Summary

The absorption spectra of rhenium(VII), rhenium(V), and various rhenium(IV) species have been determined, and the reactivity of these valence states determined for common oxidizing and reducing agents. Reduction of rhenium(VII) in 4 formal hydrochloric acid with tin(II) gives first green rhenium(V) and then a yellow-brown variety of rhenium(IV). A similar but not identical yellow-brown form of rhenium(IV) may be obtained by dissolving freshly precipitated rhenium dioxide in hydrochloric acid, and this form is converted to hexachlororhenate(IV) by digestion with hot concentrated hydrochloric acid. The hexachlororhenate ion has a different absorption spectrum and is much less reactive toward oxidizing agents than the yellow-brown varieties of rhenium(IV).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE UNIVERSITY OF TEXAS]

Reactions of Some Thorium and Uranium Compounds in Liquid Ammonia

BY GEORGE W. WATT, W. A. JENKINS, JR., AND JANE M. MCCUISTON[1]

A need for simple compounds of thorium and uranium that are appreciably soluble in liquid ammonia without reaction more extensive than solvation has led to the study of the behavior of a number of compounds of these elements. In the course of this work several solvolytic reactions have been observed and a few solubility determinations have been made. These and other related studies are described below.

Experimental

Materials.—Aside from the following starting materials, all chemicals employed were reagent grade and were used without further purification or analysis.

Thorium(IV) Nitrate 4-Hydrate.—(A. D. Mackay Co.) *Anal.* Calcd. for $Th(NO_3)_4 \cdot 4H_2O$: Th, 42.0. Found: Th, 42.0.

Thorium(IV) Sulfate.—(City Chemical Corporation) *Anal.* Calcd. for $Th(SO_4)_2$: Th, 54.7. Found: Th, 54.4.

Thorium(IV) Iodate.—This salt was prepared by the reaction between pure thorium(IV) nitrate and potassium iodate. *Anal.* Calcd. for $Th(IO_3)_4$: Th, 24.9. Found: Th, 24.6.

Thorium(IV) Oxalate 2-Hydrate.—Thorium(IV) oxalate 6-hydrate was prepared from thorium(IV) nitrate and oxalic acid and dehydrated at 110° to afford the 2-hydrate. *Anal.* Calcd. for $Th(C_2O_4)_2 \cdot 2H_2O$: Th, 52.3. Found: Th, 52.3.

Uranium(IV) Chloride.—This compound was prepared by the method described by Moore[2] and purified by sublimation. *Anal.* Calcd. for UCl_4: U, 62.7; Cl, 37.3. Found: U, 62.2; Cl, 37.2.

The origin and composition of uranium peroxide 2-hydrate, uranyl nitrate 6-hydrate and 2-hydrate used in this work are given elsewhere.[3]

The Ammonolysis of Thorium(IV) Nitrate 4-Hydrate.—Because of a strongly exothermal reaction with ammonia gas and resultant caking of the solid, thorium(IV) nitrate 4-hydrate could not be treated satisfactorily with liquid ammonia in an apparatus of the type described by Watt and Moore.[4,5] Consequently, 5.1818 g. of the salt was added to 70 ml. of vigorously agitated liquid ammonia in a Dewar flask, the ammonia was then evaporated, and the resulting gross solid was dried *in vacuo* over barium oxide. A sample (5.4207 g.) of this material was then placed in the reactor,[4] and treated with anhydrous liquid ammonia for a total of four hours (including the time required for filtration and nine washings).

The ammonia-insoluble product consisted of an amorphous white solid which was insoluble in water but soluble in hot concentrated acids. Qualitative tests for nitrate ion were negative. A typical solid product contained 74.3% thorium and 1.3% nitrogen.

The solid residue from the combined filtrate and washings consisted of a small amount of white water-insoluble solid, but the major portion was water-soluble. The water extract yielded 2.38 g. of ammonium nitrate (or 3.2 moles/mole of thorium nitrate used), m. p. 169–170°, and this melting point was not depressed upon admixture with an authentic specimen (m. p. 169.6°).

These results indicate (but do not finally prove) that the thorium(IV) nitrate 4-hydrate was converted to ammonium nitrate and hydrated thorium(IV) oxide, the latter probably containing a small amount of ammonia of solvation. Complete conversion requires 2.99 g. of ammonium nitrate, but mechanical losses are considered sufficient to account for the fact that only 2.38 g. was recovered. Attention is called to the fact that these results do not necessarily depend upon the solvolytic action of ammonia. The water content of the hydrate is sufficient to permit the reactions

$$Th(NO_3)_4 \cdot 4H_2O + 4NH_3 \longrightarrow Th(NO_3)_4 + 4NH_4OH$$

$$Th(NO_3)_4 + 4NH_4OH \longrightarrow ThO_2 \cdot 2H_2O + 4NH_4NO_3$$

Alternatively, it is possible that the nitrate is directly ammonolyzed. In any event, the present results stand in sharp contrast to a report by Shatenshtein[6] that thorium (IV) nitrate 12-hydrate is soluble to the extent of 26 g./100 g. ammonia at room temperature, and to Audrieth and Yntema's statement[7] that thorium(IV) nitrate is soluble in liquid ammonia at −33°.

The Action of Liquid Ammonia upon Thorium(IV) Sulfate.—This salt (3.4667 g.) was treated with excess liquid ammonia for about three hours. Filtration could not be accomplished owing to clogging of the filter medium and take-off lines. Consequently, the ammonia was evaporated and the solid residue was dried *in vacuo* (10^{-3} mm.) for eighteen hours. A 1.0142-g. sample was leached eight times with 5–10-ml. portions of water and made up to a known volume for analysis. This solution gave a negative test for thorium but was found to contain ammonium and sulfate ions in a 2:1 ratio. Ammonium sulfate was crystallized from the aqueous extract and identified through its X-ray (CuK_α) diffraction pattern in

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(2) Moore, *J. Am. Electrochem. Soc.*, **43**, 317 (1923).

(3) Watt, Marley and Achorn, THIS JOURNAL, in press.

(4) Watt and Moore, *ibid.*, **70**, 1197 (1948).

(5) Unless otherwise indicated, all reactions in ammonia were carried out in this type of equipment.

(6) Shatenshtein, "Liquefied Gases as Solvents," Government Chemical-Technical Publishing Office, Leningrad Division, 1934.

(7) Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1902 (1930).

terms of the spacings $d = 4.36, 3.12, 3.036$ and 2.32 Å. The total sulfate ion content of the aqueous extract accounted for 91.5% of that used originally as thorium (IV) sulfate.

Analysis of the water-insoluble product showed that it contained 68.1% thorium, and that nitrogen was absent. This product gave no X-ray diffraction pattern with Cu K_α radiation.

Since thorium(IV) sulfate is readily soluble in water, it appears that this salt was largely converted to ammonium sulfate and probably a basic sulfate of thorium. In addition to the possibility of direct ammonolysis, these products could have arisen from the hydrolysis of the product of an initial solvolytic reaction between the thorium(IV) sulfate and liquid ammonia.

The Solubility of Thorium(IV) Iodate in Liquid Ammonia.—Four grams of thorium(IV) iodate was treated with 70 ml. of liquid ammonia for three hours, washed, and dried *in vacuo*. There was no visual evidence of reaction and the starting material was recovered unchanged except for a small retention of ammonia.

Anal. Calcd. for $Th(IO_3)_4$: Th, 24.9. Found: Th, 24.0; N, 0.5.

The solubility of this salt in liquid ammonia at 25°, as determined by the method of Watt, Jenkins and Robertson,[8] was found to be 0.08 g. $Th(IO_3)_4$/100 g. NH_3.

The Solubility of Thorium(IV) Oxalate 2-Hydrate in Liquid Ammonia.—Treatment of a 2-g. sample of this salt with liquid ammonia gave essentially the same results as given above for the iodate. The residual solid phase consisted of unchanged oxalate.

Anal. Calcd. for $Th(C_2O_4)_2 \cdot 2H_2O$: Th, 52.3. Found: Th, 53.2; N, 0.4.

The solubility of this salt was found to be 0.51 g. $Th(C_2O_4)_2 \cdot 2H_2O$/100 g. NH_3.

Reactions of Uranium Peroxide 2-Hydrate in Liquid Ammonia.[9]—This compound gave no evidence of reaction when 0.9060 g. was treated with liquid ammonia for two hours. The washed solid gave a positive test for peroxidic oxygen and a negative test for nitrogen.

Anal. Calcd. for $UO_4 \cdot 2H_2O$: U, 70.4. Found: U, 70.9.

The peroxide (1 g.) also proved to be unreactive toward 1.3 g. (4.5 molar equivalents) of ammonium bromide (an acid in liquid ammonia) over a period of *ca.* two hours. The peroxide was recovered unchanged.

Anal. Calcd. for $UO_4 \cdot 2H_2O$: U, 70.4. Found: U, 70.1.

To the potassium amide (5 molar equivalents) formed catalytically from 1.00 g. of potassium in 50 ml. of liquid ammonia was added 1.68 g. of finely divided uranium peroxide 2-hydrate. The yellow solid was immediately converted to deep orange colored potassium peruranate which was allowed to remain in contact with the excess potassium amide for three hours, then washed eight times with liquid ammonia.

Anal. Calcd. for K_2UO_5: U, 60.1; K, 19.7; peroxidic oxygen, 8.1. Found: U, 60.4; K, 23.3; peroxidic oxygen, 7.8.

Uranium peroxide as the 2-hydrate was regenerated from the potassium peruranate when the latter was treated with 0.1 *M* sulfuric acid and the resulting light yellow solid was dried at 110°.

Anal. Calcd. for $UO_4 \cdot 2H_2O$: U, 70.4; peroxidic oxygen, 9.4. Found: U, 69.9; peroxidic oxygen, 8.9.

One attempt was made to reduce uranium peroxide 2-hydrate (1.089 g.) suspended in anhydrous liquid ammonia by addition of 0.506 g. of potassium. The ensuing reaction was extremely slow and a small amount of potassium remained after twelve hours. The yellow peroxide was converted to a flocculent brown solid which was not homogeneous; hydrogen was evolved slowly, thus indicating the progressive formation of potassium amide. Examination of the final solid product (Found: U, 51.0; K, 23.5; N, 0.1) led to no definite conclusions. Since it appeared unlikely that it would be possible to distinguish between the results of the reaction due to potassium solution and those due to potassium amide (*vide supra*), this reaction was not further investigated.

The Action of Liquid Ammonia upon Uranyl Nitrate Hydrates.—Approximately 3 g. of uranyl nitrate 6-hydrate was treated with 75 ml. of liquid ammonia. The nitrate was immediately converted to ammonium diuranate which was washed with ammonia and dried *in vacuo*.

Anal. Calcd. for $(NH_4)_2U_2O_7$: U, 76.3; N, 4.5. Found: U, 76.3; N, 4.5.

When treated as described above, uranyl nitrate 2-hydrate was also converted to ammonium diuranate.

Anal. Calcd. for $(NH_4)_2U_2O_7$: U, 76.3; N, 4.5. Found: U, 76.6; N, 4.4.

The identity of these products was further established by comparison of their X-ray (Cu K_α) diffraction patterns with the pattern obtained using ammonium diuranate prepared by the reaction between uranyl nitrate and aqueous ammonia.[10] These data are given in Table I.

TABLE I

X-RAY DIFFRACTION DATA FOR AMMONIUM DIURANATE PREPARED IN WATER AND IN LIQUID AMMONIA

$(NH_4)_2U_2O_7$ from H_2O		$(NH_4)_2U_2O_7$ from NH_3	
d, Å.	I/I_1	d, Å.	I/I_1
3.15	1.00	3.15	1.00
3.50	0.94	3.47	0.98
3.41	.87	3.34	.85
7.16	.82	7.10	.66
1.91	.32	1.90	.27
2.52	.27	2.51	.22

When treated with solutions of potassium in liquid ammonia, ammonium diuranate reacted extremely slowly, potassium was slowly converted to the amide, and the brown solid reaction product was distinctly heterogeneous.

The Action of Liquid Ammonia upon Uranium Halides.—Condensation of ammonia on approximately 1 g. of uranium(IV) chloride resulted in an extremely vigorous exothermal reaction. The ammonolysis product was washed exhaustively with liquid ammonia but low concentrations of chloride ion persisted in the washings. This suggests the presence of a slightly soluble partial ammonolysis product containing chlorine. The washed product was treated *in situ* with 4 atomic equivalents of potassium. Slow evolution of hydrogen was observed over a period of two hours; thereafter the unreacted potassium was converted to potassium amide by addition of an iron wire catalyst. The total hydrogen collected corresponded exactly to the quantity of potassium employed. The insoluble product was washed, dried *in vacuo*, and found to contain 73.8% uranium and 1.6% nitrogen.

Similar ammonolytic reactions have been observed using uranium(III) chloride and uranium(IV) bromide. Since the objective of these studies was the reduction of the halides to elemental uranium, the behavior of these compounds in ammonia was not further investigated.

Attempts to Prepare Ammonates of Uranyl Nitrate.—The thermal dehydration of uranyl nitrate 6-hydrate at 170–180° in a carbon dioxide atmosphere was carried out by the procedure described by Markétos.[11] Although the resulting solid had a uranium content close to that of the anhydrous nitrate [calcd. for $UO_2(NO_3)_2$: U, 60.4. Found: U, 61.0, 60.8], ammonation by ammonia gas at 170–180° and at room temperature, or by liquid ammonia at −33.5° led to extremely heterogeneous solids containing black, deep red, orange and yellow particles. No definite

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[8] Watt, Jenkins and Robertson, *Anal. Chem.*, **22**, 330 (1950).

[9] The assistance of Miss Siegried L. Achorn in carrying out these experiments is gratefully acknowledged.

[10] Carson and Norton, *Am. Chem. J.*, **10**, 219 (1888).

[11] Markétos, *Compt. rend.*, **155**, 210 (1912).

or reproducible ammonate could be isolated. In view of the heterogeneous character of the ammonation products together with the fact that the decomposition temperature of uranyl nitrate is 200°,[12] it seems unlikely that the thermal dehydration product is a single substance.

Uranyl nitrate 2-hydrate 3-ammonate was prepared as follows. Twenty-five grams of uranyl nitrate 6-hydrate was dissolved in 300 ml. of anhydrous ether and cooled in a Dry Ice–acetone-bath so long as crystals of ice continued to separate. The supernatant ether solution was decanted into a glass-stoppered flask, dried for twenty-five hours over 75 g. of anhydrous copper(II) sulfate, and filtered in an atmosphere of anhydrous nitrogen. Subsequent addition of anhydrous ammonia gas resulted in precipitation of a brilliant yellow solid which was dried *in vacuo* over barium oxide and thereafter maintained in an atmosphere of anhydrous ammonia gas at atmospheric pressure.

Anal. Calcd. for $UO_2(NO_3)_2 \cdot 2H_2O \cdot 3NH_3$: U, 49.5; N, 8.7. Found: U, 49.7; N, 8.5.

Summary

1. Thorium(IV) nitrate 4-hydrate reacts with liquid ammonia at −33.5° to form ammonium nitrate and, probably, hydrated thorium(IV) oxide.
2. The ammonolysis of thorium(IV) sulfate by liquid ammonia at −33.5° yields ammonium sulfate and other products believed to be basic sulfates of thorium.
3. The solubilities of thorium(IV) iodate and thorium(IV) oxalate 2-hydrate in liquid ammonia at 25° have been measured. These salts are unreactive toward liquid ammonia at 25° and at −33.5°.
4. Uranium peroxide 2-hydrate does not react with liquid ammonia or with liquid ammonia solutions of ammonium bromide at −33.5°. The peroxide reacts with potassium amide to form potassium peruranate, but is only slowly reduced by solutions of potassium.
5. Uranyl nitrate 6- and 2-hydrates react with liquid ammonia at −33.5° to form ammonium diuranate, *e. g.*, $2UO_2(NO_3)_2 \cdot 2H_2O + 6NH_3 \rightarrow (NH_4)_2U_2O_7 + 4NH_4NO_3 + H_2O$.
6. Uranium(III and IV) chlorides and bromides are ammonolyzed by liquid ammonia at −33.5° and the resulting ammonolysis products are not reduced to elemental uranium by solutions of potassium.
7. The preparation of uranyl nitrate 2-hydrate 3-ammonate is described.

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[12] Lebeau, *Compt. rend.*, **152**, 439 (1911); **155**, 163 (1912).

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

High-Temperature Heat Contents of Some Zirconium-containing Substances[1]

BY J. P. COUGHLIN AND E. G. KING

Current interest in development of commercial means of producing ductile zirconium has emphasized the need for thermal data for zirconium and its simpler compounds. This paper reports high-temperature heat-content measurements of five zirconium-containing substances—the metal, oxide (ZrO_2), nitride (ZrN), silicate ($ZrSiO_4$), and chloride ($ZrCl_4$). No previous similar data are available for the nitride, silicate, and chloride. A previous study[2] of the metal had given reproducible results to about 900°K., and there are available also results for the oxide[2] at three temperatures in the range 673 to 1073°K.

Experimental

Materials.—Zirconium, in the form of trimmings from rolled sheet, was furnished for this work by the Foote Mineral Company, through the courtesy of W. F. Luckenbach, Jr. The metal strips were sheared into small pieces and cleaned in turn with acetone, a magnet, 3 *N* hydrochloric acid, and distilled water.

Zirconium oxide was prepared by igniting at 1000° the chloride described below, thus taking advantage of the purification inherent in the chloride preparation process. The X-ray diffraction pattern showed only lines corresponding to the monoclinic variety of the oxide.

Zirconium nitride was prepared from a mixture of 94.8% zirconium nitride and 5.2% zirconium hydride obtained from the Manhattan Project through Prof. John Chipman of Massachusetts Institute of Technology. The material was treated at 1250° in a stream of nitrogen and hydrogen of 3:1 ratio until analysis indicated 86.65% zirconium, after which it was further heated in vacuum at 1250° for 14 hours. Analysis of the final product by ignition to the oxide gave 86.75% zirconium (hafnium) (theor. 86.69% Zr).

The zirconium silicate was a portion of the natural zircon sand from Lincoln, California, used previously by Kelley[3] in low-temperature heat-capacity measurements. The analysis reported by him was 66.3% ZrO_2 (HfO_2), 33.6% SiO_2 and 0.4% Fe_2O_3.

Zirconium chloride was prepared by passing chlorine gas at 500° over an intimate mixture of 4 parts of Norblack (99.7% carbon) and 1 part of C. P zirconium oxide. The sublimed and condensed tetrachloride was resublimed at 300 to 350°, ground in a dry box, and stored in a sealed container. Analysis for zirconium (hafnium) by precipitation with ammonium hydroxide and ignition to the oxide gave 39.21% (theor. 39.14% Zr).

An estimation of the hafnium contents of these materials was made by the Chemical and Physical Section of the Salt Lake City Station of the Bureau of Mines, as follows: Zr, 2.15%; ZrO_2, 1.25%; ZrN, 1.35%; $ZrSiO_4$, 1.15%; and $ZrCl_4$, 0.75%. Corrections for the hafnium contents were made on the assumption that corresponding hafnium and zirconium compounds have the same molal heat contents. These corrections increased the measured heat content values by the following amounts: Zr, 1.0%; ZrO_2, 0.6%; ZrN, 0.7%; $ZrSiO_4$, 0.6%; and $ZrCl_4$, 0.35%.

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[1] **Article not copyrighted.**

[2] **Jaeger** and **Veenstra**, *Rec. trav. chim.*, **53**, 917 (1934).

[3] **Kelley**, **THIS JOURNAL**, **63**, 2750 (1941).