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ABSTRACT

The solid produced by reaction of thorium metal with hot 12N HCl has a composition $\text{Th O}_{1.3} \text{Cl}_{0.7} \text{H}_{1.3}$. Upon heating at below 300° C, hydrogen is evolved, apparently reversibly, with a heat of activation of 2.3 kcal per mole of H_2 . At higher temperatures, hydrogen is evolved with a heat of activation of about 25 kcal. Heating to 800° C produces sublimed thorium tetrachloride and a residue of thorium dioxide and thorium metal. From chemical analysis, x-ray diffraction data, and surface area measurements, the principal initial reaction product is concluded to be a thorium (IV)-oxide-hydride-hydroxide-chloride mixed crystal that evolves hydrogen slowly by an internal reaction $\text{H}^- + \text{OH}^- = \text{O}^{-2} + \text{H}_2$.

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INTRODUCTION

Hoch and Johnson, utilizing a high-temperature x-ray diffraction technique, found that thorium and thorium dioxide react at 1850° C to form the sodium chloride modification of thorium monoxide. (2) However, this monoxide was observed to decompose to the metal and the dioxide upon cooling. Thorium monoxide had only been noted at room temperature on the surface of thorium metal samples. (3) until Katzin reported recently that the solid product of the reaction between thorium metal and aqueous hydrochloric acid is impure thorium monoxide in a zinc blende modification. (4)

The initial objective of this research was to study the chemical changes in this zinc blende modification of thorium monoxide upon heating in an inert atmosphere. The explosive oxidation reported by Katzin to occur when the material is heated above 110° C in air should not take place in an inert atmosphere, and the material was expected either to transform to the sodium chloride modification of the monoxide, or to decompose to thorium metal plus the dioxide. During the purification process, it became evident that the black product of the reaction

between metallic thorium and concentrated hydrochloric acid was not thorium monoxide contaminated by hydrogen chloride and water as believed by Katzin, but something more complex. The objective of this investigation, then, became the characterization of the black reaction product and of the materials obtained when it is heated.

After completing this work, we learned of a study by Karabash of the thorium-hydrochloric acid reaction and the reaction products. (5) Under conditions nearly identical with Katzin's, Karabash obtained a product that he concluded to be $\text{ThO}(\text{OH})\text{H}$. Our research has revealed new information on the properties of the thorium-hydrochloric acid reaction product, and leads to a somewhat different identification of the product material.

EXPERIMENTAL

Cubes of 98+% thorium metal, each weighing about 5 grams, were allowed to react with excess 12N hydrochloric acid in a Pyrex flask in a dry-box containing an argon atmosphere. The reaction caused the solution to boil. A black-green precipitate was formed that remained undissolved even when more HCl was added and heated to boiling on a hot plate. The solution and precipitate were centrifuged until the supernatant liquid was clear. This clear greenish liquid was decanted and discarded. The gummy precipitate was added to fresh 12N HCl in a clean Pyrex flask. The flask was heated to insure dispersion of the dark precipitate and solution of any thorium metal that might remain. Washing and centrifuging were repeated for a total of

six washes, after which the then colorless supernatant liquid was discarded. The residue, which for convenience can be called wet $\text{ThO}_x\text{Cl}_y\text{H}_z$, was put into a small glass vacuum flask and evacuated at about 25 μ pressure for 5 days. As it dried, the $\text{ThO}_x\text{Cl}_y\text{H}_z$ shrank and lost its green cast, leaving shiny black angular lumps. [μ -mu]

Some of the $\text{ThO}_x\text{Cl}_y\text{H}_z$ was ground under an inert atmosphere and was sealed in 0.2-mm. capillaries for x-ray diffraction study in a North American Philips powder camera. Fifteen-hour exposures with copper K- α radiation ($\lambda = 1.5418 \text{ \AA}$) were used. [α -alpha]
[λ -lambda]

The pattern showed a number of broad diffuse lines, the centers of which indicated a structure with thorium positions the same as those in thorium dioxide, but with probably a slightly larger lattice ($a = 5.62 \pm 0.05 \text{ \AA}$) in substantial agreement with the constants reported both by Katzin and by Karabash. No other lines were observed.

A portion of the $\text{ThO}_x\text{Cl}_y\text{H}_z$ was heated under vacuum to 200° C, during which large quantities of permanent gas were evolved. The run was repeated with an evacuated 250-cc. glass bulb attached to the apparatus. Analysis by a Consolidated mass spectrometer of the contents of the bulb showed the gas to be essentially pure hydrogen. The runs were repeated three times in a glass apparatus that allowed measurements to be made of the pressure, temperature, and volume of hydrogen liberated. To be sure of removing nearly all of the hydrogen, the samples were heated to about 500° C in quartz thimbles. The hydrogen evolution results at standard temperature and pressure were: from 1.1437 g. (sample), 61 cm.³; from 0.5457 g., 27.5 cm.³; and from 2.2212 g., 113.8 cm.³.

Another portion of the $\text{ThO}_x\text{Cl}_y\text{H}_z$ was heated, but without complete removal of the hydrogen. The temperature, measured by a chromel-alumel thermocouple, was held constant at each setting until apparent pressure equilibrium was established (20 to 40 minutes). At every second setting, the hydrogen was partly pumped out and the sample was re-equilibrated. No attempt was made to approach equilibrium by reducing the temperature except at temperatures below about 300°C , where it was found that the partial pressure of hydrogen decreased on cooling to 27°C to the original 1μ value. The data are plotted in Fig. 1. As indicated in the figure, some of the hydrogen required that 2300 cal. be supplied for removal of one mole of H_2 , while the remainder required 25000 cal. per mole. The material after hydrogen removal may be called ThO_xCl_y .

A B.E.T. surface area determination, as described by Bugge and Kerlogue, (6) was performed on one of the outgassed ThO_xCl_y samples, to see whether adsorbed hydrogen could account for the copious gas evolution. The area, as found by nitrogen adsorption, was 19.4 M.^2 per gram of sample. According to McConnell and Roberts, however, a substance with this surface area and with properties similar to those of thorium dioxide could chemisorb about 5 cm.^3 of hydrogen measured at standard conditions. (7) The total hydrogen evolved from the dried material was about $52\text{ cm.}^3/\text{g}$. The surface area measurements suggest, therefore, that about 10% of the hydrogen was present as a weakly adsorbed layer.

To see if further decomposition of the ThO_xCl_y could be induced, a fresh sample was placed in the vacuum apparatus in a quartz tube and

was slowly heated under vacuum to 800° C. After the hydrogen was pumped off, a white deposit formed above the black sample on the cooler portion of the quartz thimble. Wet chemical analysis of the sublimed material gave 60.94 mg. of thorium and 37.40 mg. of chlorine from 0.4353 g. of ThO_xCl_y . A second sample gave 41.79 mg. of thorium and 25.50 mg. of chlorine from 0.3096 g. of ThO_xCl_y . The chlorine to thorium mole ratios were, respectively, 4.02 and 3.99, so the white solid that sublimed from the ThO_xCl_y appeared to be thorium tetrachloride. This identification was partially confirmed when a similar sample showed a diffraction pattern characteristic of ThCl_4 as well as lines of thorium dioxide produced, presumably, when a power failure exposed the sublimed ThCl_4 to moist air.

Two weighed samples of $\text{Th}_{(y-4)/4}\text{O}_x$ residues from the sublimation were oxidized by introducing oxygen into the vacuum line. The reacting mass glowed white-hot and yielded a partially sintered white powder. A sample that initially weighed 0.4559 g. gained 0.0115 g., and a sample that weighed 0.3038 g. gained 0.0079 g. The powder after oxidation had a B. E. T. surface area of 5 m.²/g. and exhibited only sharp thorium dioxide x-ray diffraction lines ($a = 5.60 \pm 0.01$). The composition of the $\text{Th}_{(y-4)/4}\text{O}_x$ was, therefore, $\text{ThO}_{1.57 \pm 0.01}$; the composition of the ThO_xCl_y was $\text{ThO}_{1.31 \pm 0.02}\text{Cl}_{0.67 \pm 0.02}$; and the composition of the dried $\text{ThO}_x\text{Cl}_y\text{H}_z$ was $\text{ThO}_{1.31 \pm 0.02}\text{Cl}_{0.67 \pm 0.02}\text{H}_{1.28 \pm 0.05}$.

When a $\text{Th}_{(y-4)/4}\text{O}_x$ sample was removed from the vacuum system, it became slightly warm to the touch, implying a slower spontaneous oxidation by air. Such samples remained black but gave only the typical thorium dioxide x-ray powder pattern with $a = 5.597 \pm 0.005 \text{ \AA}$.

Donnay and Nowacki report that thorium dioxide has the fluorite structure with $a = 5.584 \pm 0.010$, (8) so it seems certain that the black powder was oxygen-deficient thorium dioxide.

A sample was prepared for x-ray diffraction examination after successive stages of decomposition. After vacuum drying for five days at room temperature only the diffuse pattern characteristic of thorium dioxide was obtained. No appreciable change in this thorium dioxide diffraction pattern was produced by heating for one day at 180° C, for an additional three days at 300° C and for one day at 450° C. Some very weak and very broad lines that were observed at low scattering angles are also found on standard thorium dioxide samples. These have been shown to arise because ordinary x-ray diffraction technique does not produce perfectly monochromatic radiation. (9) After an additional one-day period at 620° C, weak thorium lines and a sharper thorium dioxide pattern were found. Two or three very weak but sharp lines of a third phase were also present, and were still present after 1 day at 800° C.

DISCUSSION

Because of the explosive character of his dried material, Katzin had difficulty in obtaining a complete elemental analysis. He reports the composition of material vacuum dried for 16 hours at room temperature to be $\text{ThC}_{1.78} \text{Cl}_{0.61} \text{H}_{2.12}$. If this material is assumed to contain 0.47 mole of water, the remainder of the material would have a composition $\text{ThC}_{1.31} \text{Cl}_{0.61} \text{H}_{1.29}$, in reasonable agreement

with the composition of the material analyzed in this research after five days of vacuum drying at room temperature. Katzin was led principally by two items of information to conclude that the crystalline portion of his material was ThO. First, catalytic oxidation of the material by HCl solution yielded (usually, but not always) just the quantity of hydrogen gas to be expected from raising the thorium present from the +2 to the +4 oxidation state. Second, a neutron-diffraction study performed by Siegel showed oxygen arrangements characteristic of the ZnS-type crystal structure. (10) However, Katzin states: "A few weak extra lines may indicate the possibility of some unrecognized superstructure, though a second phase seems more likely to be the source."

Katzin concluded that the considerable quantity of chlorine that he found in his material was probably held as hydrogen chloride and that the hydrogen also found was held partly as hydrogen chloride and partly as water.

Karabash studied the product of reaction of thorium metal with thermostatted 4-6N hydrochloric acid solutions. He found chlorine contents of his material to range from 0.12 to 0.20 atom of chlorine per atom of thorium. This chlorine content is much lower than that reported by Katzin or than that found in the present research. We used a more concentrated (12N) acid. The higher oxygen and lower chlorine content of Karabash's produce could result either from his use of a thermostatted vessel or from his use of less-concentrated HCl. Karabash found that on heating in vacuum, decomposition occurred and

left as a solid residue only white thorium dioxide. Results of our research differ, in that weak thorium metal diffraction patterns in addition to strong thorium dioxide patterns were observed after the samples had been heated to 620° C. This difference in results is consistent with the difference in initial compositions of the samples heated. In Karabash's sample sufficient oxygen and chlorine were present to convert all the thorium to thorium dioxide or thorium tetrachloride, while in this research only about four-fifths of the thorium could be converted to these compounds.

Karabash's interpretation differed sharply from Katzin's in that he considered the hydrogen to be bound as an integral part of the solid product, and in that he considered all thorium to be present in the +4 oxidation state in a $\text{ThO}(\text{OH})_2$ compound.

The dissociation studies of the work described here prove rather conclusively that Katzin's interpretation is incorrect. Neither hydrogen chloride nor water was present in significant concentrations after the sample had been vacuum dried for a period of five days at room temperature, although high concentrations of both chlorine and hydrogen remained. Even extremely gentle vacuum heating of the material yielded no water or hydrogen chloride. Furthermore, a measurable pressure of hydrogen gas could be established in apparent equilibrium with the solid. The hydrogen was shown, at least in the temperature range below 300° C, to resorb reversibly when the temperature of the sample was lowered. The observed hydrogen evolution could conceivably result from reduction of hydrogen chloride or water by thorium in

a reduced oxidation state, but for such a reaction reversibility of the hydrogen evolution would be highly improbable.

Karabash, like Katzin, did not report the fate of the chlorine in his sample, but implies it was evolved as chlorine or hydrogen chloride. However, our research proves that the chlorine is strongly bound in the lattice and is evolved only as thorium tetrachloride.

Two general formulations are consistent with the analysis $\text{ThO}_{1.31}\text{Cl}_{0.67}\text{H}_{1.28}$ obtained in this work. The material might contain thorium in the +2 oxidation state as $2/3 \text{Th}(\text{OH})_2$, $1/3 \text{ThCl}_2$, or it might contain thorium in the +4 oxidation state as a mixture or solution of ThO_2 , ThCl_4 , $\text{Th}(\text{OH})_4$, and ThH_4 , with about 0.1 mole of hydrogen gas adsorbed per mole of thorium.

For several reasons, the formulation which places the thorium in the +2 oxidation state is probably not correct. As already suggested, the observed equilibrium evolution and resorption of hydrogen from the material would be improbable with this formulation. Second, the sharp break in the plot of the logarithm of the hydrogen pressure vs. $1/T$ implies that the hydrogen is held in at least two distinct forms, in one of which the hydrogen is very weakly bound. With the hydrogen conceived to be present only as OH^- ion when heating is initiated, it is difficult to imagine what sharp change could occur at about 350°C to account for the factor-of-10 change in the hydrogen heat of dissociation. Third, as pointed out by Karabash, some chemical properties of the material are very similar to those of thorium hydride. This observation suggests that hydride ion is present. Fourth, the first formulation leaves the diffuse but distinct x-ray pattern unexplained.

Katzin's x-ray studies revealed a phase with a face-centered cubic arrangement of thorium atoms with $a = 5.63 \pm 0.01 \text{ \AA}$. He believed this to be ThO. Karabash's material contained a cubic phase with face-centered cubic arrangement of thorium atoms for which $a = 5.62 \text{ \AA}$. When his material reacted with hydrogen peroxide or other strong oxidizing agents, he obtained what he interpreted as thorium hydride-oxide-peroxide, $(\text{Th}^{+4})_2(\text{H}^-)_2(\text{O}_2^{-2})(\text{O}^{-2})_2$. This material showed the same diffraction pattern with unchanged lattice constants.

In our research the face-centered cubic phase was also found to have $a = 5.62 \text{ \AA} \pm 0.05$. When the material was heated to 620° C until almost all the hydrogen was removed, the pattern became somewhat sharper and a few additional weak lines appeared, but no measurable change in this lattice constant occurred. Thus, material of atomic proportions as different as $\text{ThO}_{1.3}\text{Cl}_{0.7}\text{H}_{1.28}$, $\text{ThO}_{1.3}\text{Cl}_{0.7}\text{H}_x$ (where x is small), $\text{ThO}_{2.0}\text{Cl}_{0.2}\text{H}_{1.8}$, and ThO_2H , all yielded diffraction patterns with lattice constants identical within the accuracies of determination.

The spacings between thorium atoms in phases of known structures are sensitive to the ratio of the number of cations to number of anions, and to the nature of the anions present. For example, the volume of the ThH_2 phase per thorium atom is 42 \AA^3 ; of the Th_4H_{15} phase per thorium atom 47 \AA^3 ; of the ThO phase 35 \AA^3 ; of the ThO_2 phase, 44 \AA^3 ; and of the ThCl_4 phase 134 \AA^3 . Single-phase materials of the variety of compositions named could not have unchanged thorium atom spacings even if, by coincidence, they all had the same basic packing of thorium atoms.

The most probable explanation of why identical diffraction patterns are found for these materials of widely different over-all compositions is that in each sample the observed pattern is that of thorium dioxide. The initial precipitates are thermodynamically unstable toward attack by HCl and by oxygen. The precipitates dissolve in HCl if a trace of hydrofluoric acid is added. Probably the survival of the precipitates depends on a protective coating of thorium dioxide. If, as is reasonable to suppose, the bulk of the material is of low crystallographic symmetry, highly disordered, and of small particle size, only the thorium dioxide pattern might be observed even though the dioxide phase constituted a small fraction of the total material.

An unusual finding of our investigation is the 2.3 kcal. heat of evolution of hydrogen from the sample at temperatures below 300° C. The heat of dissociation of thorium hydride phases is of the order of 20 to 30 kcal. (11) The heat of desorption of chemisorbed hydrogen from thorium dioxide is also 20 kcal. or more. One would expect hydrogen bound by only a 2.3 kcal. heat of adsorption to be displaced by water molecules or dipolar molecules in the original solution from which the solid was separated.

Probably the freshly prepared material contains adsorbed water or chemisorbed hydrogen. Adsorbed water could be removed by the five-day vacuum drying. The weakly held hydrogen may be liberated on standing by the solid-phase reaction $H^- + OH^- = H_2 + O^{-2}$. Katzin's observation that the quantity of reducing agent present decreased with time is consistent with this hypothesis.

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The initial dried precipitate from our research is believed, therefore, to have the composition $\text{ThC}_{1.0}\text{H}_{1.0}\text{Cl}_{0.7}(\text{OH})_{0.3}$ and that of Karabash to have the composition $\text{ThC}_{1.0}\text{H}_{0.84}\text{Cl}_{0.16}(\text{OH})_{1.0}$. Probably between 10 and 20% of each of these precipitates consists of a separate thorium dioxide phase. The remainder is probably a highly disordered solid solution that gradually changes in composition through the reaction $\text{H}^- + \text{OH}^- = \text{H}_2 + \text{C}^{-2}$. On heating, this reaction is accelerated and all the hydrogen is driven from the solid solution. Thorium metal precipitates as a separate phase, if insufficient oxide and chlorine ions are present to maintain all the thorium in an average oxidation state close to +4.

The materials prepared by the analogous reaction of uranium metal are probably similar, except that the oxidation state of the uranium in the product is about +3, as concluded by Karabash.

Several lines of further study should be of interest. The variation in composition and in properties of metal-hydrochloric acid reaction products with acidity of the solution should be investigated. Studies of the kinetics of decomposition of the reaction products should be made to test the hypothesis of the $\text{H}^- + \text{OH}^-$ reaction proposed here. Analysis of the products of reaction with other acids, especially with hydrofluoric, hydrobromic, and hydroiodic acids, would be of interest. Various measurements sensitive to the nature of the bonds should be used to test the hypothesis made by Karabash and by us that hydrogen is initially present both as hydride ions and as hydroxyl ions. We would welcome work by other investigators.

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LEGEND

Figure 1

Equilibrium pressure of H_2 over (ThO)

