[CONTRIBUTION FROM THE LABORATOIRE DE CHIMIE MINÉRALE OF THE COLLÈGE DE FRANCE]

The Ammonolysis of Tantalum Pentachloride

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In a recent note[2] the authors have given evidence that the primary product of the reaction of liquid ammonia on tantalum pentachloride was the heptammine of the trichlorodiamide whose formation was accounted for by the equation

$$TaCl_5 + 17NH_3 \longrightarrow Ta(NH_2)_2Cl_3{\cdot}7NH_3 + 2NH_4Cl{\cdot}3NH_3$$

It was found that this compound, on progressive heating to 170° in a vacuum, not only was separated from the ammonium chloride formed in the initial reaction but also underwent loss of the seven molecules of ammonia held by secondary valence.

The trichlorodiamide of tantalum could thus be isolated and its properties studied. Thus, it was possible to show that on heating to 1180° in a current of dry ammonia, the mononitride of tantalum was produced

$$3Ta(NH_2)_2Cl_3 + 8NH_3 \longrightarrow 3TaN + 9NH_4Cl + N_2$$

We have since not only obtained additional data confirming these reactions but have also been able to isolate the pentanitride which is formed at an intermediate stage in this latter reaction and to investigate some previously unrecorded properties of these compounds.

Preparation of Tantalum Pentachloride.—This material was made from tantalum pentoxide by a modification of the method discovered by Demarçay[3] and subsequently used by Ruff and Schiller.[4] The oxide was of high purity, having been separated from columbium pentoxide by fractional crystallization of the potassium heptafluotantalate salt. After three sublimations in a vacuum, the practically colorless pentachloride was collected in small Pyrex tubes which were sealed off. Chlorine analysis of this product, after hydrolysis and separation of tantalum by the method of Hönigschmid and Schlee,[5] showed it to be pure tantalum pentachloride within the limits of the analytical precision. Found: 49.12, 49.31%; calcd., 49.49%.

Formation of $Ta(NH_2)_2Cl_3{\cdot}7NH_3$ by the Action of Liquid Ammonia on Tantalum Pentachloride.—When several volumes of liquid ammonia were condensed on tantalum pentachloride and the mixture allowed to warm up slowly to its boiling point at atmospheric pressure, reaction took place, the heat evolved thereby causing the ammonia to be boiled vigorously, and resulted in the practically complete dissolution of the solid to form a pale greenish-yellow solution.

Evaporation of the ammonia left a residue which was composed obviously of at least two different substances, one white and the other pale yellow, and which continued to evolve ammonia even at room temperature. From the quantity of tantalum pentachloride used and its increase in weight on being treated in this manner, it was ascertained that at 20° between ten and eleven (found: 10.12, 10.70, 10.62, 10.80, 10.34, 10.22) moles of ammonia were fixed per mole of tantalum pentachloride originally taken. It was apparent that the mixture consisted of components at least one of which was unstable.

An attempt to separate the ammonium chloride, for such was presumably the white portion of the residue, from the tantalum compound by extraction with anhydrous methanol, in an apparatus which permitted such an extraction to be carried out at room temperature, was of no avail. Most of the tantalum passed into solution under these conditions and instantly formed a precipitate as the extract was cycled back to the hot alcohol still. This behavior incidentally resembles the action of ethanol on tantalum pentachloride.[6] Extraction of the original material with liquid ammonia left only a small residue which was probably composed of unavoidable hydrolysis products.

Equilibrium Pressure–Composition Measurements.—These experiments were made with the object in view of determining the quantity of ammonium chloride formed by the initial reaction and the total quantity of ammonia fixed using a method similar to that employed by Joannis[7] in his study of the ammonia–boron chloride system. By means of liquid ammonia known quantities of tantalum pentachloride were converted to the mixture just described but instead of allowing the residue to warm up to room temperature, it was maintained at 0° by means of an ice-bath, excess ammonia having been evaporated at a pressure always greater than 1035 mm. which at 0° is the pressure of dissociation of the triammine of ammonium chloride, $NH_4Cl{\cdot}3NH_3$, reported by Troost.[8] By measuring equilibrium pressures and volumes of ammonia evolved a series of points on the pressure–composition curve was then determined. Data obtained in three experiments (I, II, III) are tabulated in Table I.

Composition in this table represents the number of molecules of ammonia fixed by the mixture per atom of tantalum present, or x in the over-all formulas $TaCl_5{\cdot}xNH_3$ (including ammonium chloride triammine). The values obtained in experiment I, in which measurements were carried down to low pressures during the course of four months, are plotted in Fig. 1, Curve A. It is to be noted that only one well characterized monovariant region of composition can be detected in the curve, that this is at a pressure corresponding

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[1] Recipient of the Moore Traveling Fellowship from the Massachusetts Institute of Technology for the academic year 1934–1935.

[2] Moureu and Hamblet, *Compt. rend.*, **200**, 2184 (1935).

[3] Demarçay, *ibid.*, **104**, 111 (1887).

[4] Ruff and Schiller, *Z. anorg. Chem.*, **72**, 330 (1911).

[5] Hönigschmid and Schlee, *ibid.*, **221**, 129 (1934).

[6] Lindner and Feit, *ibid.*, **132**, 10 (1924).

[7] Joannis, *Compt. rend.*, **135**, 1106 (1902); **139**, 364 (1904).

[8] Troost, *ibid.*, **88**, 578 (1879).

TABLE I

Eq. press., mm.	Compn., x	Eq. press., mm.	Compn., x
I, $TaCl_5$ taken 0.9758 g. ≎ 2.723 millimoles		III, $TaCl_5$ taken 2.3939 g. ≎ 6.6893 millimoles	
1379	17.59	1057.2	16.66
1241	17.59	1040.0	16.36
1153	17.43	1033.9	16.33
1069	17.36	1036.6	16.03
1003	17.01	1030.3	15.69
1018	16.65	1025.8	13.46
1001	16.53	1017.6	11.28
1008	15.22	1006.6	10.94
1021	14.47	922.3	10.75
1003	10.81	816.6	10.70
824	10.59	680.9	10.67
628	10.38	578.4	10.66
433	10.26		
288	10.00		
171	9.61		
88.4	9.23		
48.8	9.11		
7.6	8.49		
2.3	8.34		
1.5	8.28		
0.8	8.23		
0.5	8.18		
II, $TaCl_5$ taken 0.3812 g. ≎ 1.064 millimole		VIII, $TaCl_5$ taken 4.8079 g. ≎ 13.42 millimoles	
1082.6	17.23	884	10.24
1035.4	15.34	704	10.15
1023.3	12.43	527	10.04
927.3	11.06	430	9.96
748.9	10.92	385	9.92
537.3	10.76	334	9.86
454.4	10.62	302	9.80
		290	9.75
		247	9.68
		220	9.57
		176	9.32
		116	9.08
		54	8.82
		12	8.55
		6	8.43

sensibly to that of dissociation of the triammine of ammonium chloride, and that on either side of this region the equilibrium pressure changes abruptly in a linear manner. In fact, as the pressure decreases the composition remains practically constant until a pressure of 300 mm. is reached. Figure 2 shows the data obtained in experiment II in the monovariant region plotted to larger scale.

Equilibrium was only slowly attained, possibly due to the formation of a coating on the surface of the decomposing crystals of reaction product which hindered the diffusion of ammonia out from the undecomposed interior part of the crystals. A similar phenomenon was mentioned by Klemm[9] in the case of the ammines of indium.

In deriving from these curves the amount of ammonia evolved by the triammine of ammonium chloride and the quantity fixed by the solid at the end of this decomposition, the points of intersection of the linear parts of the curve with the theoretical 1035-mm. isobar were used. The results are tabulated in the first three lines of Table II.

TABLE II

Experiment	Initial ammonia	Final ammonia	Difference	Ammonium chloride
I	17.20	10.88	6.32	2.11
II	17.17	11.14	6.03	2.01
III	16.66	10.79	5.87	1.96
IV	...	...	7.34	2.45
V	18.12	10.79	7.33	2.44
VI	19.73	9.93	9.80	3.27
VII	19.79	9.63	10.16	3.39

Initial ammonia content values correspond to the point of commencement of decomposition of the triammine of ammonium chloride and final ammonia content represents the composition when all of the triammine has decomposed. The difference between these quantities divided by three gives the moles of ammonium chloride formed per mole of tantalum pentachloride originally taken.

It can be concluded from these experiments that when liquid ammonia reacts with tantalum pentachloride, two atoms of chlorine in the latter are replaced, forming two molecules of ammonium chloride. Furthermore, the over-all content of ammonia in the mixture obtained after the triammine of ammonium chloride has completely decomposed corresponds to the fixation of eleven molecules per atom of tantalum present. Consequently, each atom of tantalum must be combined with nine atoms of nitrogen, if a mixture of tantalum compounds is not formed which is improbable in view of the duplicatibility of results under different conditions in these three experiments.

Since our analogy with the reaction product of phosphorus pentachloride with liquid ammonia[10] indicates that under these conditions of temperature and ammonia pressure an amide rather than an imide or a nitride is to be expected, the most likely formula that can be assigned to this tantalum compound is that of the heptammine of the

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(9) Klemm, *Z. anorg. Chem.*, **163**, 240 (1927).

(10) Moureu and Rocquet, *Compt. rend.*, **200**, 1407 (1935); *Bull. soc. chim.*, **3**, 829 (1936).

diamidotrichloride of tantalum, formed by the reaction

$$TaCl_5 + 17NH_3 \longrightarrow Ta(NH_2)_2Cl_3 \cdot 7NH_3 + 2NH_4Cl \cdot 3NH_3$$

Confirmatory evidence for this formula will be presented later in this article under the study of the thermal decomposition of this compound.

It is to be noted that a composition corresponding to the fixation of nine moles of ammonia there is a slight change of curvature, indicating the possible presence of pentammine, $Ta(NH_2)_2Cl_3 \cdot 5NH_3$. This is shown more clearly when plotted to larger scale as in Fig. 1-B. To verify the existence of this compound, equilibrium pressure–composition measurements were carried out at 24.5° on a new sample of the ammine of the diamino trichloride. The results are given in Table I, experiment VIII, and are plotted in Fig. 1-C and Fig. 1-D to larger scale. Although there is a definite change of curvature in this plot, it is so gradual that the point of inflection cannot be ascertained definitely. It is to be observed, however, that this pressure curve intersects the one obtained at 0°, indicating that another phenomenon is taking place. It is probable that slight replacement of more chlorine in tantalum pentachloride occurs at this temperature under an appreciable ammonia pressure. Experiments about to be described bear out this supposition.

It seemed advisable at this stage to investigate the tendency of the remaining three atoms of chlorine still attached to the tantalum to be ammonolyzed off by repeated treatment with liquid ammonia and intermediate heating to various temperatures. Since it was by a procedure similar to this that Schwarz and Jeanmaire[11] succeeded in decomposing an ammonium chloride complex of triamido stannic chloride, it was felt that a further replacement of chlorine in $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ might be accomplished in this manner. This actually did occur, for more than three gram atoms of the original five in the pentachloride were ammonolyzed. The procedure, however led to mixtures and consequently the exact nature of the compounds formed could not be ascertained. Experimental conditions in four experiments (IV, V, VI, VII) are summarized in Table III and the corresponding results are tabulated in Table II.

TABLE III

Experiment	IV	V	VI	VII
Heating temp., °C.	100	100	160	240–250
Time, hrs.	5.5	1	1	1
Times performed	1	4	4	4

It is seen that even heating to 100° causes half an additional gram atom of chlorine to be replaced. This was the justification for the assumption previously made that at 24.5° slow replacement of chlorine occurred which interfered with vapor pressure measurements extending over a period of several months. Furthermore, the number of moles of ammonium chloride formed per mole of tantalum pentachloride originally present increases while the quantity of ammonia fixed after the triammine of ammonium chloride has decomposed increases as the severity of treatment is increased. This is not regular, however, as the results obtained in experiments VI and VII approach similarity even though the temperature to which the mixture has been heated differs by almost 100°. This would seem to indicate the formation of stable tantalum compounds but since the molal quantities obtained differ considerably from whole numbers, it is apparently a question of a mixture of two or more substances, the formulas of which cannot be derived directly from the data.

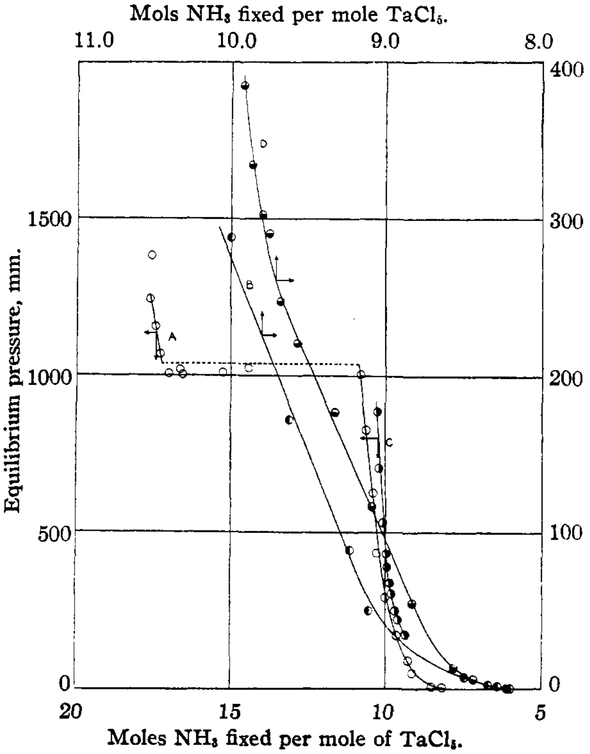

Fig. 1.

Thermal Decomposition of $Ta(NH_2)_2Cl_3 \cdot 7NH_3$.—When the mixture ($Ta(NH_2)_2Cl_3 \cdot 7NH_3$ +

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(11) Schwarz and Jeanmaire, *Ber.*, **66**, 1443 (1932).

$2NH_4Cl$) primarily formed by the action of liquid ammonia on tantalum pentachloride was heated in vacuum, ammonia was evolved continuously as the temperature was raised to 170° and ammonium chloride sublimed onto the cooler parts of the apparatus. At this latter temperature, the evolution of ammonia ceased and hydrogen chloride began to be evolved, showing the commencement of a new reaction. Up to this point seven moles of ammonia had been evolved and two moles of ammonium chloride appeared in the sublimate.

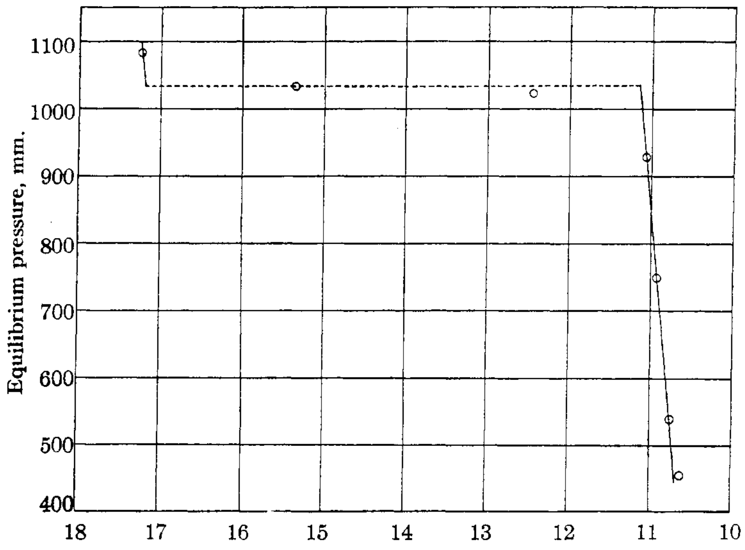

Fig. 2.

As shown by the data in Table IV and by the plot in Fig. 3 there was no indication of a temperature range throughout which there was any discontinuity of evolution, although evolution decreased gradually as the temperature was raised. It is not probable, therefore, that any well-defined intermediate compounds are formed between the heptammine and the amido chloride itself. The data obtained in two experiments are summarized in Table V, all quantities being expressed as total moles per mole of tantalum pentachloride originally present.

TABLE IV

Temp., °C.	NH_3 evolved per mol. $TaCl_5$, mols.	Composition of total solid,[a] x
20–22	2.24	8.72
25–27	2.45	8.51
44–47	3.14	7.82
72–76	4.92	6.04
117	6.03	4.93
170–172	6.62	4.34

[a] Including ammonium chloride.

It is to be noted that although the quantity of ammonia fixed in the end by the tantalum and chlorine (as NH_4Cl) is greater than four by an amount greater than the probable experimental error, nevertheless this deviation was markedly decreased in Experiment II where greater precautions were taken toward the end of the decomposition. Undoubtedly secondary reactions take place to a slight extent with the gaseous ammonia for there was apparently only a very small intermediate temperature range, if any, between cessation of ammonia and commencement of hydrogen chloride evolution, for when the solid residue obtained in expt. 1 was again heated in vacuum to 170°, a small but appreciable hydrogen chloride pressure developed. Another fact which was noted and which undoubtedly did cause a slight error was the formation of a very small quantity of a volatile yellowish tantalum compound of unknown composition which appeared in the sublimate, for a small quantity of white precipitate formed when the latter

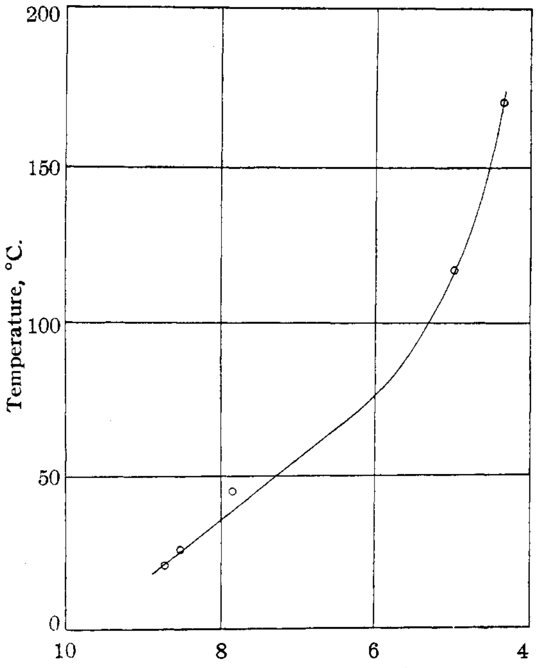

Fig. 3.

TABLE V

Experiment		I	II
Tantalum pentachloride	g.	5.9847	10.859
	mml.	16.70	30.32
NH_3 initially combined		10.53	6.654
Uncombined NH_3 in apparatus		0.43	Negligible
NH_3 evolved			
(1) Determined gasometrically		6.62	2.50
(2) Determined by direct weighing		6.77	2.52
NH_4Cl sublimed			
(1) From direct weighing		2.04	2.08
(2) From Cl analysis		2.05	2.07
(3) From NH_3 analysis		..	2.08
Final NH_3 content of residue			
(1) From gas evolved		4.34	4.15
(2) From change in wt.		4.19	4.13

was treated with water and was shown to be tantalum hydroxide by microscopic examination of the K_2TaF_7 derivative. However, these factors are both so small that it is felt that they do not seriously impair the conclusions that are to be drawn from these results and are merely suggested as probable explanations of deviations from the main reaction taking place.

The preceding experiments show, then, that when the mixture $[Ta(NH_2)_2Cl_3\cdot 7NH_3 + 2NH_4Cl]$ undergoes thermal decomposition, no further replacement of chlorine occurs, provided that the ammonia evolved be removed from the system. The ammonium chloride present sublimes off unchanged and the seven molecules of ammonia coordinately bound are evolved completely.

$$Ta(NH_2)_2Cl_3\cdot 7NH_3 + 2NH_4Cl \longrightarrow Ta(NH_2)_2Cl_3 + 7NH_3 + 2NH_4Cl$$

The composition of this residual tantalum compound was confirmed by analysis.

Analysis of $Ta(NH_2)_2Cl_3$.—The residue in the flask was found to react vigorously with water with evolution of hydrogen chloride and consequently could not be allowed to be exposed to the atmospheric moisture. To determine *nitrogen* content, samples were decomposed with concentrated sulfuric acid, in which reagent gentle heating caused complete dissolution. The ammonia was distilled off from the alkalinized solution and titrated. *Chlorine* was determined by dissolving samples in 33% potassium hydroxide solution (evolution of ammonia), cautious neutralization with nitric acid after dilution, and immediate precipitation of tantalum hydroxide by means of an excess of ammonium hydroxide. The hydroxide was filtered off and washed with dilute ammoniacal ammonium nitrate solution, and chloride in the filtrate determined as silver chloride. Due to occlusion of chloride ion by the colloidal hydroxide[5] it was found helpful, to obtain consistent results, to heat the precipitate of tantalum hydroxide on the water-bath for two days before filtration. *Tantalum* was determined by the method employed by Hahn and Putter,[12] which consisted in treatment of the sample with an excess of sulfuric acid in a weighed platinum crucible and careful evaporation to dryness, the ignited residue being weighed as Ta_2O_5.

Experiment	I	II	Calcd. for $Ta(NH_2)_2Cl_3$
Nitrogen, %	8.8	8.15	8.77
	8.9	8.32	
Chlorine, %	32.86	32.88	33.31
	33.04	33.52	
Tantalum, %	56.40	56.77	56.65
	56.62	56.82	

Due to the fact that the substance could not be ground up and mixed to obtain a homogeneous mixture, the analytical results vary slightly. Taking into consideration this factor along with the fact that any impurities introduced were accumulated in the residue along with incidental hydrolysis products from which purification could not be made at any step of the synthesis, the concordance of the results with the theoretical is satisfactory.

Properties of $Ta(NH_2)_2Cl_3$.—The diamido trichloride of tantalum obtained in this manner is a light yellow solid which decomposes on heating above 170° in vacuum. It is decomposed rapidly by moisture and reacts vigorously with water with evolution of hydrogen chloride and precipitation of hydrated tantalic oxide. That this precipitate contained only negligible quantities of nitrogen was demonstrated by ammonia analysis of its solution in concentrated sulfuric acid. Hence, the hydrolysis can be represented by the equation $2Ta(NH_2)_2Cl_3 + (x + 5)H_2O \longrightarrow Ta_2O_5\cdot xH_2O + 2HCl + 4NH_4Cl$. When fused with potassium hydroxide, ammonia is evolved and the melt is totally soluble in water. On gentle heating, the diamido trichloride dissolves in concentrated sulfuric acid with liberation of hydrogen chloride. Both of these reactions are in accordance with the above hydrolysis and known properties of tantalic oxide.

Conversion of $Ta(NH_2)_2Cl_3$ **to** Ta_3N_5.—The more easily prepared ammine–ammonium chlo-

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[12] Hahn and Putter, *Z. anorg. Chem.*, **127**, 153 (1923).

ride mixture was employed in one experiment. It was heated continuously in the ammonia current at 750° for six days, at which time the sublimation of ammonium chloride to the cooler parts of the tube had ceased. The non-volatile residue remaining in the boat was red with a few purple spots. It was analyzed by the methods described for the diamide. Chlorine was not present. The data are summarized in Table VI.

TABLE VI

			Calcd. for Ta_3N_5
Solid reactant, g.	2.6886		
Ta_3N_5, g.	1.0780		
Ta in Ta_3N_5, %	87.41	88.00	88.57
N in Ta_3N_5, %	11.16	10.97	11.43
Average % Ta	87.39		
Average % N	11.06		
Total % found	98.45		
Atomic ratio of N/Ta	1.640		1.667

The pure diamide gave similar results. At 650–670° the product obtained was brighter red, more homogeneous in appearance and contained no dark spots. The variation of the analytical results among themselves is due to lack of homogeneity as the product was not ground up before analysis. The sum of the percentages of tantalum and nitrogen lacks 1.55% of being 100. Oxide formed from unavoidable reaction of the initial reactants with moisture of the air during experimental manipulation before the conversion is doubtless partly the cause of this discrepancy. The ratio N/Ta is somewhat better than the only other value found in the literature. Joly[13] prepared tantalum pentanitride directly by the action of gaseous ammonia on tantalum pentachloride at elevated temperature and found the corresponding ratio in his product to be 1.61.

It is to be concluded that when the diamido trichloride of tantalum, or its ammine, is heated in a current of ammonia, all of its chlorine is evolved as ammonium chloride which sublimes off and leaves a residue consisting essentially of the red pentanitride of tantalum. Its formation is accounted for by the equation

$$3Ta(NH_2)_2Cl_3 + 8NH_3 \longrightarrow Ta_3N_5 + 9NH_4Cl$$

Physical Properties of Ta_3N_5.—Although the X-ray spectrum of tantalum mononitride is known and the compound has been found to be crystalline,[14] the corresponding data for the pentanitride are lacking. On submitting the latter to X-ray analysis, it showed several well-defined, characteristic lines which were different from those of the mononitride later prepared. Hence, it is to be concluded that the pentanitride is also crystalline. Its density was found to be 8.5 and it was slightly diamagnetic.

Conversion of $Ta(NH_2)_2Cl_3$ to TaN.—Joly[13] found that the pentanitride was converted to the black mononitride by heating in a current of ammonia to red heat. The same conversion takes place as an intermediate step if the diamido trichloride or its ammine be treated similarly as we have already shown in the previous paper.[2] We have evidence that this step consists merely in the decomposition of the pentanitride, the presence of ammonia having no essential bearing on the reaction, which goes according to the equation

$$Ta_3N_5 \longrightarrow 3TaN + N_2$$

The conversion from the ammine was carried out in the same manner as for the pentanitride but at a higher temperature. A 2.1-g. sample of the mixture obtained by the action of liquid ammonia on tantalum pentachloride was heated in a current of dry ammonia gas at 1190° for twenty-four hours. Even under these conditions the conversion was not complete for the black residue obtained still contained more than theoretical nitrogen as shown by the following analysis which was carried out in the manner described for the pentanitride. No chlorine was found to be present.

	Found		Calcd. for TaN
Tantalum, %	91.61	91.75	92.81
Nitrogen, %	8.34	8.11	7.18

When heated in a vacuum the red pentanitride, made from $Ta(NH_2)_2Cl_3$ by heating in a current of ammonia at 750°, evolved nitrogen at 730°. A certain amount of hydrogen, however, was given off simultaneously (0.218 mole per mole of Ta_3N_5), indicating that the initial material contained a hydrogen compound, perhaps a small quantity of an imide, which underwent a decomposition similar to that observed by Moureu and Wetroff[15] in the case of phosphorus compounds. On the other hand, analysis of the black product obtained showed it to contain 8.01% nitrogen and the amount of nitrogen evolved corresponded to only 78% of the theoretical amount for formation of TaN even after six hundred hours of heating in vacuum at 800–850°. It appears that at these temperatures transformation of the pentanitride in vacuum is very slow.

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(13) Joly, *Compt. rend.*, **82**, 1195 (1876).

(14) Van Arkel, *Physica*, **4**, 294 (1924).

(15) Moureu and Wetroff, *Compt. rend.*, **201**, 1381 (1935).

Thermal Decomposition of $Ta(NH_2)_2Cl_3$ in Vacuum.—Due to the complicated character of this reaction it was not possible to arrive at any definite conclusions concerning its mechanism although it can be said with certainty that the two nitrides mentioned are among the products. The main reaction involved seems to be the following, although the change is evidently much more complicated.

$$3Ta(NH_2)_2Cl_3 \longrightarrow Ta_3N_5 + NH_4Cl + 8HCl$$

When heated in vacuum the first gaseous product, hydrogen chloride, commenced to be evolved at 170°. Ammonium chloride sublimed to the cooler parts of the apparatus along with a yellow to green tantalum compound which decomposed with evolution of hydrogen chloride and formation of a dark green to black compound on heating with a free flame. As shown by the data summarized in Table VII for experiments in which samples of the diamido trichloride were heated to various temperatures in vacuum and the residues obtained analyzed, temperatures as high as 800° are required to expel the chlorine completely.

TABLE VII

Experiment		(A)	(B)	(C)	(D)
Temp. of decomposition, °C.		400	600	600	800
Time of decomposition		Several days	3–4 hrs.	2 days	5–6 hrs.
Wt. of sample, g.		1.1006	1.5353	0.4616	1.6080
Millimoles $Ta(NH_2)_2Cl_3$		3.447	4.808	1.445	5.036
Millimoles HCl evolved		1.82	....	1.47	6.80
Millimoles N_2 evolved		0.00	....	0.08	0.31
Wt. of residue, g.		0.7169	0.8938	0.2005	0.7324
Composition of residue, %	Ta	75.3	80.33 78.98	....	86.12 86.12
	N	6.8	7.12 7.04	9.80	10.03 10.01
	Cl	16.5	5.90 5.81	3.4	0.0

The residue obtained varied from greenish brown to black as the temperature of decomposition was raised. In all cases, however, sulfur dioxide was liberated from concentrated sulfuric acid in the nitrogen analysis while the dissolving solid became bright red in experiments (B), (C) and (D), indicating that a superficial coating of mononitride hid the color of the pentanitride. That pentanitride actually was the chief component of the residue in experiment IV was confirmed by its X-ray spectrum. Although the other residues failed to show clearly defined lines, in the latter case well-defined lines corresponding in position to those previously obtained from the pentanitride were found.

The composition of the volatile tantalum compound could not be ascertained because of its small quantity and because of its rapid decomposition by the moisture of the atmosphere. Due to the fact that it underwent a color change on heating it could not have been tantalum pentachloride.

Magnetism of Tantalum Pentachloride.—It might be supposed that the difference in reactivity of the chlorine in tantalum pentachloride to liquid ammonia might be due to dissimilarity in bonding, for example the attachment of three chlorine atoms by doublets, while that of the remaining two by singlets with the formation of an octet structure around the tantalum. In this case it was to be expected that the pentachloride would be paramagnetic. Actual determination of the magnetism of iron-free pentachloride, however, showed it to be slightly diamagnetic. An average of three determinations made on a Curie balance in which the pentachloride was both packed and fused in the determination tube gave for x the value $-0.231 \pm 0.002 \times 10^{-6}$. Hence some other explanation must be sought for this difference in reactivity.

Discussion

Schwarz and Jeanmaire[11] found that with the normal valence halides of Group IV of the periodic classification those of the more metallic high atomic weight elements differed considerably from those of less metallic low atomic weight elements in the ease with which chlorine atoms were ammonolyzed by liquid ammonia. While the tetrahalides of silicon and germanium suffered complete ammonolysis, that of tin required special treatment to bring about complete replacement of chlorine and lead tetrachloride formed a stable chloramide, $Sn(NH_2)_3Cl$, which decomposed to a chloronitride, SnNCl. In the reactions of the chlorides of Group V with liquid ammonia there is an analogous behavior: the pentachloride of phosphorus suffers complete ammonolysis[16] while the halides of bismuth, BiX_3, form ammines but are not ammonolyzed.[17] The transitional element, tantalum, on the other hand, has intermediate properties between phosphorus and bismuth and its pentachloride undergoes only partial replacement of chlorine to form an ammoniated diamido trichloride.

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(16) Moureu and Rocquet, *Compt. rend.*, **200**, 1407 (1935).

(17) Schwarz and Striebich, *Z. anorg. Chem.*, **223**, 399 (1935).

Summary

1. From equilibrium pressure–composition measurements it has been shown that the primary product of the action of liquid ammonia on tantalum pentachloride is soluble $Ta(NH_2)_2Cl_3 \cdot 7NH_3$ which is deposited from solution, along with the ammonium chloride simultaneously produced, in the form of a light yellow crystalline mass.
2. When heated in a vacuum this compound first loses its seven molecules of ammonia coordinatively bound to form the yellow diamido trichloride of tantalum. Study of this reaction revealed a slight discontinuity at the point where the total ammonia fixed by the solid material was nine moles per gram atom of tantalum present, indicating the formation of the pentammine of the diamido trichloride.
3. By repeated alternate heating and submission to the action of liquid ammonia more than three of the original five chlorine atoms in tantalum pentachloride can be ammonolyzed off to form a mixture the components of which were of undetermined character.
4. Some properties of $Ta(NH_2)_2Cl_3$ have been described and its thermal decomposition both in the presence of gaseous ammonia and in vacuum studied. In the presence of gaseous ammonia, the first product isolated was the pentanitride while in a vacuum at the same temperature the pentanitride is accompanied by some mononitride and a small amount of a volatile tantalum compound of undetermined composition.
5. At elevated temperature, in either an atmosphere of ammonia or in a vacuum, the pentanitride is found to decompose to the mononitride with the evolution of nitrogen.
6. Tantalum pentanitride has been shown to be crystalline from its X-ray spectrum and its density has been determined.
7. The magnetic constant of tantalum pentachloride has been measured.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Separation of Gallium and its Colorimetric Determination by Means of Quinalizarin[1]

BY H. H. WILLARD AND H. C. FOGG[2]

Practically the only method available for the detection and estimation of small amounts of gallium is by means of the spectroscope. This furnishes a specific and sensitive method for detection, and one which in the hands of experienced manipulators is quite accurate for its determination. However, it has the disadvantages of requring an apparatus which not all laboratories possess, and a technique which everyone has not had an opportunity to develop.

Dennis and Bridgman[3] using a spark were able to detect, by means of a direct vision spectroscope, the gallium line, 4172, in a concentration of 3 mg. of gallium per 100 ml. when 0.15 ml. of the solution, corresponding to 0.0046 mg. of gallium, was placed in the small cup used to hold the solution. Approximately five times this amount of gallium was required for the line 4033 to be visible. The spectrograph has also been employed by Papish and Holt[4] for the direct detection and semi-quantitative estimation of gallium in certain minerals. Kimura, Nakamura and Kusibe[5] combined chemical concentration with the spectrographic method for the qualitative examination of a large number of Japanese minerals for gallium.

A colorimetric method, even if not as specific, is desirable and an investigation was, therefore, made to find a dye which would form with gallium, a suitable lake.

Experimental

Aurin tricarboxylic acid, alizarin red-S, titan yellow and quinalizarin (1,2,5,8-tetrahydroxyanthraquinone) were tried. Although the first dye gave a color with small amounts of gallium, as stated by Corey and Rogers,[6] no suitable experimental conditions could be established which would allow an accurate colorimetric determination.

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(1) This manuscript was originally received on August 14, 1933, but was withdrawn and resubmitted after additional experimental work had been done.—EDITOR.

(2) Holder of the J. T. Baker Chemical Company Fellowship in Analytical Chemistry for the Mid-Western Division for the academic year, 1931–1932.

(3) Dennis and Bridgman, THIS JOURNAL, **40**, 1531 (1918).

(4) Papish and Holt, *J. Phys. Chem.*, **32**, 142 (1928).

(5) Kimura, Nakamura and Kusibe, *J. Chem. Soc. Japan*, **52**, 55–62 (1931).

(6) Corey and Rogers, THIS JOURNAL, **49**, 216 (1927).