[CONTRIBUTION FROM THE McPHERSON CHEMISTRY LABORATORIES OF THE OHIO STATE UNIVERSITY]

An X-Ray Study of Titanium Tetrabromide, Titanium Tetraiodide and Titanium Triiodide

BY ROBERT F. ROLSTEN AND HARRY H. SISLER[1]

RECEIVED JULY 24, 1957

X-Ray diffraction data on the pure compounds titanium tetrabromide, titanium tetraiodide and titanium triiodide have been obtained. Titanium tetraiodide undergoes a crystal transformation in the temperature range 100–125°.

Introduction

As a part of our current research program on the formation of molecular addition compounds by metal tetrahalides,[2] it became necessary to prepare pure titanium tetrabromide and titanium tetraiodide. Hassel and Kringstad[3] have reported X-ray diffraction studies on these two compounds and state that $TiBr_4$ is body-centered cubic with an a_0 value of 11.250 ± 0.004 Å. whereas TiI_4 is of the type $T_h^6(P_a3)$ with an a_0 value of 12.002 ± 0.001 Å. Titanium triiodide has not been previously examined by X-ray diffraction. It was, therefore, decided to check the results of Hassel and Kringstad and to obtain similar data for titanium triiodide.

Experimental

The titanium tetrabromide, prepared[4] by the direct reaction of liquid bromine and titanium metal prepared by the de Boer process,[5] was purified by distillation in a Pyrex glass distillation column (30 theoretical plates) with a fixed reflux ratio of 3/1 and packed with Fenske glass helices. The titanium tetraiodide was prepared by three methods: (a) by the reaction of gaseous iodine with pure titanium metal, (b) by the disproportionation of pure titanium triiodide, and (c) the reaction of hydrogen iodide and titanium tetrachloride.

$$Ti(c) + 2I_2(g) \longrightarrow TiI_4(liq) \quad (1)$$

$$2TiI_3(c) \longrightarrow TiI_4(g) + TiI_2(c) \quad (2)$$

$$4HI(g) + TiCl_4(liq) \longrightarrow TiI_4(liq) + 4HCl(g) \quad (3)$$

In the reaction designated (2), 200 g. of purified TiI_3 was added to the 64 mm. Pyrex bulb of an L-shaped apparatus. The unit was removed from the dry-box and hermetically sealed. A temperature gradient was maintained, 290° for the TiI_4 collection tube, 300° for the connecting tube and 310° for the TiI_3 bulb. Contamination of the tetraiodide with the triiodide and/or diiodide can be neglected since their respective vapor pressures are very low at these temperatures and the partial pressure of the tetraiodide over the mixture is high. Analysis of the TiI_4 bears out this conclusion. The experiment was terminated after 24 hours and the unit removed to a dry-box where the test-tube containing the tetraiodide was broken open and its contents placed in weighing flask and stored in a desiccator over phosphorus(V) oxide. Titanium triiodide was prepared by the reduction of titanium tetraiodide with metallic titanium. Pure tetraiodide was charged to the Vycor reaction bulb which contained a small perforated molybdenum disc to support the pure titanium turnings prepared by the iodide method. The system was evacuated and the reaction bulb slowly warmed to vaporize the tetraiodide. A plug of solid tetraiodide was frozen in the capillary which served to isolate the reaction bulb from the vacuum system. Under these conditions triiodide which was produced condensed in the reaction tube in the area just above the titanium turnings. During the course of the experiment a temperature gradient was maintained in the reaction tube (bases 300°; middle, 340°; top, 600°). At the end of 96 hours, the reaction was terminated, the reaction tube cooled to room temperature, the plug of solid tetraiodide removed from the capillary and the system pressurized to one atmosphere dry argon. The reaction tube was sealed off at the constriction and removed to a dry-box where the cake and acicular crystals of TiI_3 were transferred to storage flasks and stored in a desiccator over phosphorus(V) oxide.

Analytical Results

Titanium was determined as TiO_2 and halogen by the modified Volhard technique.[6] Results of the analyses are shown in Table I.

TABLE I

CHEMICAL ANALYSES OF $TiBr_4$, TiI_4 AND TiI_3

	Ti, %	I, %	Mole ratio halogen titanium
TiI_3 exptl.	11.3	89.2	2.98
TiI_3 exptl.	11.2	89.4	3.01
TiI_3 theor.	11.17	88.83	3.00
TiI_4 exptl.[a]	8.55	91.4	4.03
TiI_4 exptl.[a]	8.71	89.0	3.86
TiI_4 exptl.[a]	...	89.7	..
TiI_4 exptl.[b]	8.61	91.3	4.00
TiI_4 exptl.[c]	8.64	91.1	3.98
TiI_4 exptl.[c]	8.62	90.9	3.98
TiI_4 theor.	8.62	91.38	4.00
$TiBr_4$ exptl.	13.2	86.8	3.94
$TiBr_4$ exptl.	13.1	86.7	3.97
$TiBr_4$ theor.	13.04	86.96	4.00

[a] Prepared by direct synthesis. [b] Prepared by the reaction HI + $TiCl_4$. [c] Prepared by disproportionation of TiI_3.

X-Ray Method and Data

The K-alpha radiation was supplied by a Philips Model 5700 X-ray diffraction unit. The halides, which are extremely hygroscopic, were contained in Lindemann glass capillary tubes that were filled in a dry-box and then hermetically sealed. Different preparations of the compounds were checked in order to establish the reproducibility of the preparative method as well as to ensure the absence of hydrolysis before and during irradiation by X-rays.

Titanium Tetrabromide.—Solid titanium tetrabromide contained in a 0.5 mm. Lindemann capillary tube was exposed five hours to the K-alpha radiation of iron using a manganese filter to remove the β-radiation. The camera diameter was 57.3 mm. A summary of the data obtained from two samples is given in Table II, with similar data from the literature as well as Miller indices and relative intensities. The observed *d*-spacings were cor-

---

(1) Department of Chemistry, University of Florida, Gainesville, Florida.

(2) R. F. Rolsten and H. H. Sisler, THIS JOURNAL, **79**, 1068 (1957).

(3) O. Hassel and H. Kringstad, *Z. physik. Chem.*, **15**, 274 (1932).

(4) J. M. Blocher, Jr., R. F. Rolsten and I. E. Campbell, *J. Electro. Soc.* (Nov., 1957).

(5) J. H. de Boer and A. E. van Arkel, U. S. Patent 1,709,781 (April 16, 1929).

(6) J. R. Caldwell and H. B. Moyer, *Ind. Eng. Chem., Anal. Ed.*, **7**, 38 (1935).

rected for sample absorption and the unit-cell dimension determined by the method of Floyd and Taylor[7] in which the observed a_0 values were plotted *versus* a function of the Bragg angle, θ. This function was extrapolated to θ equal to 90° to obtain the true value of a_0 of 11.298 ± 0.012 Å. for sample no. 1 and 11.301 ± 0.010 Å. for sample no. 2. Both sets of data were treated by the method of least squares with the resulting value for a_0 of 11.300 ± 0.007 Å.

TABLE II

X-RAY RESULTS FOR TITANIUM TETRABROMIDE

$a_0 = 11.300 \pm 0.007$ Å.

d-Spacings, Å. Sample 1	2	Cor.	Lit.[8]	(*hkl*)	Intensity (obsd.)
4.46	4.44	4.613		211	30
3.50	3.48	3.573		310	40
3.18	3.17	3.262	3.26	222	100
2.76	2.77	2.825	2.82	400	90
2.613	2.616	2.663		(411)(330)	10
2.362	2.374	2.409		332	10
2.170	2.176	2.216		(510)(431)	20
1.966	1.962	1.998	1.99	440	100
1.853	1.855	1.883		600–442	10
1.814	1.809	1.833		611–532	10
1.686	1.686	1.704	1.70	622	100
1.649	1.647	1.666		631	40
1.614	1.609	1.631	1.63	444	40
1.398	1.398	1.413	1.41	800	10
1.292	1.290	1.296	1.29	662	10
1.258	1.259	1.263	1.26	840	10
1.149	1.150	1.153	1.15	844	10
1.085	1.085	1.087	1.09	(666)(10.22)	10
0.997	0.997	0.999	0.998	880	10
...	...	...	0.953	10.62	..

The X-ray density was calculated to be 3.383 g. cc.$^{-1}$ with eight molecules per unit cell.

Titanium Tetraiodide.—X-Ray diffraction patterns obtained from representative samples of different preparations of titanium tetraiodide, prepared by direct synthesis, by the disproportionation of titanium triiodide and by the reaction between HI and $TiCl_4$, are mutually consistent and independent of the method of preparation. Samples were contained in sealed 0.3 mm. Lindemann glass capillary tubes and exposed for 24 hours to the K-alpha radiation of copper with a nickel filter. The observed *d*-spacings with the visually observed intensities are 3.66 Å., F; 3.45, M_1; 3.28, M_1; 3.06, S; 3.01 (?), F; 2.39, M_2; 2.16, VF; 2.01, M; 1.99, M_1; 1.87, M_1; 1.84, M_2; 1.72, M; 1.70, F; 1.68, M; 1.65, VF; 1.53, VF; 1.49, M; 1.36, M; 1.32, F; 1.29, M; 1.28, M; 1.27, M; 1.24, M; 1.21, M; 1.18, VF; 1.16, VF; 1.14, VF; 1.13, VF; 1.12, M; 1.108, VF; 1.052, VF.

One sample of TiI_4 was hermetically sealed in a 0.2 mm. Lindemann glass capillary and mounted in a Model HC-101 high temperature X-ray diffraction powder camera. Sixteen-hour exposures were obtained at room temperature, 100°, 125° and 150°. The sample underwent a crystal transformation between 100 and 125° and the observed *d*-spacings, determined from the 125° photograph, are given in Table III. This results in a cell constant, $a_0 = 12.21$ Å.

TABLE III

X-RAY RESULTS FOR TITANIUM TETRAIODIDE (CUBIC)

d-Spacings[a]	Intensity[a]	*d*-Spacing[8]	I/I_0[8]
3.520	S	3.47	100
3.048	M_2	3.01	60
2.156	M_1	2.13	80
1.843	M_1	1.81	100
1.762	F	1.74	10
1.526	F	1.50	20
1.400	F	1.38	40
1.386	VF	..	..
1.365	F	1.34	40
1.284	VF	..	..
1.246	F	1.23	20
1.175	F	1.16	40

[a] Determined from the powder pattern obtained at 125°.

Titanium Triiodide.—Representative samples of titanium triiodide from different preparations gave identical diffraction patterns when contained in 0.3 mm. Lindemann glass capillary tubes and exposed for five hours to the unresolved K-alpha radiation of either iron or copper, using a Phillips 114.6 mm. camera. A manganese filter was used with iron; a nickel filter with copper. In addition, a single acicular crystal of titanium triiodide was hermetically sealed in a 0.5 Lindemann glass capillary tube and exposed to K-alpha radiation from copper.

The observed *d*-spacings ($\lambda = 1.5418$ Å.) and visually observed intensities as determined from the powder diffraction data and the calculated *d* spacings and corresponding Miller indices from the single crystal data are summarized in Table IV. The data were corrected for sample absorption and the unit cell dimensions determined by the method of Floyd and Taylor.[7] As a result of this, it was concluded that TiI_3 needles are hexagonal with the following lattice parameters: $a_0 = 7.173 \pm 0.003$ Å. and $c_0 = 6.47$ Å.

TABLE IV

X-RAY RESULTS FOR TITANIUM TRIIODIDE (HEXAGONAL)

d-spacings, Å. Obs.	Calcd.	(*HKL*)	Intensity
5.99	6.212	100	F
3.49	3.587	110	M_2
3.20	3.235	002	VF
3.08	3.106	200	S
	3.137	111	
2.37	2.402	112	M_2
2.25	2.241	202	VF
2.13	2.157	003	VF
2.04	2.071	300	S
1.84	1.848	113	VF
1.77	1.793	220	F
1.73	1.744	302	M_2
1.71	1.723	310	M_1
	1.728	221	
1.56	1.553	400	VF
	1.568	222	
1.35	1.356	410	VF
1.32	1.327	411	M_1
1.24	1.242	500	M_2
	1.250	412	

---

[7] A. Taylor and R. W. Floyd, *Acta Cryst.*, **3**, 285 (1950).

[8] A.S.T.M. X-Ray Card File.

Discussion

The results obtained in this study indicate that titanium tetrabromide crystallizes in the body-centered cubic form with the unit cell dimension $a_0 = 11.300 \pm 0.007$ A. This value can be compared to the reported value[3] of 11.250 Å. which was obtained by averaging five observed a_0 values. This average value was corrected[8] to 11.282 Å. The precision in our powder diffraction data can be seen from the plot of the observed a_0 *versus* $f(\theta)$ and the standard deviation of ± 0.007 Å. in the true a_0 value. The additional diffraction lines obtained in this investigation over those reported by Hassel and Kringstad[3] are of relative intensity 40 or less, and can, perhaps, be attributed to a longer time of exposure and/or to the use of a fluorescent filter. Not to be overlooked is the possibility that the observed line at 1.666 Å. could also have been observed by Hassel but was coincident with the CdO (internal standard) line at 1.661 Å. and was, therefore, not reported. The X-ray density of 3.383 g. cc.$^{-1}$, calculated with eight molecules per unit cell, can be compared to the values[9,10] obtained by direct pycnometric measurement, $d_4^{20} = 3.254$ g. cc.$^{-1}$ and $d_4^{25} = 3.37$ g. cc.$^{-1}$, respectively.

Titanium tetraiodide is dimorphic (−15° is the transformation temperature for $TiBr_4$) with the room temperature modification of less symmetry than the high temperature, 100–125°, cubic form. It should be observed that the room temperature form yields a powder pattern with weak and not well-defined back reflections. Also, there is doubt about the existence of two lines at 3.06 and 3.01 Å. This could be the result of sample absorption effects and was apparently eliminated since molybdenum radiation resulted in a single line at 3.04 Å. The observed lines index quite well as hexagonal with $a_0 = 7.978$ Å. and $c_0 = 19.68$ Å. but little credence can be placed in these values until single crystal (we were unable to prepare them) data are available. The cubic form of the tetraiodide has a cell dimension of 12.21 Å. at about 125° which was obtained as an average of ten observed values and not refined by extrapolation techniques. This results in an X-ray density, with eight molecules per unit cell, of 4.01 g. cc.$^{-1}$ and can be compared to the pycnometric value[10] of $d_4^{25} = 4.40$ g. cc.$^{-1}$ and the X-ray density according to Hassel of 4.27 cc.$^{-1}$.

Powder and single crystal X-ray data indicate that acicular titanium triiodide crystallizes in the hexagonal form with the lattice parameters $a_0 = 7.173 \pm 0.003$ Å. and $c_0 = 6.47$ Å. It has an X-ray density of 4.937 g. cc.$^{-1}$ if it is assumed that there are two TiI_3 units per unit cell. Table IV shows that four *d*-spacings can be assigned two different sets of Miller indices. The more probable indices are (111), (221), (222) and (412) rather than (200), (310), (400), and (500), respectively, as determined from a comparison of observed and calculated intensities. The space group d_{3h}^3 can be assumed tentatively.

Acknowledgments.—We wish to thank Dr. Robert E. Gilbert of Oak Ridge and Mr. Neil D. Veigel of Battelle Memorial Institute for their suggestions concerning the preparation of the titanium iodides.

COLUMBUS, OHIO

---

[9] J. B. Olsen and E. P. Ryan, THIS JOURNAL, **54**, 2215 (1932).

[10] W. Klemm, W. Tilk and S. von Mullenheim, *Z. anorg. Chem.*, **176**, (1928).

[CONTRIBUTION FROM THE NATIONAL LEAD COMPANY, TITANIUM DIVISION, RESEARCH LABORATORY]

A Spectrophotometric Study of the System Titanium(IV)–Peroxide–Fluoride

BY KERMIT HERRINGTON AND DORRIS E. KINGSBURY

RECEIVED MAY 21, 1957

Absorption spectrum measurements are reported for sulfuric acid solutions containing titanium(IV), peroxide and fluoride In the presence of sufficient excess peroxide so that dissociation of the peroxy–titanium(IV) is negligible, the bleaching of the color of this complex by fluoride has been found to be only about 20% in the presence of a hundred-fold excess of fluoride. No evidence was found for any new complex ion in this system in the presence of fluoride. The stability of the peroxy–titanium(IV) complex was found to be unaffected by the presence of fluoride.

Introduction

The yellow color produced when peroxide is added to aqueous titanium(IV) is commonly used as an analytical method for titanium(IV).[1] That the color is due to a peroxy–titanium(IV) complex ion has been well established, and Schaeppi and Treadwell[2] have shown, by the method of continuous variations, that this ion has a 1:1 stoichiometry. In his excellent discussion of the limitations of this method, Woldbye[3] concludes that the system titanium(IV)–peroxide is sufficiently uncomplicated so that there should be no reason to doubt the validity of the results obtained by Schaeppi and Treadwell. The absorption spectrum of the ion has a maximum density at 410 mμ and it has been found that Beer's law is followed at titanium(IV) concentrations less than about 10^{-3} molar.[4] Above this concentration, the deviations which occur have been attributed by Reeves and Jonassen to polymerization of the titanium(IV). The color of the ion (both the position of the absorption band and the molar extinction coefficient) has been found to be independent of many common anions; fluoride, however, is reported to

---

[1] W. W. Scott, "Standard Methods of Chemical Analysis," 5th Ed., D. Van Nostrand, Inc., New York, N. Y., 1939, p. 987.

[2] Y. Schaeppi and W. D. Treadwell, *Helv. Chim. Acta*, **31**, 577 (1948).

[3] F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

[4] See for example, R. E. Reeves and H. B. Jonassen, THIS JOURNAL, **76**, 5354 (1954).