

material, reduction to Ir(III) by the ligand must accompany complexation.

PAPHY appears to be bidentate in I, II, and IV.  $\text{Ir}(\text{C}_{11}\text{H}_{10}\text{N}_4)_3^{3+}$ , the cation in I, is the analog of the Rh(III) complex ion described earlier.<sup>1</sup> The isolation of the *cis*-dichloro complex, II, is an illustration of the kinetic inertness to substitution shown by cationic complexes of iridium. Four of the chlorines in  $\text{IrCl}_6^{3-}$  are replaced by two bidentate PAPHY molecules to produce the *cis*-dichlorobis(pyridine-2-carboxaldehyde 2'-pyridylhydrazone)iridium(III) cation, but further substitution of chlorines appears to be difficult. It has been reported that 1,10-phenanthroline reacts with  $\text{IrCl}_6^{3-}$  to give similarly the *cis*-dichlorobis(1,10-phenanthroline)iridium(III) cation.<sup>8</sup>

The coordination behavior of PAPHY toward the three members of the cobalt subgroup in an oxidation state of +3 has now been established. Toward Co(III), it is tridentate.<sup>9</sup> Toward Rh(III), it can be either tri- or bidentate, although the tris complex containing bidentate PAPHY is labile in aqueous solution and readily changes to the bis complex. In three of the Ir(III) complexes reported here PAPHY appears to be bidentate, but tridentate in complex III.

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## The Red and White Forms of Thorium Oxydiiodide and Their Transport Reactions<sup>1</sup>

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During an earlier study<sup>2</sup> of the synthesis and properties of the metallic thorium diiodide, traces of a remarkably voluminous, red product were found in the cooler ends of the tantalum container, well separated

from the diiodide and thorium metal. Analytically, the material corresponded to the composition  $\text{ThOI}_2$ , and the amounts obtained were typically such as would result from an average oxygen contamination of only 100 ppm in the reactants. Since that time Scaife and coworkers<sup>3</sup> have described some of the properties of  $\text{ThOI}_2$  as prepared by the direct reaction of thorium oxide and excess tetraiodide in a silica container at 600° followed by removal of the unreacted tetrahalide under vacuum. Their results contrasted with our earlier observations in two respects: their product was white rather than red, and they made no mention of the apparent sublimation or transport of the compound to cooler zones. The present paper describes work done to clarify the synthesis and interconversion reactions of the white and red forms and the character of the transport reaction.

### Results and Discussion

**Synthesis Reactions.**—As before,<sup>3</sup> the *white*, acicular  $\text{ThOI}_2$  is easily obtained by the direct reaction of unsintered  $\text{ThO}_2$  and excess  $\text{ThI}_4$  (or the elements), at 780–850° for several days followed by vacuum sublimation of the excess halide at 530°. In Vycor containers small amounts of  $\text{SiI}_4$  and  $\text{ThO}_2$  (on the walls) are sometimes produced by extensive heating at or above 850°, and the attack becomes substantial by 1000°. Tantalum is a generally more satisfactory container.

The *red* modification is always (and, to date, only) obtained after heating  $\text{ThO}_2$  and  $\text{ThI}_4$  reactants or white  $\text{ThOI}_2$  in the presence of, but not necessarily in contact with, excess thorium metal (or  $\text{ThI}_2$ ). This reaction is best accomplished in tantalum though on rare occasions the red form has been obtained in a Vycor apparatus. Oxide on the thorium (or tantalum) can also function as the sole oxygen source although at these temperatures the oxygen solubility and diffusion rate in thorium are too low to allow purification of more than the surface.

With either the red or the white form the product is usually found as a compact mat in which crystal growth is evident and as a crystalline mass of very low density which has obviously sublimed or been transported to the cooler end of the container. This transport also allows the colorless form to be separated after more complex reactions wherein silica furnishes the oxygen, such as from  $\text{SiO}_2$  plus  $\text{ThI}_4$  in tantalum at 850° or from  $\text{ThI}_4$  plus thorium or tantalum in Vycor at 860° for several days. The second type of reaction with tantalum present gives the clearest indication of the course of the reaction. At least as long as  $\text{ThI}_4$  is in excess, the  $\text{ThOI}_2$  together with  $\text{Ta}_2\text{Si}$  are found on the tantalum while the volatile  $\text{TaI}_5$  occurs throughout. The silica is transported to the metal, probably as  $\text{SiI}_4$  and  $\text{TaOI}_3$  judging from the simpler  $\text{Ta}-\text{I}_2-\text{SiO}_2$  system.<sup>4</sup> The net reaction in the present system

(3) D. E. Scaife, A. G. Turnbull, and A. W. Wylie, *J. Chem. Soc.*, 1432 (1965).

(4) H. Schäfer, E. Schibilla, R. Gerken, and H. Scholz, *J. Less-Common Metals*, **6**, 239 (1964).

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would be  $5\text{SiO}_2 + 10\text{ThI}_4 + 14\text{Ta} = 4\text{TaI}_5 + 5\text{Ta}_2\text{Si} + 10\text{ThOI}_2$ .

The red form is evidently colored because of a slight reduction and hence can be converted to the white, oxidized modification by heating with a trace of iodine at  $300\text{--}400^\circ$  or by heating alone in sealed Vycor or tantalum containers at  $700\text{--}900^\circ$ , probably because of a slight outgassing or attack of the walls. The conversion of white to red  $\text{ThOI}_2$  is *not* accomplished by hydrogen at  $500\text{--}1000^\circ$  or aluminum at  $850^\circ$ .

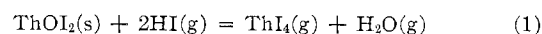
**Properties of  $\text{ThOI}_2$ .**—Both forms after transport usually dissolve completely in water without gas evolution. The untransported products may yield a precipitate of  $\text{ThO}_2$  but this is eliminated if they are heated further with  $\text{ThI}_4$ . The red oxyiodide also gives a small oxide precipitate if it has been made by heating the stoichiometric white form with thorium because of equilibrium dissociation to gaseous  $\text{ThI}_4$  which occurs in the process. Analytically the two modifications appear indistinguishable and very close to the simple stoichiometry; for white, Th = 46.27, 46.02, 45.87% (theory 46.24%); I = 50.45, 50.45, 50.11% (theory 50.57%); I/Th = 1.999 average; for red, Th = 46.00, 46.30; I = 50.32, 50.45; I/Th = 1.997 average. An approximate oxygen analysis by the inert gas fusion method gave 3–6% which compares with a theoretical 3.2%. The previously<sup>3</sup> reported I/Th ratio of 2.064 was presumed to have been high because of excess  $\text{ThI}_4$ . Powders of the two materials appear qualitatively identical with X-rays. The diffraction data are in good agreement with those reported earlier,<sup>3</sup> but close inspection reveals that two lines appear to be present only in the pattern of the red form ( $d = 1.250, 1.142 \text{ \AA}$ ).

The diffuse reflectance spectrum of the white material exhibits what is probably charge-transfer absorption at 264–270 nm, together with a small, broad band at about 400 nm. The red shows an additional absorption band at 542 nm with shoulders at 615 and 430 nm. There is no indication of  $\text{ThI}_4$  (445, 400 nm) in either. The white material gives no signal in esr measurements, but the red contains very roughly  $2 \times 10^{15}$  spins  $\text{mol}^{-1}$  with a  $g$  value close to 2. If this number represents the entire difference between the two forms, their analytic similarity and the ease of oxidation of the red modification by trace impurities is quite reasonable.

**Transport Reaction.**—The occurrence of an apparent sublimation of  $\text{ThOI}_2$  to the cooler end of the container during the above synthesis and interconversion reactions was erratic and unpredictable. The process appears to be a chemical-transport reaction<sup>5</sup> which results after adventitious contamination with traces of moisture and hence hydrogen iodide during handling and storage of the samples. Transport was not observed when extensive precautions were taken against contamination whereas transport did occur when HI was purposely introduced. In the latter case 3 torr

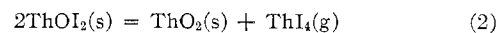
of HI together with 0.5 atm of helium or argon was typically introduced into Vycor or tantalum tubes containing the oxyiodide, and the tubes were sealed and heated in a furnace with a  $780\text{--}530$  to  $850\text{--}600^\circ$  gradient for several days. (The actual gradients were certainly less with the metal containers.) The transport reaction is relatively slow under these conditions, 10–30 mg/day. The same effects are observed when transported material is reused. Transport does not result with CO or with HI at only  $650^\circ - T_1$ , whereas it does after purposeful contamination with air. The red form is again obtained if thorium metal is present.

The evidence supports the occurrence of the endothermic transport reaction

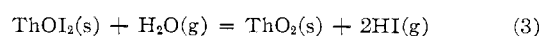


The enthalpy change for this is about 45 kcal at  $1000^\circ\text{K}$  based on standard data for HI and  $\text{H}_2\text{O}$ ,<sup>6</sup> recent values at  $298^\circ\text{K}$  for solid  $\text{ThI}_4$  and  $\text{ThOI}_2$ ,<sup>3</sup> the heat of vaporization,<sup>7</sup> and an estimated heat of fusion of 8 kcal for  $\text{ThI}_4$ . ( $H_{1000} - H_{298}$  increments for  $\text{ZrI}_4$ <sup>6</sup> were substituted for  $\text{ThI}_4$  and in the mean of the  $\text{ThO}_2$  and  $\text{ThI}_4$  data used for the oxyiodide.) Although the magnitude of  $\Delta H_{1000}^\circ$  is relatively large, the distribution of mass makes the entropy change likewise rather positive,  $> \sim 13$  eu at  $1000^\circ\text{K}$  using similar data<sup>6–8</sup> and approximations. The value of  $K_{1000}$  is then of the order of  $10^{-7}$ .

It will be noted that the (unknown) pressure of  $\text{ThI}_4$  is fixed by the equilibrium



and pressures of the other gaseous species in an inert container are defined by the difference of eq 1 and 2



for which  $K_{1000}$  is about 850 from available data<sup>3,6,8</sup> and estimates as before. With the typical amount of HI added  $P_{\text{H}_2\text{O}}$  is  $7 \times 10^{-5}$  torr, and  $P_{\text{H}_2}$  from dissociation is 1.6 torr. In the presence of the tantalum container traces of gaseous  $\text{TaI}_5$  (or  $\text{TaOI}_3$ ) are presumably formed from the HI (and  $\text{H}_2\text{O}$ ), but solid  $\text{Ta}_2\text{O}_5$  will not be formed<sup>9</sup> if the reaction of HI with tantalum increases the  $P_{\text{H}_2}/P_{\text{H}_2\text{O}}$  ratio by a factor of  $10^2$  over that present in an inert container. This condition appears to hold with the Ta– $\text{ThI}_4$ – $\text{SiO}_2$  reaction cited earlier. The transport in tantalum is perhaps slightly slower than in glass, as expected from the above considerations.

Rather different conditions apply when thorium metal is present since the typical amount of HI employed should lead to the formation of  $\text{ThI}_2$ . The

(6) "JANAF Thermochemical Tables," Dow Chemical Co., Midland, Mich., 1964.

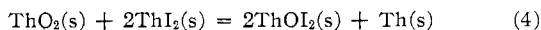
(7) "Selected Values of Chemical Thermodynamic Properties," National Bureau of Standards Circular 500, U. S. Government Printing Office, Washington, D. C. 1950, Series II, Table 83-1.

(8) K. K. Kelley, U. S. Bureau of Mines Bulletin 584, U. S. Government Printing Office, Washington, D. C., 1960, p 189; K. K. Kelley and E. G. King, U. S. Bureau of Mines Bulletin 592, U. S. Government Printing Office, Washington, D. C., 1961, p 115.

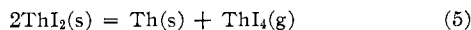
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(5) H. Schäfer, "Chemical Transport Reactions," Academic Press, New York, N. Y., 1964.

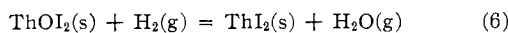
presence of  $\text{ThI}_2$  means that  $\text{ThO}_2$  is no longer a component of the system since the reaction



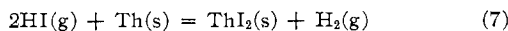
is known to occur at these temperatures.<sup>2</sup> In this case the pressure of  $\text{ThI}_4$  is larger and fixed by the disproportionation of  $\text{ThI}_2$



The transport reaction now is probably governed by equilibria 5 and 6 in the hot zone followed by the same



reverse of reaction 1 in the colder zone and at the metal



The necessary thermodynamic data for  $\text{ThI}_4$  and  $\text{ThI}_2$  are not available, but it will be noted that the value of  $K_{1000}$  for eq 6 will be less than the  $10^{-17}$  calculated<sup>9</sup> for the couple  $\text{ThO}_2(\text{s})\text{-Th}(\text{s})$ . (It is assumed that neither thorium nor tantalum has a substantial effect on the hydrogen pressures in the above systems since neither absorbs hydrogen very strongly at these temperatures.) The very low  $P_{\text{H}_2\text{O}}$  so estimated is consistent with the markedly slower transport of  $\text{ThOI}_2$  in the presence of thorium, the reverse of reaction 1 in the colder zone being controlling. In fact, one may question whether a different transport reaction may be involved which is insignificant in the absence of thorium. However, no direct evidence for such is available, and the addition of HI is clearly important in the presence of thorium as well.

The means by which the red and apparently slightly reduced form is colored during the transport process is by no means obvious. At the possible impurity levels indicated, a trace of a volatile, reduced thorium species could be involved although there is no direct evidence for such. No volatilization or transport of  $\text{ThI}_2$  or  $\text{ThI}_3$  has ever been noted in tantalum containers up to  $850^\circ$ .<sup>2</sup> The attack of these materials on glass becomes important above about  $550^\circ$ <sup>2</sup> and although vaporization of  $\text{ThI}_3$  has been suggested to be responsible,<sup>10</sup> the possibility that conventional transport reactions may instead be involved has not been eliminated. On the other hand, the extremely high ratio of hydrogen to water indicated in the presence of thorium or  $\text{ThI}_2$  suggests a slight reduction of  $\text{ThOI}_2$  by very pure hydrogen. Obviously tank hydrogen is not likely to meet such a stringent water limit, but hydrogen generated from  $\text{UH}_3$  and sealed with  $\text{ThOI}_2$  in Vycor or tantalum containers which had first been baked out at  $800^\circ$  does not produce the coloration either. However, it is questionable whether a water content of the order of  $10^{-11}$  ppm can be obtained in hydrogen handled under any conditions rather than generated within a closed system.

The red form of  $\text{ThOI}_2$  may be compared with the blue crystals of  $\text{ThO}_2$  which are obtained when the dioxide is heated to  $1700^\circ$  in hydrogen.<sup>11</sup> The fact

that the transitions observed in  $\text{ThO}_2$  are in part at lower energies (710 and 403 nm) than in red  $\text{ThOI}_2$  suggests that the coloration mechanisms may not be very comparable. Subsequent oxidation of the blue dioxide in air at  $1000^\circ$  produces a tan sample with a new band at 306 nm.

#### Experimental Section

Materials, techniques, and analytical methods were similar to those employed earlier.<sup>2</sup> A reactive form of  $\text{ThO}_2$  was prepared by heating the oxalate (a precursor of the high-purity metal) with a Meeker burner for several minutes. Reflectance spectra were secured with 100-mesh samples diluted with strongly ignited  $\text{ThO}_2$ . Data were taken from the cutoff at 216–218 nm to 1200 nm on a Beckman DU instrument with a no. 2580 reflectance attachment.

Gaseous HI for the transport studies was generated by the reaction of aqueous HI with  $\text{P}_4\text{O}_{10}$  at  $-78^\circ$  and was further dried by condensation on  $\text{P}_4\text{O}_{10}$ . In order to avoid contamination or loss of HI during transfer to or evacuation in the tantalum welder, a 6-mm tantalum tube was electron-beam-welded to a Kovar-to-glass seal. This was then attached through a stopcock to the vacuum line for the introduction of HI and the inert atmosphere. The metal part was then crimped and the apparatus was transferred and welded while closed at the stopcock.

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### High-Pressure Polymorphism and Reactions of Dysprosium Sesquioxide

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The close relationship between ionic size and the structure type assumed by the rare earth sesquioxides was first pointed out by Goldschmidt, Barth, and Lunde.<sup>1</sup> Recent work has provided a more detailed description of the distribution of these oxides among the three structure types A, B, and C, as a function of temperature at atmospheric pressure<sup>2–4</sup> and, later, as a function of pressure and temperature.<sup>5,6</sup>

This work was directed toward determining the  $p$ - $t$  dependence of the B-C polymorphism of one of these sesquioxides over as broad a range as possible. The specific goal was the establishment of the equilibrium boundary and the general one was to seek a cross comparison of performance of various high-pressure systems.

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