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Concerning a Lower Oxide of Thorium and Related Compounds of the Last Row Elements<sup>1,2</sup>

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The black residue found on treating thorium metal with concentrated HCl is shown by chemical tests to be equivalent to Th(II) in the form of ThO. Neutron diffraction indicates a lattice probably of the ZnS-type, which is consistent with ThO. Though its composition is more a function of acid concentration, the residue left on treating uranium metal with HCl apparently starts also as monoxide. It is inferred that similar residues seen on treating other of the last row metals with HCl are also monoxides.

## Introduction

It has been known since early work with thorium metal that it will dissolve on treatment with HCl, usually leaving a residue which customarily has been ascribed to ThO<sub>2</sub> present in the starting material or produced during the reduction procedure. One investigator,<sup>3</sup> however, has argued that the residue was a lower oxide formed in the process of reaction. Our results, commencing with rediscovery of the effect during Manhattan District work, make the recent suggestion that the residue is finely divided metal, coated with oxide,<sup>4</sup> impossible and give definite support to the guess of von Bolton<sup>3</sup>: the residue is basically ThO. It further can be shown that this must be formed in the solution process and is not present in the original metal.

Others of the last-row metals show a similar phenomenon on reaction with HCl.

## Experimental

**Thorium.**—Pieces of good quality (>99%) massive thorium metal, 11–14 grams in weight, were sawed from larger billets. Excess hydrochloric acid, from 2 to 12 N in concentration, as desired, was allowed to react with the metal in a flask to which a water-cooled condenser was attached. The spontaneous reaction drove the solution to boiling, and the metal dispersed to a black suspension. When gas evolution was largely terminated, the solution was heated to boiling for short periods until ebullition stopped when the source of heat was removed. Allowed to stand, the black matter settled out fairly rapidly. To free it from dissolved thorium, the solid was slurried, transferred to 15-ml. centrifuge tubes fitted with male 14/20 ground joints or larger tubes made from female 24/40 joints and separated from the supernatant. Several washes with fresh HCl and separation of the wash liquid by centrifugation removed soluble thorium.

Thorium dioxide originally present in the metal (see below) appears in these manipulations as a white, dense, finely granular material, which settles out faster than the dark reaction product. Some can be made to adhere to the original reaction vessel in transferring to the centrifuge tubes and thus is eliminated. However, some is usually still visible as a small white ring near the bottom of the centrifuge tube. In mass it represents less than 1% of the total thorium in the residue. The residue itself contains some 20–25% of the thorium in the original metal.

The centrifuge tubes could be attached directly to an apparatus for measuring gas evolution by water displacement, without further manipulation of the washed residue. When ready for measurement, HCl containing a few drops

of HF or fluosilicic acid<sup>5</sup> was added to the residue, the tube was coupled to the apparatus and hydrogen was evolved at a rate controlled by heating the centrifuge tube. The apparatus was operated in such a way as to keep a minimum difference from atmospheric pressure throughout the system, avoiding pressure differences that might favor hydrogen leakage. The reaction was complete when the solution in the centrifuge tube was clear, and only white ThO<sub>2</sub> was left. This was identified spectroscopically and by X-ray analysis ( $a = 5.5875$  kx.). The volume of hydrogen evolved was measured, and the Th(IV) which had gone into solution was determined by oxalate precipitation and ignition of the precipitate to ThO<sub>2</sub>. Some typical data and hydrogen–thorium ratios for residues produced by concentrated HCl on metal are shown in Table I. It is seen that one mole of hydrogen gas is evolved per gram atom of thorium dissolved.

TABLE I

RESIDUE OF THORIUM METAL TREATED WITH CONCENTRATED HCl. HYDROGEN EVOLVED ON TREATMENT OF RESIDUE WITH FLUORIDE-CATALYZED HCl

| No. | H <sub>2</sub><br>(cor.)<br>20°, cc. | Th<br>dissolved,<br>g. | Mole ratio,<br>H <sub>2</sub> /Th |   |
|-----|--------------------------------------|------------------------|-----------------------------------|---|
| 1   | 80.2                                 | 0.781                  | 0.994                             | a |
| 2   | 57                                   | 0.518                  | 1.06                              |   |
| 3a  | 190                                  | 1.761                  | 1.043                             | b |
| 3b  | 141                                  | 1.318                  | 1.035                             | c |
| 4a  | 180.5                                | 1.723                  | 1.014                             |   |
| 4b  | 140                                  | 1.323                  | 1.023                             |   |
| 5   | 188                                  | 1.912                  | 0.951                             | b |

<sup>a</sup> Yellow residue, much ThO<sub>2</sub>. <sup>b</sup> Pumped dry before experiment. <sup>c</sup> Not dried before experiment.

A tube containing washed and centrifuged residue was connected to a vacuum pump and trap, through a ground-joint, and the remaining water and HCl were pumped off, at room temperature, continuing for 2–3 days, and leaving dry residue. The ratio of hydrogen evolved to thorium dissolved from the dry residue was not distinguishably different from that for a portion of the same residue which had not been so dried (No. 3a and 3b). At room temperatures, the decomposition rate of the residue is quite low, and over 80% of the reducing power remains after two months. A sample kept for some 6 weeks gave a hydrogen–thorium ratio of 0.92, with a larger residue of oxide than usual.

A sample of residue which had been pumped dry for 16 hours was analyzed. Hydrogen was determined by igniting a portion of residue in a train and capturing the water in magnesium perchlorate (Anhydron). This analysis, which is critical, could be slightly high, inasmuch as in the ignition of the residue, which oxidizes explosively when heated to about 110°, some hydrogen appears as HCl as well as H<sub>2</sub>O. The HCl which passes through the train is captured at the end with silver, and a correction can be made for this. However, any small amounts of HCl that might be trapped in the magnesium perchlorate have a mass hydrogen equivalent over 4 times that of water, which could lead to slightly high hydrogen values. Oxygen was determined by the

(1) Presented in part in Proceedings of International Conference on Peaceful Uses of Atomic Energy, Geneva, Vol. VII, 1955, pp. 407–413 (U.N., 1956).

(2) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(3) W. von Bolton, *Z. Elektrochem.*, **14**, 768 (1908).

(4) C. J. Rodden and J. C. Warf, "Analytical Chemistry of the Manhattan Project," C. J. Rodden, Editor, NRES, Div. VIII, Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 163.

(5) F. L. Steahly and R. W. Stoughton, U. S. Patent No. 2,546,933 (March 27, 1951); F. W. Shuler, F. L. Steahly and R. W. Stoughton, "Production and Separation of U<sup>233</sup>," Collected Papers, L. I. Katzin, Editor, U.S.A.E.C. Doc. No. TID-5223 (1952), p. 307.

KBrF<sub>4</sub> procedure.<sup>6</sup> Samples for thorium analysis were dissolved in dilute sulfuric acid, with fluoride catalysis, and the thorium was precipitated with oxalic acid. Chloride was determined gravimetrically after distillation from the supernatant.

The analytical results showed hydrogen, 0.75%; chloride, 7.72%; oxygen, 10.12%; thorium, 82.36%; material balance, 100.95%. There is therefore no gross constituent overlooked. The atomic ratios, per thorium, in the above analysis, are hydrogen, 2.12; chloride, 0.61; oxygen, 1.78. Assuming all the chloride to be HCl and all the residual hydrogen to be water, the thorium-oxygen residual composition is representable as ThO<sub>1.03</sub>. A small percentage of ThO<sub>2</sub> is known to be in the dried solid, so the oxygen may be expected to be a little high for ThO. As there is but 0.75 water molecule per thorium, the dried material is probably not Th(OH)<sub>2</sub>. In other similar experiments, the amount of chloride is variable, in correspondence to the details of the washing procedure, and oxygen was usually taken by difference, but the general conclusion was the same. The agreement between the hydrogen-thorium ratios and the analytical results is satisfactory.

The residue in preparation seems black, but during handling it develops more of a brownish character. It is rather like a dense gummy mud when wet. Handling wet facilitates appearance of a yellow color. If residue material is left in a centrifuge tube with a layer of HCl over it, in the course of time a yellowing is seen to work down from the top layers. If the residue is treated with 6 *N* ammonia, the yellowing takes place quite rapidly, in contrast to the rate of the process in HCl. Nitric acid (6 *N*) quickly turns the solid to bright orange-yellow. The dry residue will not change color in the same way that the wet residue does, on exposure to air. It has not yet been possible to find an analytical change to correspond to the color change, but it is suspected that oxidation to ThO<sub>2</sub> is involved. In canary-yellow samples, obtained by prolonged standing in air of wet residues, the hydrogen evolution-thorium solution ratio is still close to unity, though the amount of residual oxide is noticeably increased. Residues which had been treated with nitric acid and with ammonia, respectively, gave hydrogen-thorium ratios of 1.12 and 1.08. Hydrogen peroxide, in 30% concentration, reacted with the fresh residue with gas evolution. The bulk of solid remaining after gas evolution ceased was of a light yellow color. The material was inactive to dilute HCl, but dissolved in HCl and catalytic fluoride with gas evolution. The original residue, dried and heated to 110–115°, will ignite explosively to white ThO<sub>2</sub>. Warmed in an inert gas atmosphere, a permanent gas is evolved, probably hydrogen.

**Uranium Residue.**—The reaction of uranium with hydrochloric acid yields rather similar results. The superficial oxide layer was removed from cubes of uranium metal about 19 grams in weight, with a nitric acid wash. Following the spontaneous reaction of the metal with HCl, the residue was washed and separated as for thorium. Some ratios of hydrogen evolved to uranium dissolved with fluoride-catalyzed HCl are shown in Table II.

Experiments with partially diluted HCl as the reagent used to dissolve the metal yielded voluminous residues, as with the thorium but, in contrast to the thorium, the hydrogen-uranium dissolved ratios, with some variability, centered around the value 0.65. Because the color of UO<sub>2</sub> is brown and the solutions formed are deeply colored by the U(IV), it is difficult to tell if one is dissolving oxide which might have been in the original metal and thus bringing the ratio down. Experiments in which the solution process for the residue was carried out in two stages showed a somewhat lower hydrogen-uranium ratio for the second stage, but not as different as might have been sought. Another possibility for the lower ratios would be solution of the uranium to the U(III) state in part, either with or without subsequent air oxidation to U(IV). It has been shown by others that when uranium metal is attacked by fluoride-catalyzed HCl, solution is clean to the U(IV) state.<sup>7</sup> Investigations of our own show that all the uranium in solution at the end of an experiment is U(IV), which does not, however, completely eliminate a possible U(III) stage under the experimental conditions. In the earliest stages of the catalyzed reaction

on the residue, a violet color sometimes may be observed, but as the solution and its immediate atmosphere are quickly flushed by hydrogen released in the solution reaction, it seems doubtful that enough U(III) would be formed and air-oxidized to U(IV) to account for the large effects found.

The major explanation for the deviation from a hydrogen evolved-uranium dissolved value of unity is probably contained in the following observations. In the course of testing various acid concentrations and acid volumes in the metal solution step, it was observed that the amount of residue formed was a function of the acid concentration, suggesting a significant hydrolytic contribution compared to the thorium situation. When precautions were taken to use large excesses of concentrated HCl, it was found that the amount of uranium in the residue was perhaps one-fifth that when 25% acid (3 vol. of water to one vol. of concentrated acid) was used but that the hydrogen evolved-uranium dissolved ratio was 1.0–1.1 (see Table II).

TABLE II  
RESIDUE OF URANIUM METAL TREATED WITH HCl, AND INFLUENCE OF ACID CONCENTRATION HYDROGEN EVOLVED ON TREATMENT OF RESIDUE WITH FLUORIDE-CATALYZED HCl

| No. | Acid concn. in metal treatment | H <sub>2</sub> (cor.) 20°, cc. | U dissolved, g. | H <sub>2</sub> /U mole ratio |          |
|-----|--------------------------------|--------------------------------|-----------------|------------------------------|----------|
| 1   | ..                             | 72.5                           | 1.000           | 0.72                         |          |
| 2   | ..                             | 127                            | 1.986           | .63                          |          |
| 2a  | 70%                            | 117                            | 1.797           | .645                         |          |
| 2b  | 70%                            | 75                             | 1.099           | .676                         |          |
| 3   | 25%                            | 71.4                           | 1.092           | .649                         |          |
| 7   | 25%                            | 292                            | 3.147           | .921                         | <i>a</i> |
| 8   | 20%                            | 181                            | 3.045           | .590                         | <i>a</i> |
| 7–8 | ..                             | 80                             | 1.582           | .501                         | <i>b</i> |
| 9a  | 50%                            | 75                             | 0.960           | .756                         |          |
| 9b  | 50%                            | 103                            | 1.240           | .803                         |          |
| 10  | 100%                           | 44                             | 0.429           | .995                         |          |
| 11  | 100%                           | 152                            | 2.022           | .726                         | <i>c</i> |
| 12  | 100%                           | 76                             | 0.662           | 1.11                         | <i>d</i> |
| 13  | 25%                            | 206                            | 2.815           | 0.71                         |          |

<sup>a</sup> Some residue left and separated. <sup>b</sup> Combined residues of 7 and 8. <sup>c</sup> Two cubes metal but same volume acid as 10. <sup>d</sup> Two cubes metal and twice volume acid as 10.

The conclusion may be derived that the primary insoluble material formed in the solution process is of the U(II) type. When the acid concentration is maximal, this primary product tends to dissolve further, so that small amounts of residue (ca. 0.5 g. out of 19.5 g. metal) are left. At lower acid concentrations, possibly assisted by hydrolysis, there tends to form a material with some contribution from higher uranium oxidation states. Not only does the bulk of the insoluble material increase, to the order of 3 g. for 25% acid, but so does the effective amount of U(II) equivalent. This is the basis for the suggestion that the U(II) material is the primary solid product in this instance too and that some sort of protective action from higher-valence uranium materials resists the action of the HCl so that more material remains than for the concentrated acid. As there is a strong tendency for the hydrogen evolved-uranium dissolved ratio to approximate 0.65 over a considerable range of acid concentrations, there is room for the suggestion that the stabilization might consist of formation of a solid phase which might be formulated 2UO·UO<sub>2</sub>. There is no other evidence for such a phase at the moment, however.

Following this discovery for the uranium solution process, a survey of the data for thorium residue showed that although the residue composition was much less sensitive to acid conditions than was the case for uranium, the use of 50% HCl in the metal-attack step dropped the hydrogen-thorium ratio to about 0.9, and for 6-fold diluted acid, the residue showed a ratio of about 0.8. This could be a consequence of the less ready hydrolysis of Th(IV) compared to U(IV).

Uranium residue which had been pumped dry under high vacuum became very hot when air was readmitted and probably oxidized to U<sub>3</sub>O<sub>8</sub> spontaneously. In larger amounts the material might be pyrophoric.

(6) I. Sheft, A. F. Martin and J. J. Katz, *THIS JOURNAL*, **78**, 1557 (1956).

(7) C. V. Banks and J. C. Warf, Manhattan District Report CC-2942 (1945), declassified.

**Structural Investigation.**—X-Ray diffraction investigation of the thorium residue, both wet and dried, showed it to be essentially amorphous or of very finely divided crystals. With very long exposures, a weak pattern with diffuse lines could be obtained. If the material were pumped dry while heated at about 75°, a slight intensification, particularly of lines with greater deviation, could be achieved, without noticeably sharpening the lines. The pattern resembles that of ThO<sub>2</sub>, but with a slightly larger lattice spacing, and without the line sharpness which is characteristic of ThO<sub>2</sub>. There is no evidence for any residual thorium metal. The data allow certain differentiation from the ThO of cubic structure reported by Rundle, *et al.*,<sup>8</sup> to form on the surface of freshly cleaned thorium metal.

The uranium residue likewise shows a very weak X-ray pattern with diffuse lines. Again, the spacing suggests a slightly larger cell than UO<sub>2</sub>. When the trends in the uranium oxide cell size against oxygen content<sup>9</sup> are considered, the pattern would be consistent with less than two oxygens per uranium.

The X-ray investigation of the heavy-element compounds with light elements suffers from the fact that direct information is obtained only on the heavy atom positions. Neutron diffraction techniques were therefore applied to some 20 g. of thorium residue which had been pumped dry on the vacuum line, and the pattern obtained was clearly not of the ThO<sub>2</sub> (fluorite) type but seemed to be of the ZnS type. A heavy background of hydrogen scattering made work with the weaker lines difficult, so the same sample was equilibrated with D<sub>2</sub>O and pumped dry again. (Even 0.4% hydrogen represents about as many atoms of hydrogen as of thorium.) Neutron diffraction investigation of the sample again showed the same pattern with a more favorable intensity to background relation, and it is clearly indicated to be of the ZnS type.<sup>10</sup> However, a few weak extra lines indicate the possibility of some unrecognized superstructure, though a second phase seems more likely to be the source. Hydride structures clearly do not fit. The unit cell is  $a = 5.63 \pm 0.01$  kX.

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### Discussion

Salts of thorium, in solution or in the solid state, thorium dioxide and volatile compounds such as thorium acetylacetonate all contain thorium clearly in the 4+ oxidation state. Compounds such as ThS and Th<sub>2</sub>S<sub>3</sub> are known only in the solid state. They would appear stoichiometrically to represent compounds with thorium in subnormal oxidation states, but crystallographically<sup>11</sup> the characteristics are those of thorium atoms in the metallic state. The physical properties of these sulfides agree with such a characterization.<sup>12</sup> On the other hand, although actinium, uranium, neptunium and plutonium all show tripositive states in solution, two sulfides of the four (uranium and neptunium) with formula X<sub>2</sub>S<sub>3</sub> are, like the thorium compound, crystallographically metallic.<sup>13</sup>

Hayek, Rehner and Frank<sup>13,14</sup> and Anderson and

(8) R. E. Rundle, N. C. Baenziger, A. Wilson, R. A. McDonald and P. Chiotti, unpublished data, cited in R. E. Rundle, *Acta Cryst.*, **1**, 180 (1948).

(9) R. F. Ackermann, ANL Report 5482, 1955; Thesis, Univ. of Kansas, 1955.

(10) Detailed discussion to be published elsewhere by S. Siegel.

(11) W. H. Zachariasen, *Acta Cryst.*, **2**, 291 (1949).

(12) E. D. Eastman, I. Brewer, L. A. Bromley, P. W. Gilles and N. L. Lofgren, *This Journal*, **72**, 4019 (1950).

(13) E. Hayek and Th. Rehner, *Experientia*, **5**, 114 (1949).

D'Eye<sup>15</sup> have reported reaction products between ThI<sub>4</sub> and Th metal, in the proper proportion, which they have interpreted as ThI<sub>2</sub> and ThI<sub>3</sub>. More structural data must be obtained before the true nature of these materials is elucidated. In contrast to the thorium sulfides, and to our apparent ThO, these iodides are very sensitive to moisture.

The composition ThO has been reported<sup>8</sup> as a temporary surface film forming on fresh Th metal surfaces, but there is some uncertainty at present as to the status of this compound and of analogs such as ThN. On the other hand, in metal oxidation studies such as that of Levesque and Cubicciotti,<sup>16</sup> there are described two types of oxides—the normal white ThO<sub>2</sub>, as an outer layer, and a layer next to the metal of a black oxide. Our residue seems to be some form of ThO, perhaps stabilized by hydration, or perhaps simply by being formed at relatively low temperature, in a relatively non-reactive form compared to the oriented layer on the metal surface (though consider the implications of the Levesque and Cubicciotti<sup>16</sup> observations of possible ThO formation). The ZnS-type structure may be looked on as a fluorite-defect lattice with half the oxygens missing. The yellowing reaction might then well be surface oxidation of the fine crystallites of ThO to ThO<sub>2</sub>. The increased residue of ThO<sub>2</sub> found with time would be consistent with this interpretation. In the case of UO, with trivalent uranium states available, and generally easier oxidation, compositions with higher oxygen-uranium ratios than UO form more readily, and the dried lower oxide is extremely readily attacked by atmospheric oxygen. It cannot yet be said whether ThO is the equivalent of an intermetallic compound like the sulfides of thorium or a more ionic material which legitimately represents divalent thorium.

Though the neutron diffraction data are not available, the chemical evidence indicates that UO forms also in concentrated acid. Whether the apparent centering on a composition such as 2UO:UO<sub>2</sub> at lower acid concentrations is real is still not certain.

In addition to thorium and uranium, neptunium<sup>17</sup> and also plutonium form black residues on treatment of metal with HCl. It is to be assumed that formation of these residues, in all cases dissolved with the help of catalytic fluoride, is related to monoxide formation, as with thorium and uranium, and that protactinium metal should show the same sort of behavior. This sort of analogy in chemical reaction is undoubtedly related to other analogies in the chemistry of the last-row elements.

### LEMONT, ILLINOIS

(14) E. Hayek, Th. Rehner and A. Frank, *Monatsh. Chem.*, **82**, 575 (1951).

(15) J. S. Anderson and R. W. D'Eye, *J. Chem. Soc., Suppl.* 2 S244 (1949).

(16) P. Levesque and D. Cubicciotti, *This Journal*, **73**, 2028 (1951).

(17) E. F. Westrum, Jr., and L. Eyring, *ibid.*, **74**, 2045 (1952).