252. *Thorium Oxyiodide.*

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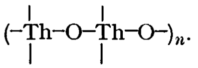
Synthesis of the remarkably acicular thorium oxyiodide has been investigated by differential thermal analysis, and the compound has been examined by *X*-ray diffraction, optical and electron microscopy, and spectroscopy in the visible and infrared regions. Strong exothermal reaction occurs between thorium oxide and molten thorium tetraiodide. The heat of formation, based on heat of solution in hydrochloric acid, is $-237 \cdot 4 \pm 1 \cdot 0$ kcal./mole. Comparison with other oxyhalides of thorium shows that there is a steady increase in stability from oxyiodide to oxyfluoride against disproportionation to oxide and gaseous tetrahalide. A useful relationship between the heat of formation of the oxyhalides and the heat of the disproportionation gives the heat of formation of thorium oxybromide as $-268 \cdot 4 \pm 2$ kcal./mole.

Thorium oxyiodide undergoes no phase or other thermal transformations when heated in a closed system to 950°. There is no evidence of a " thoryl " group, and the characteristic physical properties of the oxyiodide are attributed to the existence of an infinite chain of thorium and oxygen atoms



$(-\overset{|}{\underset{|}{\mathrm{Th}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Th}}}-\mathrm{O}-)_n$.

CHAUVENET[1] claimed to have prepared thorium oxyiodide by thermally degrading a hydrate of basic thorium iodide. It seems doubtful from his description of the product and its reported heat of solution in water whether he obtained the pure material. An unequivocal preparation was given by Heyek, Rehner, and Frank[2] who described the reaction of thorium oxide with thorium tetraiodide at 600° and obtained a white, hygroscopic product of composition $\mathrm{ThOI_{2\cdot06}}$. Scaife and Wylie[3] used vacuum techniques to obtain a pure product. The synthesis from oxide and tetraiodide has now been further investigated by differential thermal analysis, and pure preparations of this unusually acicular substance have been characterised by *X*-ray diffraction and by determination of the density, various spectral properties, and the heat of formation. The thermodynamic properties of the thorium oxyhalides are discussed and a possible structural unit suggested for the oxyiodide.

EXPERIMENTAL

Preparation.—Thorium oxide of nuclear grade, containing less than 60 p.p.m. total impurities, was degassed at 950° in a vacuum ($<10^{-4}$ mm.); the oxide was then mixed in an argon-filled glove-box (dew-point $<-60°$) with pure, sublimed thorium tetraiodide prepared from thorium carbide as described elsewhere.[3,4] There was a 20% excess of tetraiodide over that required by the equation:

$$\mathrm{ThI_4 + ThO_2 \longrightarrow 2ThOI_2} \qquad (1)$$

This mixture was transferred to a clear silica tube and heated *in vacuo* for 60 hr. at 600°. Finally, excess of tetraiodide was sublimed from the product over 60 hr. at 530°. The voluminous, white, very hygroscopic product was freely soluble in water and hydroxylic solvents. The otherwise clear solutions, however, contained a few particles of carbon derived from the tetraiodide, despite use of a sintered glass filter designed to prevent carry-over of carbon from thorium carbide to thorium tetraiodide. These totalled less than 0·1% of the total solids.

At the temperature of these preparations, thorium tetraiodide did not attack Pyrex glass and neither the tetraiodide nor the oxyiodide attacked silica.

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[1] Chauvenet, *Ann. Chim. Phys.*, 1911, **23**, 472.

[2] Heyek, Rehner, and Frank, *Monatsh.*, 1951, **82**, 475.

[3] Scaife and Wylie, Second Internat. Conf. Peaceful Uses Atomic Energy, Geneva, 1958, Vol. 4, p. 215.

[4] Scaife and Wylie, *J.*, 1964, 5450.

Chemical Analysis.—Thorium and iodine were determined as described in a previous Paper,[4] the same precautions being taken to prevent loss of iodine vapour. Typical results were: for thorium oxyiodide, Th, 45·55; I, 51·41% ($ThOI_2$ requires Th, 46·2; I, 50·6%); for thorium tetraiodide, Th, 31·4; I, 68·4% (ThI_4 requires Th, 31·4; I, 68·6%).

Differential Thermal Analysis of the Reaction Between Oxide and Tetraiodide.—Degassed thorium oxide (0·33 mmole) and sublimed thorium tetraiodide (0·30 mmole), after being thoroughly ground together in a glove-box, were compressed in dry argon into a small platinum capsule. The technique of sealing this capsule in the glove-box and the method of differential thermal analysis have been fully described.[4] The heating rate was 8°/min. Thorium oxyiodide was treated similarly.

Optical and Electron-microscopic Examination.—Fluorocarbon oil, dried by pumping *in vacuo* at high temperatures, proved a satisfactory medium for optical examination of the oxyiodide. Filtered perfluoroiso-octane, dried by contact with thoroughly degassed molecular sieves, was used to suspend the oxyiodide for preparation of electron micrographs.

Density Determination.—The densities of thorium oxyiodide, thorium oxide, and thorium tetraiodide were measured at 20° ± 2° with a simplified helium densitometer,[5] calibrated with mercury. Samples were loaded in dry argon, quickly attached to the equipment, and evacuated before admission of helium. A correction of 0·1 g./c.c. was made for the small amount of thorium tetraiodide (3 wt.-%) in the thorium oxyiodide sample.

X-*Ray Examination.*—Powder patterns were obtained on an 11·46-cm. Philips Debye–Scherrer camera, using Cu–K_α radiation and 0·50-mm. beam collimator. Samples were sealed in 0·3-mm. Lindemann glass capillaries in the glove-box. Films were calibrated for absorption and other errors by incorporating a small quantity of degassed thorium oxide in the samples, the correct position of the thorium oxide lines being found from extrapolated lattice constants.

Line positions measured on a travelling microscope showed scatter between six films not exceeding ±0·03 mm. Intensities were measured on a Joyce densitometer. More accurate low-angle measurements were made with a Guinier camera and air-tight sample-holders loaded in dry argon. Results were in good agreement with those obtained with the Philips camera.

Attempts to grow single crystals of oxyiodide for *X*-ray examination resulted in a lengthening, but virtually no broadening, of the crystals.

Spectral Examination.—The diffuse reflectance spectrum of powdered thorium oxyiodide was measured over the range 200—2500 mμ with the reflectance attachment of a Beckman model DK2A recording spectrophotometer. The sample was contained behind a clear silica window in a gastight sample-holder.[6] The infrared spectrum was obtained on a Perkin-Elmer model 21 instrument. Samples were made up between rocksalt windows in both dry nujol and fluorocarbon mulls, which adequately protected the oxyiodide against atmospheric moisture.

Heats of Solution.—The platinum, isothermal-wall calorimeter has been previously described.[7] Samples were loaded under dry argon into Pyrex bulbs with wax-coated rubber stoppers, the bulbs being broken under 1M-hydrochloric acid with negligible heat of breaking. Heat was evolved for 5—10 min. giving a final temperature of 24° ± 1° (corrections to 25° were negligible). The solutions were continuously flushed with water-saturated nitrogen to avoid iodide oxidation, and were clear and colourless after reaction except for carbon. Since no thorium oxide impurity was observed after dissolving thorium oxyiodide, the only impurity was assumed to be thorium tetraiodide in amounts varying from 3 to 5 wt.-% calculated from the Th and I analysis of each solution (Table 2). Approximately this quantity of tetraiodide was visible under the microscope. Total weights from such calculations agreed well with those from direct weighing of the samples. Corrections of 0·3—0·4 kcal. were made to the heat of solution of thorium oxyiodide, assuming that the thorium tetraiodide impurity liberated 75 kcal./mole on solution, a value found in preliminary work on its heat of formation.

Samples of hydriodic acid (57%) were prepared by distillation with orthophosphoric acid to give the constant-boiling acid (HI, 5·37 H_2O). The heat of solution of hydriodic acid (2—4 mmole) in 1M-hydrochloric acid (110 g.) containing thorium was measured as described above, giving concentrations similar to those used for thorium oxyiodide.

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[5] Pearson, U.S. Atomic Energy Comm. Report, 1960, U.C.R.L.-6639.

[6] Wailes, Reid, and Scaife, *Spectrochim. Acta*, 1964, **20**, 1257.

[7] Turnbull, *Austral. J. Chem.*, 1964, **17**, 1063.

RESULTS

Differential Thermal Analysis.—No thermal effects could be detected on heating pure thorium oxyiodide to 900° in a closed system. Thorium tetraiodide gave a single, *endo*thermal peak at the m. p., 560°. Equimolar mixtures of thorium oxide and thorium tetraiodide under the same conditions showed *endo*thermal peaks at 540—555° and *exo*thermal peaks at 640—655°. In one experiment an additional exothermal peak appeared at 555°. There were other minor and irreproducible peaks on the chart, but after the mixture had been heated to equilibrium at 900° no thermal reactions of any kind could be detected on subsequent heating and cooling cycles.

When heated on a microscope hot-stage in dry, flowing argon at 1 atm. pressure, crystals of oxyiodide showed some shrinkage and distortion on decomposition, but at 1000° left a thorium oxide residue, a relic structure of the original oxyiodide crystals. Sublimation of thorium tetraiodide increased progressively as the temperature was raised above 600° and was almost complete at 900—1000°.[8]

Microscopic Observations and Density.—Microscopic examination showed thorium oxyiodide to consist of a felted mass of colourless, highly acicular crystals with moderate birefringence and extinction parallel to the axis of elongation. Electron micrographs showed that typical crystals varying in length from 7 to over 50 μ were 0·5—1 μ wide. Curved cystals were often visible. The unusual morphology is responsible for the very low bulk density, *ca.* 0·35 g./c.c., or a void fraction of 0·96. The true density of the oxyiodide, ρ_{20}, was found to be 8·2 ± 0·5 g./c.c., the low bulk density accounting for the large limits of error. For thorium oxide ρ_{20} was found to be 9·85 ± 0·1 g./c.c., in good agreement with 9·86 g./c.c. reported by Hevesy[9] for a pycnometric determination and with 10·06 g./c.c. calculated from the corrected lattice spacing, 5·586 ± 0·01 Å, for the oxide used in this work. For thorium tetraiodide ρ_{20} was found to be 6·1 ± 0·1 g./c.c. No pycnometric value has been reported but the value 5·94 g./c.c. has been calculated from the *X*-ray data given by D'Eye, Ferguson, and McIver.[10]

TABLE 1.

X-ray powder diffraction pattern of thorium oxyiodide.

d	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
10·57	20	3·72	40	2·890	70	2·360	20	1·886	25	*1·591* *	20
8·75	80	3·51	40	2·855	50	2·316	10	1·823	10	1·563	20
7·74	10	3·33	10	2·764	50	2·248	10	1·766	20	1·554	25
6·39	30	3·19$_1$	50	2·642	50	2·155	25	1·735	20	1·485	25
4·40	30	3·08$_3$	15	2·586	60	2·103	60	1·713	20	1·448	20
4·22	30	3·035	40	2·525	25	2·041	20	1·689	30	1·436	20
4·02	5	2·972	100	2·474	5	1·946	40	1·670	40	1·335	30
2·75	25	2·925	15	2·421	25	1·913	25	1·632	10	1·212	20
										1·183	25
										1·044	20

* There were many other lines below 1·591 but only the strongest are reported.

X-Ray Diffraction Pattern.—The complex powder pattern of thorium oxyiodide is given in Table 1. The data could not be indexed on the basis of a unit cell of orthorhombic or higher symmetry, and it appears that the unit cell is either very large and orthorhombic, or of lower, possibly monoclinic symmetry. Optical observations do not conflict with this conclusion. The pattern of thorium tetraiodide confirmed the orthorhombic indexing of D'Eye, Ferguson, and McIver.[10]

Spectral Observations.—The diffuse reflexion spectrum of thorium oxyiodide showed no absorption bands in the visible portion. There was however a strong charge-transfer-type absorption band below approximately 300 mμ, with a weak shoulder at 400 mμ. The infrared spectrum is also devoid of bands in the region 4000—650 cm.$^{-1}$.

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[8] Reid, Wilmshurst, and Wylie, *J. Electrochem. Soc.*, 1963, **110**, 429.
[9] Hevesy, *J.*, 1931, 10.
[10] D'Eye, Ferguson, and McIver, *Compt. rend.*, 16*th Cong.* I.U.P.A.C., 1957, 341.

Heat of Formation.—The following reaction scheme was used to evaluate ΔH°_f 298 for thorium oxyiodide:

$$ThOI_2(c) + 4(HCl)_{1M\text{-}HCl} \longrightarrow (ThCl_4,\ 2HI,\ H_2O)_{0{\cdot}94M\text{-}HCl} \qquad (2)$$

$$ThCl_4(c) \longrightarrow (ThCl_4)_{0{\cdot}94M\text{-}HCl} \qquad (3)$$

$$2(HI)_{57wt.\text{-}\%HI} + (ThCl_4)_{0{\cdot}94M\text{-}HCl} \longrightarrow (ThCl_4,\ 2HI)_{0{\cdot}94M\text{-}HCl} \qquad (4)$$

$$(ThCl_4,\ 2HI)_{0{\cdot}94M\text{-}HCl} + H_2O(l) \longrightarrow (ThCl_4,\ 2HI,\ H_2O)_{0{\cdot}94M\text{-}HCl} \qquad (5)$$

Reaction (2) represents the experimental heat of solution of thorium oxyiodide in 1M-hydrochloric acid given in Table 2. The average of four samples, corrected for thorium tetraiodide content, was −40·6 ± 0·4 kcal./mole, using an average mole ratio of Th : HCl : H_2O = 1 : 105·5 : 5890.

TABLE 2.

Heat of solution of thorium oxyiodide in 1M-hydrochloric acid.

Sample wt. (g.)	$ThOI_2$ (mmole)	ThI_4 (mmole)	$-\Delta H$ (calorie)	$-\Delta H$ (corrd.) (kcal./mole)
0·4996	0·9655	0·0204	40·43	40·3
0·4872	0·9320	0·02635	40·28	41·05
0·6897	1·3125	0·0420	56·86	40·95
0·7841	1·4875	0·0508	63·46	40·1

Reaction (3) represents the heat of solution of thorium tetrachloride in 0·94M-hydrochloric acid. The results of Westrum and Robinson [11] for the heat of solution of the tetrachloride in 1M-, 6M-, and 9M-hydrochloric acid respectively were extrapolated slightly to give −57·6 ± 0·1 kcal./mole in 0·94M hydrochloric acid with mole ratios averaging Th : CHl : H_2O = 1 : 235 : 12970. This heat of solution may be adopted for the slightly higher thorium concentration of reaction (2) with negligible error.

Reaction (4) represents the heat of solution of 57% hydriodic acid in 0·94M-hydrochloric acid containing thorium tetrachloride, found in separate experiments to be −1·50 ± 0·03 kcal./mole of hydriodic acid. The heat of dilution represented by reaction (5) may be taken as zero with negligible error.

The above reaction heats were combined with the heats of formation of thorium tetrachloride, −284·5 ± 0·5 kcal./mole, reported by Eyring and Westrum,[12] of hydriodic acid in 57% aqueous solution, −11·50 ± 0·05 kcal./mole, and hydrochloric acid in 1M-solution, −39·60 ± 0·05 kcal./mole, reported by Rossini *et al.*,[13] to calculate the heat of formation of solid, crystalline thorium oxyiodide, −237·4 ± 1·0 kcal./mole.

Further discussion demands the heats and entropies of other thorium oxyhalides, given in Table 3. The heats of formation based on early measurements of Chauvenet [1] differ considerably and are considered to be in error due to inadequate preparative methods. The value for thorium oxychloride,[14] based on its heat of solution in sodium hydroxide and on equilibrium-pressure measurements, appears to be reliable. However, that for thorium oxyfluoride [15]

TABLE 3.

Thermodynamic properties of thorium oxyhalides.*

Compound	$-\Delta H_f{}^\circ{}_{298}$ (kcal./mole)	$\Delta H_{disp.}$ (kcal./mole)	$S^0{}_{298}$ (e.u.)	$-\Delta S_f{}^\circ{}_{298}$ (e.u.)	$-\Delta G_f{}^\circ{}_{298}$ (kcal./mole)
$ThOI_2$	237·4 ± 1·0	10·3	(40·3)	24·9	230·0 ± 1·3
$ThOBr_2$	(268·4 ± 2)	(8·3)	(35·8)	38·2	257·0 ± 2·3
$ThOCl_2$	295·4 ± 1·5	6·6	(31·8)	58·8	277·9 ± 1·8
$ThOF_2$	398·8 ± 1·5	1·8	(24·8)	61·0	380·6 ± 1·8

* Estimated values in parentheses.

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[11] Westrum and Robinson, " The Transuranic Elements," National Nuclear Energy Series IV-14B, McGraw-Hill, New York, 1949, Paper 6.50.

[12] Eyring and Westrum, *J. Amer. Chem. Soc.*, 1950, **72**, 5555.

[13] Rossini, Wagman, Evans, Levine, and Jaffe, Nat. Bur. Stand., Circular 500, 1952.

[14] Yen Kung-Fan, Li Shao-Chung, and Novikov, *Russ. J. Inorg. Chem.*, 1963, **8**, 89.

[15] Darnell, U.S. Atomic Energy Comm. Report, 1960, NAA-SR-5045.

has been recalculated from a revised heat of formation of thorium tetrafluoride. The latter was based [16] on the pressure of silicon tetrafluoride gas in the equilibrium:

$$\mathrm{ThF_4(c) + SiO_2(c) \rightleftharpoons ThO_2(c) + SiF_4(g)} \qquad (6)$$

Recent improved values for the heats of formation of silicon tetrafluoride gas,[17] $-385{\cdot}98 \pm 0{\cdot}2$ kcal./mole, and of silica [17] (α quartz), $-217{\cdot}72 \pm 0{\cdot}34$ kcal./mole, give a new value for the heat of formation of thorium tetrafluoride, $-500{\cdot}86 \pm 0{\cdot}7$ kcal./mole. From the pressure of thorium tetrafluoride in the equilibrium:

$$\mathrm{ThOF_2(c) \rightleftharpoons \tfrac{1}{2}ThO_2(c) + \tfrac{1}{2}ThF_4(c)} \qquad (7)$$

the heat of this reaction was found [15] to be $1{\cdot}75 \pm 1$ kcal./mole at 298° K, assuming $\Delta C_p = 0$, giving a new value for the heat of formation of thorium oxyfluoride, $-398{\cdot}8 \pm 1{\cdot}5$ kcal./mole,

The heats of disproportionation, ΔH(disp.) given in Table 3 for the reaction:

$$\mathrm{ThOX_2(c) \longrightarrow ThO_2(c) + ThX_4(c)} \qquad (8)$$

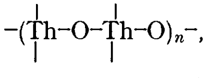
are based on the heats of formation discussed above and on the following values (kcal./mole) for the solid compounds: thorium oxide,[18] $-293{\cdot}2$; thorium tetrabromide,[18] $-227{\cdot}0$; and thorium tetraiodide, -161 (this last being based on its heat of solution in 1M-hydrochloric acid, reported later).

The entropies in Table 2 have been estimated on an additive basis from those of solid thorium oxide and the various solid tetrahalides,[18] a relationship confirmed by a review of all available oxyhalide data.

DISCUSSION

Differential thermal analysis shows that the rate of the exothermal reaction between thorium oxide and thorium tetraiodide in a closed system increases rapidly when the tetraiodide melts. The main reaction evidently occurs in stages over the range 550—650° as the oxide is progressively wetted by the molten salts. Due to interactions in the system: thorium oxide–thorium oxyiodide–thorium tetraiodide, there may be other, less-marked thermal effects such as a small eutectic lowering of the melting point of thorium tetraiodide at the onset of reaction. Since these thermal effects all disappear on heating the mixture to equilibrium at 900°, thorium oxyiodide undergoes no phase-transformations under such conditions. Presumably the disproportionation to liquid thorium tetraiodide and solid oxide proceeds rather slowly in a closed system.

That disproportionation on heating is the reverse of reaction (1), uncomplicated by simultaneous volatilisation of oxyiodide, follows from previous experimental work on the thermal deposition of thorium metal from thorium tetraiodide vapour.[8] The low oxygen-content of the deposited metal, <100 p.p.m., establishes the vapour pressure of the oxyiodide as $<0{\cdot}1\ \mu$ at 500°.

Density measurements indicate that average molar volumes are only a little less in the oxyiodide than in a mixture of oxide and tetraiodide. The absence of characteristic absorption frequencies in the visible and infrared regions differentiates the compound from oxyhalides of the uranyl and vanadyl type and confirms the absence of a short thorium–oxygen bond in a well-defined molecular entity in the oxyiodide lattice. Except for the oxyfluoride,[19] little is known of the structures of the thorium oxyhalides, $\mathrm{ThOX_2}$. For the oxyiodide a layer lattice seems precluded by the physical properties, but a structure containing thorium and oxygen atoms linked in an infinite chain,  $-(\overset{|}{\underset{|}{\mathrm{Th}}}-\mathrm{O}-\overset{|}{\underset{|}{\mathrm{Th}}}-\mathrm{O})_n-$, could offer a satisfactory explanation.

The heats of formation of the four oxyhalides of thorium (Table 3) show the expected increase from oxyiodide to oxyfluoride. The fact that the heat of formation of thorium

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[16] Darnell, *J. Inorg. Nuclear Chem.*, 1960, **15**, 359.

[17] Wise, Margrave, Feder, and Hubbard, *J. Phys. Chem.*, 1963, **67**, 815.

[18] Kubashewski and Evans, " Metallurgical Thermochemistry," Pergamon, London, 1958, p. 276.

[19] Zachariasen, *Acta Cryst.*, 1949, **2**, 388.

oxyfluoride is very close to the average for thorium oxide and thorium tetrafluoride suggests that bonding is similarly ionic in all three of these compounds. This is in keeping with the structures. The greater disparity in the system thorium oxyiodide–thorium oxide–thorium tetraiodide reflects the substantial difference in size and polarisability of iodide and fluoride ions.

There is an almost linear relationship between $-\Delta H^\circ_{f\,298}$ of the solid tetrahalide and $\Delta H_{\text{disp.}}$, which enables the unknown value for thorium oxybromide to be predicted (Table 3) and may also be useful in considering other metal oxyhalides. Since $\Delta S_{\text{disp.}}$ is assumed zero, then $\Delta G_{\text{disp.}} \sim \Delta H_{\text{disp.}}$, and the values in Table 3 indicate a steady increase in stability towards disproportionation to solid products from fluoride to iodide. In practice, the oxyhalides disproportionate to gaseous tetrahalides, for which stability decreases from fluoride to iodide owing to the increasing volatility of the tetrahalides.

No experimental data exist for thorium(III) oxyhalides, but it has been shown [4] that thorium metal does not reduce thorium oxyiodide when heated for many hours in a closed system at 600°.

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