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TRANSPORT REACTIONS OF THORIUM OXYDIODIDE

by

Douglas Guy Adolphson

M.S. Thesis, February 1969

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TRANSPORT REACTIONS OF THORIUM OXYDIODIDE

by

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TRANSPORT REACTIONS OF THORIUM OXYDIODIDE

Douglas Guy Adolphson

ABSTRACT

Traces of a remarkably voluminous red product corresponding to the composition ThOI_2 were found in the cooler ends of the tantalum container in an earlier study of the synthesis and properties of thorium diiodide. Since that time Scaife and co-workers have prepared white ThOI_2 and described some of its properties, but they made no mention of the red modification or the migration of the compound from hotter to cooler zones. In this work white ThOI_2 was obtained by the direct reaction of ThO_2 and ThI_4 in either tantalum or fused silica apparatus. The transport reaction $\text{ThOI}_2(\text{s}) + 2\text{HI}(\text{g}) = \text{ThI}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$ was established as the cause of the migration of the compound to cooler zones. The red modification was obtained when white ThOI_2 was heated in the presence of thorium metal in tantalum apparatus. While the means of coloration is not completely obvious, the evidence suggests that a stoichiometric excess of thorium may be responsible.

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INTRODUCTION

Thorium was discovered by Berzelius (1) in 1828 in a sample of the mineral now known as thorite. Thorium derives its name from the god Thor of Scandinavian mythology. While thorium has some promise as an alloying constituent, its low strength, moderately high density, poor corrosion resistance, and relatively high cost limits its usefulness as a structural material (2). The largest potential use of the metal is in the field of nuclear energy (3, 4). The natural element consists essentially of the isotope ^{232}Th (5). Neutron bombardment of ^{232}Th produces ^{233}Th which has a relatively short half-life and decays to ^{233}U .

The isotope ^{233}U is relatively long-lived and can be made to fission like ^{235}U and ^{239}Pu . The interest aroused by this property of thorium resulted in active work on the element since 1940 and the large scale production of the metal in the early 1950's.

Historically, thorium was the second element which was demonstrated to be radioactive. M. Curie (6) and G. C. Schmidt (7) independently made the discovery in 1898. However, the half-life is sufficiently long (1.39×10^{10} yr) (8) that the nucleus can be regarded as almost

stable. The chemical investigation of thorium is unhampered by the radioactivity, and ordinary chemical methods may be used. Thorium metal is chemically very reactive, particularly at elevated temperatures (2). The enthalpies of formation of thorium compounds are typically greater than those for the corresponding tetravalent compounds of uranium, titanium, chromium, manganese, and tungsten. The oxide and the halides cannot be reduced to the metal with hydrogen at temperatures as high as 2000° . Finely-divided thorium reacts spontaneously with the atmosphere at ambient temperature to form the oxide. Contamination by the atmosphere or by reaction with many containers readily occurs.

The valence electron shells of thorium have the form $6d^2 7s^2$ (9). The formal oxidation state of thorium does not exceed four, and in aqueous solution there is no evidence for a state lower than four. Thorium(III) presumably would reduce water strongly, and at best lower oxidation states would have a transitory existence in water (10). The study of the lower halides of thorium (9) poses a serious experimental problem. They are best made by heating thorium metal with the appropriate tetrahalide, and they are all reactive, hygroscopic substances which are converted to thorium(IV) compounds in the presence of air or moisture. Several reports of reduced thorium halides (11-14) have appeared in the literature; some of

the workers were plagued with poor quality metal or by side reactions with the glass containers or by lack of equilibrium between phases (15). The recent availability of substantially higher purity thorium metal and the superior container material tantalum has permitted accurate investigation of reduced thorium halides. Clark and Corbett (15) prepared metallic, gold-colored thorium diiodide by reacting sublimed thorium tetraiodide and excess, high purity thorium metal in sealed tantalum containers at 800° . Guggenberger and Jacobson (16) have recently determined the crystal structure of thorium diiodide. The structure consists of two-dimensional infinite layers in which the thorium atom is encompassed in alternate layers by trigonal prismatic and trigonal antiprismatic polyhedra of iodine atoms, respectively. Both types of coordination polyhedra are linked by sharing edges. They found that the Th-I distances were the same as those in ThI_4 . This supports the formulation of ThI_2 as $\text{Th}^{4+}(\text{I}^-)_2(\text{e}^-)_2$ predicted by Clark and Corbett (15). Scaife and Wylie (17) have partially characterized three lower iodides of thorium: the triiodide, α -thorium diiodide, and β -thorium diiodide (high temperature form). Thorium triiodide is black. The β -diiodide corresponds to the gold-colored compound prepared by Clark and Corbett, and the α -diiodide is dark-colored. The simi-

larity of the powder patterns of the α - and β -diiodides reported by Scaife and Wylie suggest that the two forms may not be separate phases. In view of the structure (16) Guggenberger and Jacobson suggest that different polytypes might be obtained under different reaction conditions or sample treatment and that Scaife and Wylie's α -diiodide could well be explained in this manner. However, Guggenberger and Jacobson (16) found it difficult to rationalize Scaife and Wylie's 7.13 Å powder line on the basis of a layered structure with an a cell edge similar to that of the β -phase.

Lucas and Rannou (18) have recently obtained the oxyfluoride of thorium(III) by reaction of a stoichiometric mixture of thorium, ThF_4 , and ThO_2 at 1200° in a sealed nickel tube for four days. The compound is neither hygroscopic nor oxidizable at room temperature. The stability of the compound is attributed to the partial substitution of fluoride for oxide in the fluorite lattice. Both ThO_2 and ThOF crystallize in the face-centered cubic system; the lattice parameter of the oxyfluoride is $a = 5.68$ Å as compared with $a = 5.59$ Å for thorium oxide.

In the preparation of thorium diiodide (15), Clark frequently observed a remarkably acicular material at the ends of the reaction vessels, well separated from the metal and the diiodide. The color of the material

ranged from white to red, and it was quite voluminous and had an extremely low effective density. The compound readily dissolved in water without evolution of hydrogen. Partial analytical data suggested that the compound was thorium oxydiiodide. The amount of the oxydiiodide typically observed could have resulted from an average oxygen contamination of the reactants on the order of only 100 ppm. The fact that the ThOI_2 obtained in the thorium diiodide preparations had migrated to the cooler ends of the reaction vessels was puzzling since a preparation of the material by the reaction of thorium tetraiodide and thorium oxide did not show this effect.

The first report of thorium oxydiiodide was made by Chauvenet (19), who thermally degraded $\text{Th}(\text{OH})\text{I}_3 \cdot 10 \text{H}_2\text{O}$ which he had prepared by the evaporation of a solution of $\text{Th}(\text{OH})_4$ in HI. He claims to have prepared $\text{ThOI}_2 \cdot 3.5 \text{H}_2\text{O}$ by drying the product in air and ThOI_2 by drying at 50° in a stream of hydrogen. It is doubtful that he obtained the pure material. Hayek, Rehner, and Frank (12) described the reaction of thorium oxide and thorium tetraiodide at 600° which produced a white, hygroscopic product of composition $\text{ThOI}_{2.06}$. Scaife, Turnbull, and Wylie (20) obtained a product of composition $\text{I/Th} = 2.064$ by reaction of thorium oxide with a 20 percent excess of thorium tetraiodide in a fused silica tube

"in vacuo" at 600° for 60 hours. They examined the compound by X-ray diffraction, optical and electron microscopy, and visible and infrared spectroscopy and described some of the properties of ThOI_2 but made no mention of the red modification or of the migration of the compound to cooler zones as observed by Clark (15). Recently a general preparation (21) has been given for the quadrivalent oxydihalides of thorium, protactinium, uranium and neptunium. Oxydihalides of the type MOX_2 ($X = \text{Cl}, \text{Br}, \text{and I}$) for the four metals were prepared by the reaction of antimony(III) oxide, Sb_2O_3 , with the appropriate tetrahalide at 400° in vacuum. Although the reaction between a particular metal(IV) dioxide and the corresponding tetrahalide is normally an excellent preparative route, this reaction offers an attractive alternative, especially in the case of protactinium since the only satisfactory preparation of protactinium(IV) dioxide at present is the hydrogen reduction of the pentoxide at 1600° .

In following up the earlier observations of Clark, Guidotti (22) obtained white thorium oxydiiodide from the reaction of thorium oxide and thorium tetraiodide. He observed that a substantial amount of the product migrated to the ends of the reaction tube and ascertained that the portion that had migrated and the portion that had not migrated were the same compound. The interconversion of

the red and white modifications was also investigated. The red form of thorium oxydiiodide was always obtained after heating the ThO_2 and ThI_4 reactants or white ThOI_2 in the presence of but not necessarily in contact with excess thorium metal or ThI_2 . This reaction was best carried out in tantalum apparatus. The red form appears to be colored because of a slight reduction. It was established that it can be converted to the white modification by heating with a trace of iodine in Vycor at 300 to 400° or by heating alone in either sealed Vycor or tantalum tubes at 700 to 900°, probably because of a slight outgassing or attack of the walls.

The two modifications appeared to be indistinguishable analytically and are very close to the stoichiometry ThOI_2 ; for the white form: Th = 46.2₇, 46.0₂, 45.8₇% (46.24% theory); I = 50.4₅, 50.4₅, 50.1₁, respectively, (50.57%); I/Th = 1.99₉ average; and for the red form: Th = 46.0₀, 46.3₀; I = 50.3₂, 50.4₅; I/Th = 1.99₇ average. The X-ray powder patterns of the two forms were virtually identical, but close inspection revealed that two lines appeared to be present only in the pattern of the red form ($d = 1.250, 1.142 \text{ \AA}$). The diffraction pattern of the white form was in good agreement with that reported elsewhere (20). The diffuse reflectance spectrum of the white material exhibited what is probably a charge transfer

absorption at 264 to 270 nm and a small, broad band at about 400 nm while the red material showed an additional absorption band at about 542 nm with shoulders at 615 and 430 nm. There was no indication of ThI_4 (445, 400 nm) in either spectrum. The white material gave no esr signal, but the red contained roughly 2×10^{15} spins mole^{-1} with a g value nearly equal to two. If this number represents the difference between the two forms (22), then their analytic similarity and ease of interconversion is quite reasonable.

Throughout this work both the red and the white forms of ThOI_2 were observed to migrate to the ends of the tubes in varying amounts. The erratic nature of the process suggested that perhaps a transport reaction rather than congruent volatilization was involved. The clarification of this possibility was the purpose of this thesis.

Schäfer (23) has given a comprehensive review of transport phenomena. The term "chemical transport reaction" is used to describe a reaction involving the migration of a solid or a liquid via the gas phase as a result of heterogeneous equilibria. A solid or liquid substance A reacts with a gas B to form exclusively gaseous products, which, in turn, undergo the reverse reaction at a different place in the system to reform substance A.

Although the net process appears similar to sublimation or distillation, at the applied temperatures substance A does not possess an appreciable vapor pressure but rather undergoes chemical transport. A concentration gradient is involved as well as a reversible heterogeneous reaction. This concentration gradient can be a result of temperature gradients, changes in relative pressure, or differences in the free energy of formation of two substances. It is clear that transport of a solid substance presupposes a motion of gas. Processes which involve gas stream diffusion or thermal convection can be distinguished. If the reverse reaction proceeds rapidly and extensively with deposit of solid substance, the use of open tubes and simple flow techniques is advantageous. In all other cases, closed diffusion or convection tubes are used. In the pressure range of about 10^{-3} to three atmospheres the gas motion is essentially determined by diffusion in a properly designed apparatus. At pressures higher than this thermal convection must be taken into consideration. In most cases the rate of reaction is high compared with the gas diffusion so that the diffusion is the rate determining step as far as the transport effect is concerned. The amount of material transported depends on the partial pressure difference between the starting and the final solid substance. If the partial pressure dif-

ference is large, a relatively rapid transport generally occurs. Schäfer, Jacob, and Etzel (24) have calculated ΔP (as a measure of the transport effect) as a function of ΔH° for several values of ΔS° . For moderate absolute values of ΔH° the transport effect is larger for a larger absolute value of ΔS° . Transport does not occur to an appreciable extent for a large absolute value of ΔH° . The sign of ΔH° determines the direction of the transport; exothermic reactions transport from cooler to hotter zones while the reverse occurs for endothermic reactions.

Chemical transport reactions have been known for a long time. Bunsen (25) mentioned that the migration of Fe_2O_3 in volcanic gases is caused by the hydrogen chloride content of the gas. The controlling reaction is

Similar reactions were observed by Sainte-Claire Deville (26) for SnO_2 , TiO_2 , and MgO . Troost and Hautefeuille (27, 28) transported silicon with SiCl_4 and aluminum with AlCl_3 . These reactions are explained as the formation and disproportionation of the subchlorides:

In fact the naming of the class of reactions acknowledges the precedent of Troost and Hautefeuille who described the migration of silicon in the presence of SiCl_4 as a "transport."

A second period of investigation began in 1925 when van Arkel and de Boer (29) developed an iodide process for purifying metals which involves the vaporization of the metal as the iodide followed by decomposition of the iodide on a hot filament. The process has been applied to many metals and has become extremely well known and is of great practical importance. The investigation of transport phenomena continues to be an active field today. Transport reactions hold great potential for practical application in that they often provide a convenient means of purifying a substance and that as a rule, the substance is obtained as well-defined crystals.

EXPERIMENTAL PROCEDURE

Preparation of Thorium Tetraiodide

Thorium tetraiodide was prepared by reacting thorium metal with a 20 percent excess of iodine in a fused silica tube. The thorium metal was cut from a billet of Ames Laboratory thorium. Spectrographic impurity analysis showed 110 ppm N, 770 ppm C, 115 ppm Be, and 75 ppm Fe; oxygen was not determined, and other metals were below the limits of spectrographic detection. The iodine was resublimed Certified A. C. S. grade supplied by Fisher Scientific Co. For the preparation the tube was baked out under high vacuum (about 10^{-5} torr), and then the iodine was placed at the lower end of the tube and the thorium was placed in a fused silica cup at the upper end of the tube. The tube was positioned vertically, evacuated to a pressure of less than about 10^{-3} torr, and sealed off. The upper end of the tube was heated at 600° , and the lower end was heated at 120° . After three hours the temperature of the upper end of the tube was raised to 700° and that of the lower end to 150° . After the reaction had gone to completion, the excess iodine was condensed into an ampule attached to the lower end of the tube, and ampule was sealed off at a constriction. The product was obtained as dirty yellow needles clinging to the sides of the tube at the junction of the two furnaces.

The thorium tetraiodide was purified by sublimation. A fused silica sublimation tube was baked out under high vacuum at 850° , and then the crude thorium tetraiodide was transferred to it in an argon-filled glove box. Argon within the box was continuously circulated through a Linde Molecular Sieve in order to assure its dryness, and an open pan of P_4O_{10} in the glove box further assured a low level of moisture. The sublimation, which was carried out under dynamic vacuum (about 10^{-5} torr) at 500° , produced canary yellow crystals.

Preparation of Thorium Oxydiiodide

Thorium oxydiiodide was obtained by direct reaction of thorium oxide and thorium tetraiodide. The thorium oxide was prepared by igniting thorium oxalate with a Meeker burner for five minutes followed by degassing in high vacuum at 950° for 20 hours. The thorium oxide was mixed with a 20 percent excess of sublimed thorium tetraiodide in the glove box, and the reactants were transferred to a fused silica tube. After removing the tube from the glove box, it was evacuated and sealed off and heated at 780° for several days. Finally, the excess ThI_4 was sublimed from the product at 530° . In one preparation a tantalum tube was loaded with a stoichiometric mixture of ThO_2 and ThI_4 in the glove box. The tube was transferred to the welder in a closed container, evacuated

in the welder, and welded shut under about 0.5 atmosphere of a helium-argon mixture. The tube was then sealed within an evacuated Vycor jacket and heated at 780° for several days. The product was comparable to that obtained in glass in the presence of excess tetraiodide.

Generation of Hydrogen Iodide for Transport Studies

In order to investigate the effect of hydrogen iodide on the observed migration of ThOI_2 to the cooler end of a closed tube (15), hydrogen iodide was introduced to fused silica or tantalum tubes containing ThOI_2 which had been carefully handled to avoid contamination, and the tubes were heated in a temperature gradient for several days. The HI was generated by the reaction of 48.2 percent hydriodic acid with P_4O_{10} at -78° in an evacuated system. It was dried further by condensation on P_4O_{10} in a trap at liquid nitrogen temperature. The tube into which the ThOI_2 was placed in the glove box was connected to the vacuum line and evacuated, and then three torr of HI (30) was admitted to the tube by allowing the trap containing condensed HI to warm up to -111° , the temperature of a carbon disulfide slush (31). One-half atmosphere of argon was then admitted to the tube through a trap cooled with liquid nitrogen, and the tube was sealed off and heated in a $780-850^{\circ} \rightarrow T_1$ gradient

for about a week. In the case of tantalum the tube was electron-beam-welded to a Kovar-to-glass seal so that the tube could be connected to the vacuum system. In order to avoid contamination and loss of HI during transfer to or evacuation in the welder, the metal part of the tube was crimped and the glass part was sealed off. After welding at the crimp the tantalum tube was sealed in an evacuated Vycor jacket, and the assembly was heated in a temperature gradient. The temperature gradient within the furnace was measured with a Minneapolis-Honeywell potentiometer equipped with a Chromel-Alumel thermocouple. The actual gradient within the tube was certainly less than the one in the furnace, particularly in the case of a tantalum container.

Generation of Hydrogen

In order to determine the effect of heating ThOI_2 with hydrogen, pure hydrogen was produced from uranium hydride and sealed with ThOI_2 in either fused silica or tantalum tubes, and the tubes were heated at 750° for several days. The UH_3 was prepared by heating uranium in a fused silica tube at 250° under one atmosphere of hydrogen for an hour. The container was first baked out at 850° to eliminate as much water as possible. Uranium metal was cut into small pellets which were cleaned with

dilute nitric acid and dried under vacuum. The uranium pellets were transferred to the reaction tube in the glove box. The reaction tube was removed from the glove box and evacuated to high vacuum for two hours. Hydrogen was admitted to the tube through a liquid nitrogen trap, and the tube was heated to produce uranium hydride.

When uranium hydride is heated (32) above about 250° , it loses hydrogen; the pressure is a function of the temperature. Hydrogen produced in this manner should be free of water since UH_3 reacts vigorously with water to form hydrogen and UO_2 . After the UH_3 had been prepared, the reaction tube was allowed to cool and was then evacuated in high vacuum at room temperature for two hours. Approximately one-half atmosphere of hydrogen was produced by heating the UH_3 to 425° , and the hydrogen was allowed to expand through the vacuum system to either a fused silica or tantalum tube containing ThOI_2 . Finally, the tube was sealed and heated at 750° for several days. Again in the case of tantalum, the tube was electron-beam-welded to a Kovar-to-glass seal so that it could be connected to the vacuum line. The tantalum tube was likewise placed in an evacuated jacket before it was heated.

In one experiment the effect of heating ThOI_2 with hydrogen produced within the system was compared with that of heating ThOI_2 with externally produced hydrogen. A

fused silica tube with a constriction near the center was baked out at 850° , taken into the glove box, and loaded with ThOI_2 at one end and uranium at the other end. The end of the tube containing the uranium was heated at 250° under one atmosphere of hydrogen for an hour to generate UH_3 . The tube was allowed to cool and was evacuated in high vacuum for two hours and sealed off at the ball joint connecting it to the vacuum line. The tube was sealed into a jacket along with a thermometer which was positioned to read the temperature at the end of the tube containing the UH_3 . The end of the tube containing the ThOI_2 was heated at 750° , and the end containing the UH_3 was heated at 350° in order to generate hydrogen.

Analytical Methods

X-ray powder photography was used to identify substances before and after heating in a temperature gradient with or without a transporting agent. Samples were ground in the glove box and loaded in 0.3 mm Lindemann glass capillaries. The capillaries were sealed with Apiezon Q in the glove box and then sealed with a hot flame in the air. Diffraction patterns were determined using a Phillips Debye-Scherrer powder camera with a diameter of 114.59 mm and $\text{Cu K}\alpha$ radiation which had passed through a nickel filter. Line spacings were read for comparison

with the previously reported powder pattern (20) using a template which directly gave interplanar spacings for the camera and radiation involved. Intensities were judged visually.

EXPERIMENTAL RESULTS AND DISCUSSION

The Transport Reaction of White Thorium Oxydiiodide

The unpredictable nature of the migration of ThOI_2 in the synthesis and interconversion reactions first studied suggested that a transport reaction resulting from contamination with traces of moisture and hence hydrogen iodide might be responsible. Indeed it was shown that transport did not occur when extensive precautions were taken to prevent contamination from the atmosphere whereas transport did occur when HI was purposely introduced.

Rigorously clean containers, dry box transfers, and vacuum techniques were used throughout this work in an effort to prevent contamination. In two separate synthesis reactions ThOI_2 was obtained as a compacted matte of white crystals. No transport was observed in either preparation. The compound prepared in the first synthesis was divided and placed in two separate tantalum tubes which were heated in a $850\text{-}550^\circ$ temperature gradient for four and six days, respectively (the actual gradient was certainly less within the metal containers). Neither sample showed signs of transport. A portion of ThOI_2 obtained from the second preparation was then simultaneously heated as a control in a $780\text{-}530^\circ$ gradient for three days along with a separate portion to which three torr of HI had been admitted. The control sample did not transport;

however, about one-fourth of the sample which was heated in the presence of HI transported to the cooler end of the tube. The material which transported appeared as the acicular white crystals noted by prior workers (15, 20). It was also verified that a sample which has been transported can be transported again upon the addition of more HI. A sample which was exposed to air and subsequently heated in a 780-530° gradient also underwent transport. Addition of 12 torr of carbon monoxide and one-half atmosphere of argon to a tantalum tube containing ThOI₂ did not result in transport.

The transport of ThOI₂ was not particularly large (10 to 30 mg day⁻¹) under the typical experimental conditions of heating ThOI₂ with three torr of HI and 0.5 atmosphere of argon in fused silica or tantalum tubes in a 850-600° or a 780-530° temperature gradient for several days. The amount of mass transported was larger with the 850-600° gradient and with longer heating periods.

The evidence supports the occurrence of the endothermic transport reaction

The standard enthalpy change for Equation 1 is 43 kcal mole⁻¹. At 1000° K the enthalpy change for this reaction is about 45 kcal mole⁻¹ (22) using standard data for HI

and H_2O (33), recent data for solid ThI_4 and ThOI_2 (20), and the heat capacity. Although the magnitude of ΔH_{1000}^0 is quite large, the increase in the number of molecules and the mass in the gas phase make the entropy change also rather positive, greater than 13 eu (22) using similar data and approximations (33-36). The value of K_{1000} for Equation 1 is then of the order 10^{-7} . The equilibrium constant increases with temperature. The expression $\ln \left(\frac{K_1}{K_2} \right) = \frac{-\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$ gives $\frac{K_{1123}}{K_{1053}} =$

3.6. Transport yields in experiments carried out at those two temperatures verify that this is in the right direction.

The understanding of this transport reaction is hampered by the lack of adequate thermodynamic data. However, an idea of the relative pressures of the gases involved is obtained by noting that for an inert container the pressure of ThI_4 is fixed by the equilibrium

and the difference of Equation 2 and Equation 1 defines the equilibrium involving the other gaseous species.

The estimated value of K_{1000} for Equation 3 is about 850 (22). With three torr of HI added $P_{\text{H}_2\text{O}}$ is 7×10^{-5} torr, and P_{H_2} from dissociation of HI is 1.6 torr (22). When

tantalum is used for the container, traces of gaseous TaI_5 (or TaOI_3) are presumably formed by reaction with HI (and H_2O) although solid Ta_2O_5 will not be formed if the reaction of HI with the tantalum increases the $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$ ratio by a factor of 10^2 over that for an inert container. This condition appears to hold in the synthesis of ThOI_2 by heating ThI_4 and tantalum foil in Vycor (22). The net reaction observed here is evidently $5 \text{SiO}_2 + 10 \text{ThI}_4 + 14 \text{Ta} = 4 \text{TaI}_5 + 5 \text{Ta}_2\text{Si} + 10 \text{ThOI}_2$.

The Red Form of Thorium Oxydiiodide and its Transport Reaction

The previously reported red form of ThOI_2 (15) was again obtained by heating ThOI_2 along with a strip of thorium foil in the presence of three torr of HI and 0.5 atmosphere of argon in a tantalum tube in a $800\text{--}550^\circ$ temperature gradient for seven days. The transported product was red whereas the material that did not transport remained colorless.

The presence of thorium metal implies that ThO_2 is no longer a component of the system. Heating thorium in the presence of HI leads to the formation of ThI_2 (15).

The reaction

is known to occur (15) at these temperatures (i.e., the

reverse does not occur) thus eliminating ThO_2 from the system. The pressure of ThI_4 is larger above ThI_2 than it is above ThOI_2 and is fixed by the disproportionation of ThI_2 .

The transport reaction is probably governed by equilibria 6 and 7

in the hotter zone followed by the reverse of reaction 1 in the cooler zone. The value of K_{1000} for Equation 7 should be less than the value of 10^{-17} (37) calculated for the reaction

The means of coloration is not completely obvious. The red modification appears to result from a slight reduction. A trace of volatile, reduced thorium species could be involved although there is no direct evidence for this. No volatilization or transport of ThI_2 or ThI_3 has been noted in tantalum containers up to 850° (15). Both ThI_2 and ThI_3 attack glass above 550° (15) and while volatilization of ThI_3 has been suggested (17), the possibility of a transport reaction has not been eliminated. The high

ratio of hydrogen to water indicated by equilibrium 7 suggests a slight reduction of ThOI_2 by very pure hydrogen. Obviously, tank hydrogen is not likely to meet such a stringent water limit, but hydrogen produced by heating UH_3 and then sealed with ThOI_2 in fused silica or tantalum tubes failed to produce the coloration. The same result was obtained when hydrogen was produced by heating UH_3 to obtain hydrogen in a sealed fused silica tube containing ThOI_2 heated at 750° at the other end. It is questionable whether hydrogen with a sufficiently low water content to cause the coloration can be obtained in either case.

It is clear that hydrogen iodide is important in the transport of thorium oxydiiodide to a cooler zone within a closed tube. It has been shown that ThOI_2 which has been carefully prepared and handled to prevent contamination from the atmosphere does not undergo transport when it is heated in a $780\text{--}850^\circ \rightarrow T_1$ temperature gradient. However, transport does occur when HI is introduced to a similar sample of ThOI_2 and the latter is heated in the same gradient. At the time of writing, an explanation for the observed red coloration of ThOI_2 is less clear. The red modification may be compared with the blue crystals of ThO_2 which are obtained when ThO_2 is heated to 1700° in hydrogen (38). However, the fact that the transitions

observed in the ThO_2 are in part at lower energies than in the red ThOI_2 suggest (22) that the coloration mechanisms may not be comparable. Subsequent oxidation of the blue dioxide at 1000° in air gives a tan product with a new band at 306 nm.

BIBLIOGRAPHY

1. J. J. Berzelius, Kgl. Svenska Vetenskapsakad Handl., 9, 1 (1829); Pogg. Ann., 16, 385 (1829). Originals not available; cited by L. I. Katzin in The Chemistry of Thorium, G. T. Seaborg and J. J. Katz, eds., The Actinide Elements, p. 66, New York, New York, McGraw-Hill Book Co., Inc., 1954.
2. H. A. Wilhelm, Thorium, in H. M. Finneston and J. P. Howe, eds., Progress in Nuclear Energy, Series V, Metallurgy and Fuels, Vol. I, p. 205, London, England, Pergamon Press, Ltd., 1956.
3. L. I. Katzin, The Chemistry of Thorium, in G. T. Seaborg and J. J. Katz, eds., The Actinide Elements, p. 66, New York, New York, McGraw-Hill Book Co., Inc., 1954.
4. J. V. Dunworth, The Possible Role of Thorium in Nuclear Energy, Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955, P/867, Vol. I, p. 335, United Nations, New York, New York, 1956.
5. G. T. Seaborg, Introduction, in G. T. Seaborg and J. J. Katz, eds., The Actinide Elements, p. 3, New York, New York, McGraw-Hill Book Co., Inc., 1954.
6. M. Curie, C. R. Acad. Sci., Paris, 126, 1101 (1898).
7. G. C. Schmidt, Wied. Ann., 65, 141 (1898). Original not available; cited by G. T. Seaborg, Introduction, in G. T. Seaborg and J. J. Katz, eds., The Actinide Elements, p. 3, New York, New York, McGraw-Hill Book Co., Inc., 1954.
8. A. F. Kovaric and N. I. Adams, Phys. Rev., 54, 413 (1938).
9. A. K. Molodkin and O. M. Ivanovna, Russian J. Inorg. Chem., 11, No. 11, 1318 (1966).
10. J. J. Katz and I. Sheft, Halides of Actinide Elements, in H. J. Emeléus and A. G. Sharpe, Advances in Inorganic Chemistry and Radiochemistry, Vol. 2, p. 195, New York, New York, Academic Press, 1960.

11. J. W. M. D'Eye and J. S. Anderson, J. Chem. Soc., S-244 (1949).
12. E. Hayek, Th. Rehner, and A. Frank, Monatsh. Chem., 82, 575 (1951).
13. G. Jantsch, T. Homayr, and F. Zemack, Monatsh. Chem., 85, 526 (1954).
14. G. W. Watt, D. M. Sowards, and S. C. Malhotra, J. Amer. Chem. Soc., 79, 4908 (1957).
15. R. J. Clark and J. D. Corbett, Inorg. Chem., 2, 460 (1963).
16. L. J. Guggenberger and R. A. Jacobson, Inorg. Chem., 7, 2257 (1968).
17. D. E. Scaife and A. W. Wylie, J. Chem. Soc., 5450 (1964).
18. J. Lucas and J. Rannou, C. R. Acad. Sci., Paris, Ser. C, 266, 1056 (1968).
19. E. Chauvenet, Ann. Chim. Phys., 23, 472 (1911).
Original available but not translated; abstracted in Chem. Ab., 6, 45 (1912).
20. D. E. Scaife, A. G. Turnbull, and A. W. Wylie, J. Chem. Soc., 1432 (1965).
21. K. W. Bagnall, D. Brown, and J. F. Easey, J. Chem. Soc. (A), 288 (1968).
22. J. D. Corbett, R. A. Guidotti, and D. G. Adolphson, to be published in Inorg. Chem., ca. January, 1969.
23. H. Schäfer, Chemical Transport Reactions, New York, New York, Academic Press, 1964.
24. H. Schäfer, H. Jacob, and K. Etzel, Z. anorg. allgem. Chem., 286, 42 (1956).
25. R. Bunsen, J. prakt. Chem., 56, 53 (1852).
26. H. Sainte-Claire Deville, Ann., 120, 176 (1861).
Original not available; cited by H. Schäfer, Chemical Transport Reactions, New York, New York, Academic Press, 1964.

27. L. Troost and P. Hautefeuille, *Ann. Chim. Phys.*, (5), 7, 452 (1876).
28. L. Troost and P. Hautefeuille, *C. R. Acad. Sci.*, Paris, 100, 1220 (1885).
29. A. E. van Arkel and J. H. de Boer, *Z. anorg. allgem. Chem.*, 148, 345 (1925).
30. J. R. Bates, J. O. Halford, and L. C. Anderson, *J. Chem. Phys.*, 3, 415 (1935).
31. W. L. Jolly, *Synthetic Inorganic Chemistry*, Englewood Cliffs, New Jersey, Prentice-Hall, Inc., 1960.
32. G. Brauer, ed., *Handbook of Preparative Inorganic Chemistry*, 2nd. ed., Vol. 2, New York, New York, Academic Press, 1965.
33. JANAF Thermochemical Tables, Dow Chemical Co., Midland, Michigan, 1964.
34. Selected Values of Chemical Thermodynamic Properties, National Bureau of Standards, Circ. 500, Series II, Table 83-1, U.S. Government Printing Office, Washington, D. C., 1950.
35. K. K. Kelley, U. S. Bureau of Mines Bulletin, 584, 189 (1960).
36. K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin, 592, 115 (1961).
37. O. Kubaschewski, E. L. L. Evans, and C. B. Alcock, *Metallurgical Thermochemistry*, London, England, Pergamon Press, Ltd., 1967.
38. J. L. Bates, Report BNWL - 457, Battelle-Northwest Laboratory, Richland, Washington, July, 1967.

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