atm. and also in the presence of hydrogen, nitrogen, propane and carbon dioxide.

2. The variation of the velocity constant with pressure can be represented by the equation

$$K_{573^\circ} = \frac{7.7 \times 10^{-4}}{1 + (1400/P)} \text{ min.}^{-1}$$

from which the limiting value at infinite pressure is obtained to $K_\infty = 1.3 \times 10^5 \, e^{-26500/RT}$ sec.$^{-1}$.

3. Hydrogen and nitrogen have no effect on the reaction velocity, while propane and carbon dioxide accelerate it.

4. In the thermal equilibrium the ratio of fumaric to maleic ester is greater than unity.

5. The slowness of the activation process in the reaction is discussed and is linked to the nature of the mechanical motion responsible for the reaction.

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[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF BROOKLYN]

THE PREPARATION AND PROPERTIES OF TITANIUM TETRABROMIDE AND TITANIUM TRIBROMIDE HEXAHYDRATE[1]

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Very few of the salts of titanium have been prepared in pure form and their properties studied. Considerable work has been done at the Polytechnic Institute on titanium compounds. As a part of this research titanium tetrabromide and titanium tribromide hexahydrate have been prepared and studied.

Duppa[2] prepared the tetrabromide and describes it as an amber-yellow substance, attracting moisture with the greatest avidity and being converted into titanic and hydrobromic acids, boiling at 230° and melting at 39°. Thorpe[3] describes it as a dark yellow or orange crystalline mass melting at about 40° and boiling at 229° uncorrected. Its density is reported as 2.6 by Duppa and 3.37^{25}_{4} by Klemm, Tilk and Müllenheim.[4]

Preparation of Titanium Tetrabromide.—The tetrabromide was prepared in three ways.

[1] From the thesis submitted in partial fulfilment of the requirements for the degree of Master of Science by Emmett P. Ryan. This paper was read at the Buffalo Meeting of the American Chemical Society, August 30–September 4, 1931.

[2] Duppa, *Proc. Roy. Soc.* (London), **8**, 42 (1857).

[3] Thorpe, *J. Chem. Soc.*, **47**, 126 (1885).

[4] Klemm, Tilk and Müllenheim, *Z. anorg. allgem. Chem.*, **176**, 1–22 (1928).

(1) **A Modification of Duppa's Method.**—An intimate mixture of pure titanium dioxide and carbon black was placed in an inclined 25-mm. Pyrex tube. By means of a two-way stopcock, carbon dioxide, dry and free from oxygen, was passed either directly into the reaction tube or first into a flask containing bromine, heated to 60° to increase its vapor pressure. The tube was heated and swept free from air and moisture by the carbon dioxide after which the stopcock was turned and the bromine-saturated gas passed over the mixture of titanium dioxide and carbon heated to 640°. Titanium tetrabromide, carbon tetrabromide and excess bromine collected in the distilling flask at the end of the tube. The bromine was removed by distillation on a water-bath in a stream of carbon dioxide, and the carbon tetrabromide by later distillation. The titanium tetrabromide remained in the flask as an amber-yellow solid at room temperature. It was purified by distillation as described later.

(2) **Thorpe's Procedure.**—Hydrogen bromide was passed into titanium tetrachloride heated just below its boiling point. The hydrogen bromide, prepared by the action of bromine on red phosphorus and water, was freed from entrapped bromine fumes by passing through a U-tube filled with glass wool and red phosphorus, and dried by passing over soda lime. The hydrogen bromide was passed intermittently for thirty hours before the boiling point of the contents of the flask rose from that of titanium tetrachloride, namely, 136.4, to 228°, the boiling point of titanium tetrabromide. The hydrogen bromide was passed for five hours more, the boiling point remaining constant. This product was also purified by distillation.

(3) **Ruff and Eisner's Method.**[5]—This method is similar to (1) except that titanium carbide was used in place of titanium dioxide and carbon black. This method was abandoned after one run because we were unable to secure an iron-free sample of titanium carbide. Thorpe's method requires the longest time but gives the purest product. A large quantity can also be most easily prepared by this method. Sixty grams was made by Duppa's method in two runs, while 450 g. was made by Thorpe's method in one run.

The titanium tetrabromide made by either method was twice distilled in an atmosphere of dry carbon dioxide, collecting that portion boiling at 228° uncorrected. Samples were collected in constricted glass tubes. The air was displaced by dry carbon dioxide and the bromide distilled into the tubes, which were immediately sealed off at the constriction.

The tetrabromide was analyzed by carefully breaking these tubes under water acidulated with a small amount of nitric acid. This was made up to a known volume and aliquot portions were withdrawn. The bromine was precipitated with silver nitrate and weighed as silver bromide. The titanium was precipitated with ammonium hydroxide and weighed as titanium oxide after bringing to constant weight over a Méker burner.

Anal. Calcd. for $TiBr_4$: Ti, 13.03; Br, 86.97. Found: Ti, 13.21, 13.19, 13.30; Br, 86.62, 86.76.

The properties as determined were found to be as follows. Titanium tetrabromide is readily and completely soluble in 34% hydrobromic acid at room temperature and also in concentrated hydrochloric acid.

Concentrated nitric acid decomposes it. Nitrogen peroxide is given off, bromine settles to the bottom of the tube and titanic acid remains in solution.

Concentrated sulfuric acid decomposes the tetrabromide, liberating hydrogen bromide. Part of the hydrogen bromide reacts with the excess sulfuric acid forming bromine, water and sulfur dioxide. A reddish-brown solution is formed.

[5] Ruff and Eisner, *Ber.*, **41**, 2260 (1908).

Ammonium hydroxide and a 20% aqueous solution of sodium hydroxide decompose the tetrabromide, forming a heavy white precipitate of $Ti(OH)_4$. The reaction is analogous to that of ammonium hydroxide on titanium tetrachloride, forming a precipitate of $Ti(OH)_4$.

Titanium tetrabromide is soluble in chloroform, carbon tetrachloride, absolute ether and absolute alcohol.

Quantitative Determination of the Solubility of Titanium Tetrabromide in Alcohol and Ether.—Titanium tetrabromide was distilled in a stream of dry carbon dioxide into a small flask which was quickly stoppered. A quantity of alcohol or ether, insufficient to dissolve the tetrabromide, was added. The flask was allowed to stand overnight. It was then brought to 20° and kept there for two hours with frequent shaking. A portion of the supernatant liquid was drawn off into a pycnometer and weighed at 20°. The contents was dissolved in water and the bromine content determined.

Two hundred and eighty-seven grams of titanium tetrabromide is soluble in 100 cc. of absolute alcohol at 20°. The density of this solution is 2.29_4^{20}; 3.6 grams of titanium tetrabromide is soluble in 100 cc. of absolute ether at 20°.

Density.—As titanium bromide is hydrolyzed by water, mercury was used for the determination of density. A sample of titanium tetrabromide was distilled in an atmosphere of carbon dioxide and collected in a small test-tube drawn out near the top. On cooling, the tetrabromide solidified in the bottom of the tube and adhered firmly to the tube which was then sealed. The narrow portion of the tube was marked with a file in two places about an inch apart and the tube weighed. At the upper of the two file marks the tube was broken under mercury and filled, the temperature brought to 20° and the mercury level adjusted to the mark. The tube and contents were then weighed. The tube was now cleaned out, dried, and weighed with the glass tip broken off from the tube on filling. Its weight filled to the mark with mercury at 20° was then found. The density of the tetrabromide was 3.23_4^{20}.

The density was also determined in a vacuum. The sample was prepared as before but now the tetrabromide was but little more than covered with mercury. It was placed in a vacuum in a desiccator to wet the surface of the sample thoroughly. The tube was then removed from the desiccator, filled to the mark with mercury at 20° and weighed. The density was 3.25_4^{20}.

Duppa gives 2.6 as the density and Klemm, Tilk and Müllenheim 3.372_4^{25}. Duppa, who was the first to prepare titanium tetrabromide, does not give his method of determining the density. Handbooks have evidently taken his figure. Klemm, Tilk and Müllenheim give their method. They took especial care before filling the tubes up to the mark with mercury to place them under high vacuum to remove (as they state) any moisture that may have entered while getting the samples in the tubes. As moisture rapidly hydrolyzes titanium tetrabromide to hydrogen bromide and titanium dioxide, part of the tetrabromide would be hydrolyzed before the moisture could be removed by vacuum. As titanium dioxide has a density of from 3.75 to 4.25 any of this oxide formed would give high results especially where small samples were taken. The samples used for the two determinations which they made weighed 0.5943 and 0.3889 grams.

In filling our sample tubes, the tetrabromide was distilled in an atmosphere of dry carbon dioxide into dry test-tubes from which the air

had been displaced by carbon dioxide. They were then sealed off from the air and broken under mercury. Furthermore, samples of 8.3450 g. and 5.2538 g. were used. For these reasons we believe 3.24_4^{20}, the average of our two determinations 3.25_4^{20} and 3.23_4^{20}, more accurate than the 3.37_4^{25}, the average of Klemm, Tilk and Müllenheim's two determinations, 3.36_4^{25} and 3.38_4^{25}. Duppa's results are obviously low.

Titanium Tribromide Hexahydrate.—Stähler[6] prepared titanium tribromide hexahydrate by electrolyzing a solution of titanium tetrabromide in hydrobromic acid. He describes the crystals as dark violet, intermediate in stability between the corresponding chloride and iodide and deliquescing in air to a brown, strongly fuming liquid. We prepared the hydrated tribromide in a similar manner and present the following additional data.

Preparation.—Twenty-six grams of titanium tetrabromide was dissolved in 23 g. of 34% hydrobromic acid and placed in a porous cup 41 mm. in diameter and 76 mm. in height. This was placed in a 400-cc. beaker containing 34% hydrobromic acid. The liquids in the porous cup and beaker were kept at the same level. Two carbon rods served as the electrodes, with the porous cup as the cathode compartment. A current of 2.5 amperes was passed through the solution for two hours. When dry hydrogen bromide gas was passed into the ice cooled flask containing the violet colored solution, crystals of hydrated titanium tribromide separated out. The crystals were filtered on Gooch asbestos, washed with ether, and dried in a desiccator over soda lime until constant. The following analysis indicates that the crystals were very nearly pure $TiBr_3 \cdot 6H_2O$.

Anal. Calcd. for $TiBr_3 \cdot 6H_2O$: Ti, 12.10; Br, 60.58; $TiBr_3$, 72.69. Found by gravimetric analysis: Ti, 12.16, 11.75; Br, 59.52, 59.24; $TiBr_3$, 71.68, 70.99.

Properties.—Titanium tribromide hexahydrate is a light reddish-violet crystalline substance. It deliquesces in air to a heavy brown liquid but may be kept in a desiccator over soda lime, with but slight decomposition. The crystals melt at 115.0°.

It is soluble in water giving a violet color in concentrated solutions, and is soluble in hydrobromic acid giving a brownish solution.

Titanium tribromide hexahydrate is also soluble in methyl alcohol, absolute ethyl alcohol, and acetone, insoluble in carbon tetrachloride and benzene, and decomposes on standing with absolute ether.

Summary

Titanium tetrabromide was prepared by three methods. It is soluble in chloroform, carbon tetrachloride, absolute ether, absolute alcohol and hydrobromic and hydrochloric acids. It is decomposed by nitric acid, sulfuric acid, ammonium hydroxide and an aqueous solution of sodium hydroxide; 287 g. of titanium tetrabromide is soluble in 100 cc. of absolute alcohol at 20° and 3.6 g. in 100 cc. of absolute ether at 20°. The correct density determination is 3.25_4^{20}.

Titanium tribromide hexahydrate was prepared. It melts at 115°. Solubilities in various solvents and other properties are given.

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[6] Stähler, *Ber.*, **37**, 4409 (1904).