201. *The Reaction between Ammonia and Transition-metal Halides. Part V.* The Reaction of Ammonia with Titanium*(IV) *Bromide and Titanium*(IV) *Iodide.*

By G. W. A. Fowles and D. Nicholls.

Titanium(IV) bromide and iodide have been shown to form di- and hexa-ammoniates when ammonia is passed through their solutions in organic solvents. In liquid ammonia the halides are ammonolysed, titanium(IV) iodide being completely soluble. Ion-exchange studies indicate the formation of complex anionic species of the type $[TiX_n(NH_2)_{6-n}]^{2-}$. At −36° the compounds $TiBr_4,8NH_3$ and $TiI_4,8NH_3$ are formed, and tensimetry indicates that these are mixtures containing mainly $TiBr(NH_2)_3$ and $TiI(NH_2)_3$ respectively. On thermal decomposition, $TiBr_4,8NH_3$ gives the simple adduct $TiBr_4,2NH_3$ as a red sublimate, and a residue of TiNBr. TiN is the final product formed by the decomposition of $TiI_4,8NH_3$.

The reactions of liquid ammonia with metal halides have recently been studied in some detail. It has, for instance, been shown that titanium(IV) chloride,[1] vanadium(IV) chloride,[2] and tin(IV) chloride [3] are ammonolysed, and that when the ammonium chloride is removed by washing with liquid ammonia ammonobasic halides of formula $MCl(NH_2)_3$ are produced. Much less is known of the ammonolysis of the corresponding bromides and iodides, however, and nothing of the reaction of ammonia with titanium(IV) iodide. Work on the titanium(IV) bromide–ammonia reaction has been limited to an early investigation by Ruff and his co-workers [4,5] who obtained a compound $TiBr_4,8NH_3$, which when washed with liquid ammonia left a solid of variable composition; thermal decomposition of this product at 270° *in vacuo* gave a substance of formula TiNBr.

In view of the limitations of Ruff's study we have re-investigated the reaction of ammonia with titanium(IV) bromide, and also examined the analogous titanium(IV) iodide–ammonia reaction.

Experimental

Materials.—Titanium(IV) bromide was prepared by heating titanium metal sponge with bromine under reflux; excess of bromine was distilled off, and the titanium(IV) bromide purified by distillation *in vacuo* (Found: Ti, 13·2; Br, 86·7. Calc. for $TiBr_4$: Ti, 13·0; Br, 87·0%). Titanium(IV) iodide was prepared by heating titanium sponge and excess of iodine under reflux in carbon tetrachloride. After the removal of the excess of iodine and carbon tetrachloride, the titanium(IV) iodide was distilled *in vacuo*, the final traces of iodine being pumped off at 100° (Found: Ti, 8·85; I, 91·1. Calc. for TiI_4: Ti, 8·62; I, 91·4%). Liquid ammonia was dried over sodium. 2 : 2 : 4-Trimethylpentane was dried (P_2O_5); carbon disulphide was shaken with aqueous potassium permanganate to remove hydrogen sulphide and dried (P_2O_5). Other reagents, of "AnalaR" grade, were freed from traces of moisture by placing them in a vacuum for several hours immediately before use.

Analyses.—Nitrogen and titanium were determined as described previously.[1] Bromine was determined gravimetrically as silver bromide, and iodine by titration with potassium iodate.

Magnetic moments were measured as previously described.[6]

Reactions and tensimetry were carried out in the usual type of all-glass closed vacuum system.[1,7]

Passage of Gaseous Ammonia into Solutions of Titanium(IV) *Halides.*—Titanium(IV) bromide

---

* Part IV, *J.*, 1958, 1687.

[1] Fowles and Pollard, *J.*, 1953, 4128.
[2] Fowles and Nicholls, *J.*, 1958, 1687.
[3] Bannister and Fowles, *J.*, 1958, 751.
[4] Ruff and Eisner, *Ber.*, 1908, **41**, 2260.
[5] Ruff and Friedel, *Ber.*, 1912, **45**, 1364.
[6] Fowles and Pleass, *J.*, 1957, 1674.
[7] Fowles and Pollard, *J.*, 1952, 4938.

or iodide was dissolved in a suitable solvent, 2 : 2 : 4-trimethylpentane and carbon disulphide respectively, and ammonia, well diluted with dry oxygen-free nitrogen,[6] was bubbled through. With the bromide, a red compound formed initially, but complete reaction with excess of ammonia gave a yellow substance. The red compound was isolated by carrying out the reaction with excess of titanium(IV) bromide, collecting the product, and washing out the excess of bromide with 2 : 2 : 4-trimethylpentane. After being kept under the pump for 2 hr. at 30°, the red compound was analysed (Found: Ti, 12·2; Br, 77·3; N, 7·4. Calc. for $TiBr_4,2NH_3$: Ti, 11·9; Br, 79·6; N, 7·0%). By using excess of ammonia, the yellow compound was isolated and analysed (Found: Ti, 10·4; Br, 68·0; NH_3, 20·8. Calc. for $TiBr_4,6NH_3$: Ti, 10·2; Br, 68·2; NH_3, 21·7%). When the red compound was heated *in vacuo* to *ca.* 200° for 10 hr., most sublimed but a grey residue remained. The red sublimate again was the diammoniate, $TiBr_4,2NH_3$ (Found: Ti, 11·5; Br, 79·8; N, 6·75%). The grey residue gave analyses (Found: Ti, 34·1; Br, 55·2; N, 9·8%) corresponding to Ti : Br : N = 1·00 : 0·97 : 0·98.

Titanium(IV) iodide is not sufficiently soluble in trimethylpentane or any of the hydrocarbons or chlorinated hydrocarbons, and so carbon disulphide was used as a solvent. Since carbon disulphide reacts [8] with ammonia under some conditions, it was necessary to check whether this reaction would seriously affect the present results. When excess of ammonia was passed through carbon disulphide, however, only a white opalescence resulted, and even on prolonged passage of ammonia only a faint white precipitate was formed. On passage of ammonia through a solution of titanium(IV) iodide in carbon disulphide, a black precipitate formed at first, but this turned yellow with excess of ammonia. These two products were filtered off, washed with carbon disulphide, pumped for several hours, and analysed (Found, for black product: Ti, 8·13; I, 83·6; NH_3, 5·97%; Ti : I : N = 1·00 : 3·88 : 2·07. Calc. for $TiI_4,2NH_3$: Ti, 8·13; I, 86·1; NH_3, 5·77%. Found, for yellow product: Ti, 7·24; I, 75·0; NH_3, 16·0%; Ti : I : N = 1·00 : 3·91 : 6·22. Calc. for $TiI_4,6NH_3$: Ti, 7·28; I, 77·2; NH_3, 15·5%).

Ethylene glycol dimethyl ether was also a good solvent for titanium(IV) iodide, but when ammonia was passed through this solution only a pale yellow precipitate was formed.

Washing procedure for titanium(IV) *bromide.* Titanium(IV) bromide reacted initially with liquid ammonia to give a red compound, but with excess of ammonia an orange solid and a yellow solution were formed. After four or five washes with liquid ammonia (50 ml.), the filtrates were colourless, although if the orange solid was then pumped it partly dissolved in liquid ammonia to give a yellow solution. After some twenty washes with liquid ammonia, together with intermediate pumping, virtually all the solid had dissolved. The insoluble product was accordingly examined at various washing stages (on separate runs); it was pumped for several hours at 60° before analysis (see Table 1).

TABLE 1. *Insoluble product.*

	Analyses (%)			Ratios	
Run No.	Ti	Br	N	Ti : Br : N	Comments
1	18·3	54·6	23·1	1·0 : 1·8 : 4·3	12 washes; no intermediate pumping
2	22·2	47·5	25·9	1·00 : 1·28 : 3·98	12 washes; intermediate pumping twice
3	22·2	46·9	24·2	1·00 : 1·27 : 3·73	17 washes; intermediate pumping thrice
4 *	—	—	—	1·00 : 1·29 : 3·90	4 washes; no intermediate pumping

* In this run, a product $TiBr_4,6NH_3$ was first formed in the flow system, and then washed with liquid ammonia in the usual way. Ratios only are quoted for the analysis, since the product was hydrolysed *in situ.*

The solid was diamagnetic. It dissolved readily upon addition of a solution of ammonium bromide in liquid ammonia. Tensimetry of the insoluble product–ammonia system [Fig. 1(*a*)] at −36° shows the absence of free ammonium bromide; a 2-ammoniate appears to be formed.

Evaporation of all the washings left a heterogeneous mixture of yellow and white substances; after being pumped at 60° for several hours this mixture was hydrolysed *in situ* and analysed. Table 2 shows the results expressed in the form of an N : Br ratio. The soluble portion is assumed to be a mixture of ammonium bromide and an ammonobasic titanium(IV) bromide, and the N : Br ratio is obtained from the nitrogen and bromine still unaccounted for after deduction of that associated with the titanium.

---

[8] Sánchez and Bereau, *Anales Fis. Quim.*, 1945, **41**, 1117.

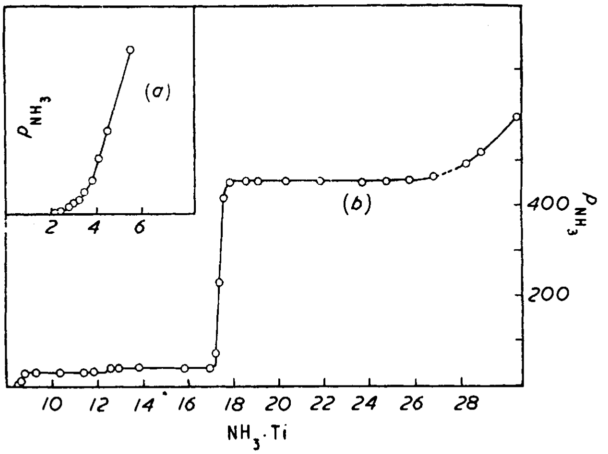
To separate this soluble compound, if possible, from the ammonium bromide, the initial reaction of titanium(IV) bromide with ammonia was carried out in the presence of excess of barium nitrate; any ammonium bromide would form the insoluble barium bromide. The whole mixture was kept at −40°, with occasional shaking, and the yellow solution was filtered from the white residue; this was washed several times with liquid ammonia to remove any soluble titanium compound. The white insoluble product was almost entirely barium bromide and contained only a negligible amount (0·10%) of titanium. The soluble product, which was hydrolysed *in situ*, on analysis gave Ti : Br : N = 1·00 : 0·06 : 5·84; some excess of barium nitrate was also present, but this was not estimated quantitatively. Since the nitrogen was determined by distillation as ammonia from sodium hydroxide solution, the nitrate nitrogen was not estimated.

TABLE 2. *Soluble portion.*

	N : Br ratio, Ti being assumed to be present as:			
Run No.	$Ti(NH_2)_4$	$TiBr(NH_2)_3$	$TiBr_2(NH_2)_2$	$TiBr_2(NH_2)_2,2NH_3$
1	1·00 : 1·52	1·00 : 0·96	1·00 : 0·55	1·00 : 0·92
2	1·00 : 1·86	1·00 : 1·06	1·00 : 0·61	1·00 : 1·08
3	1·00 : 2·14	1·00 : 1·04	1·00 : 0·52	1·00 : 1·08
4 *	1·00 : 1·69	1·00 : 0·93	1·00 : 0·51	1·00 : 0·90

* Initial product ($TiBr_4,6NH_3$) formed in a flow run.

FIG. 1.



Washing procedure for titanium(IV) *iodide.* Initially titanium(IV) iodide reacted with liquid ammonia to give a greenish-black solid, but with excess of ammonia this solid dissolved completely to give a yellow solution. After evaporation of ammonia a yellow solid remained which darkened to orange-brown on pumping at 40°. The product, which was readily hydrolysed by water or dilute acids with formation of a colourless solution, was analysed (Found: Ti, 7·10; I, 75·3; N, 13·2%; Ti : I : N = 1·00 : 4·00 : 6·33. Calc. for $TiI_4,6NH_3$: Ti, 7·28; I, 77·2; N, 12·8%). In view of the colourless solution formed on hydrolysis, it seems that the titanium is still quadrivalent.

To see whether the yellow solution contained anionic titanium species, it was passed down a column of anion-exchange resin (" De Acidite FF " in Cl^- form). The 20 cm. column of resin had been prepared previously by pumping the resin dry for 24 hr. and then washing it with liquid ammonia until several successive filtrates gave an immediate blue colour with sodium metal. The column was thermostatically controlled at −40°, and the liquid ammonia solution of titanium(IV) iodide allowed to pass slowly down it. The solution emerged colourless from the column, but on evaporation of the liquid ammonia it deposited a white solid consisting entirely of ammonium chloride. On subsequent elution of the column with a solution of sodium bromide in liquid ammonia, the eluent was found to contain titanium. It seems, therefore, that the yellow solution contains titanium in an anionic form.

Tensimetric and Thermal-decomposition Studies of the Titanium(IV) *Bromide–Ammonia and the Titanium*(IV) *Iodide–Ammonia System.*—The titanium(IV) bromide–ammonia isotherm obtained at −36° [Fig. 1(*b*)] shows the univariant portions attributable to ammonium bromide; these univariant steps have an overall length of 8·6 moles of NH_3/mole of $TiBr_4$, indicating [9] the presence of almost 3 mol. of free ammonium bromide. At −63°, the isotherm is very similar in general appearance, although the slightly shorter univariant steps (totalling 8·3 mol. of NH_3) indicate the formation of rather less ammonium bromide. In each case, the removal of excess of ammonia at the reaction temperature left a substance with overall composition $TiBr_4,8NH_3$. When this substance was heated *in vacuo*, ammonia was steadily lost (the overall composition of $TiBr_4,6NH_3$ being attained at *ca.* 60°); at 150° the product darkened to brick-red, and a bright red sublimate formed. This was resublimed (Found: Ti, 11·9; Br, 78·9; N, 7·5. Calc. for $TiBr_4,2NH_3$: Ti, 11·9; Br, 79·6; N, 6·8%). On further heating of the product to 200°, ammonium bromide also began to sublime, leaving a brown residue, which became black at 280°. Analytical figures for various products are given in Table 3.

FIG. 2.

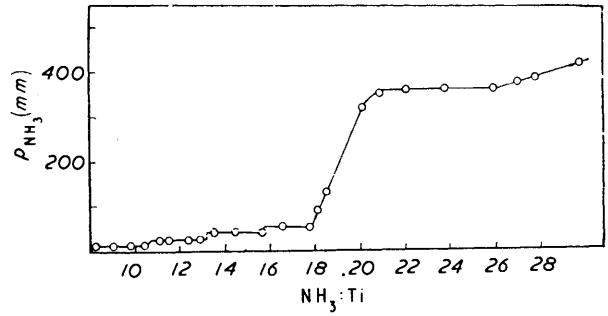


TABLE 3. *Involatile products formed by the thermal decomposition of* $TiBr_4,8NH_3$.

Temp.	Heating time (hr.)	Analyses (%) Ti	Br	N	Ratio Ti : Br : N	Comment
210°	2	14·6	75·6	8·35	1·00 : 3·09 : 1·95	Diamagnetic
210	18	28·1	62·0	8·90	1·00 : 1·32 : 1·08	—
280	4	32·2	56·1	9·70	1·00 : 1·04 : 1·03	—

The brown solid, obtained after short heating at 200°, dissolved completely in a small amount of liquid ammonia, although an orange solid was precipitated on dilution of the solution.

The titanium(IV) iodide–ammonia isotherm obtained at −36° (Fig. 2) shows univariant steps attributable to ammonium iodide, and the overall length of 9·9 moles of NH_3/mole of TiI_4 suggests the presence of some 2·5 mole of ammonium iodide. The product had an overall composition of $TiI_4,8NH_3$ when excess of ammonia was removed, but on heating *in vacuo* it steadily lost ammonia. Above 70°, iodine was given off, while ammonium iodide sublimed at 180° leaving a black product. The analysis of several products is given in Table 4.

TABLE 4. *Involatile products formed by the thermal decomposition of* $TiI_4,8NH_3$.

Temp.	Analyses (%) Ti	I	N	Ratios Ti : I : N	Comments
210°	26·2	62·2	7·70	1·00 : 0·90 : 1·00	Diamagnetic, but gives blue-green solution on hydrolysis
400	40·0	42·9	11·9	1·00 : 0·41 : 1·02	Highly pyrophoric
400	59·3	25·8	14·4	1·00 : 0·16 : 0·83	„ „ (Prolonged heating)

---

[9] Bannister and Fowles, *J.*, 1958, 4374.

DISCUSSION

In the flow runs, titanium(IV) bromide and iodide each formed a di- and a hexa-ammoniate, but there was no evidence for the formation of other products. In view of the similarity of the analogous ammoniates, it seems reasonable to consider them to have similar structures, and the arguments put forward are therefore intended to cover the products formed by both halides.

The hexa-ammoniates cannot be simple adducts, because the titanium atom is unable to assume the necessary co-ordination number of ten. It is possible, however, that the diammoniates are simple addition compounds in which the titanium(IV) halide behaves as a Lewis acid and accepts electrons from the ammonia molecules to achieve an octahedral configuration ($3d^2 4s 4p^3$). The only alternative is to consider the diammoniates as mixtures of the ammonium halide and the ammonobasic titanium(IV) halide: $NH_4X + TiX_3(NH_2)$. The sublimate which is formed by decomposing the initial product at 200° is almost certainly a simple adduct in view of its volatility and homogeneous appearance, and by analogy with the well-established volatile diammoniates of the tin(IV) halides,[3,9] and its formation is readily explained, irrespective of whether the initial diammoniate is an adduct or a mixture:

$$\left.\begin{array}{l}\text{(i) } TiBr_4,2NH_3 \longrightarrow TiBr_4 + 2NH_3 \\ \text{(ii) } TiBr_3(NH_2) + NH_4Br \longrightarrow TiBr_4 + 2NH_3\end{array}\right\} \xrightarrow[\text{surface}]{\text{on cold}} TiBr_4,2NH_3$$

Side reactions in the " hot zone " would produce the TiNBr which is also formed.

It is less certain that the original diammoniate is a simple adduct, although several observations agree with this concept. Thus, although a mixture $TiBr_3(NH_2) + NH_4Br$ has the required overall composition, the ammonobasic titanium(IV) bromide should form a strong diammoniate itself, making the overall composition that of a tetra-ammoniate. A second point is that no black product was obtained when ammonia was passed through a solution of titanium(IV) iodide in ethylene glycol dimethyl ether, even though a yellow product was formed with excess of ammonia; the ether would itself form a chelate addition compound, and it seems unlikely that ammonia would co-ordinate in preference, although ammonolysis would occur with excess of ammonia. On the whole, it is probable that the diammoniate is a simple adduct.

Since the hexa-ammoniates cannot be simple adducts, it is evident that ammonolysis has occurred with excess of ammonia, giving a mixture of ammonium halide and the corresponding ammonobasic titanium(IV) halide. On the assumption that the titanium atom has a convalency of six or less, two simple formulations are possible: (i)$TiX_2(NH_2)_2,2NH_3 + 2NH_4X$ and (ii) $TiX(NH_2)_3 + 3NH_4X$. There is no conclusive evidence in favour of either of these, and it is shown below that the washing and tensimetric experiments indicate the presence of both.

When titanium(IV) bromide reacted with excess of liquid ammonia, it mostly dissolved, although some residue (containing about 30% of the original titanium) remained even after extensive washing; the iodide, however, dissolved completely. We will consider the soluble products to be the major ones, and leave discussion of the insoluble bromide residue for the moment.

A heterogeneous solid was, for instance, obtained on evaporation of either solution, and analysis of the bromide product (cf. Table 2) showed it to be a mixture of ammonium bromide and either $TiBr(NH_2)_3$ or $TiBr_2(NH_2)_2,2NH_3$. Although the products are obviously mixtures, it is not unlikely that the solubility in liquid ammonia is caused by interaction of these constituents to form complex ions,[2] so that titanium(IV) iodide, for instance, might react with liquid ammonia according to the scheme: $TiI_4 + 6NH_3 \longrightarrow TiI(NH_2)_3 + 3NH_4I \longrightarrow [NH_4]_2[TiI_3(NH_2)_3] + NH_4I$. The ion-exchange experiments show quite conclusively that a complex titanium anion is in fact present in the iodide solution, and if we assume the titanium atom to attain a covalency of six then the anion is most likely to be

$[\mathrm{TiI_3(NH_2)_3}]^{2-}$. (This assumes that polynuclear species are not present.) The soluble bromide product probably contains similar anions, so that when the initial reaction is carried out in the presence of barium nitrate, the bromine is displaced from the labile titanium anion by nitrate ion, and precipitated as barium bromide:

$$[\mathrm{TiBr_3(NH_2)_3}]^{2-} \xrightarrow{\mathrm{NO_3^-}} [\mathrm{Ti(NO_3)_3(NH_2)_3}]^{2-} + \mathrm{Br^-}$$

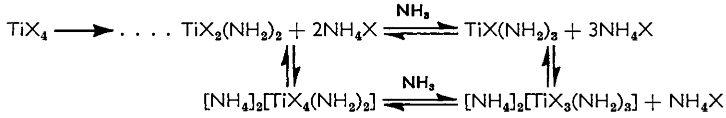
The tensimetric studies at —36° show that almost 3 mol. of ammonium bromide but only 2·5 mol. of ammonium iodide are formed in the titanium(IV) bromide- and titanium(IV) iodide–ammonium systems. A little less ammonium bromide is formed at —63°. The probable explanation of these results is that by way of the equilibrium

$$\mathrm{TiX_2(NH_2)_2 + NH_3 \rightleftharpoons TiX(NH_2)_3 + NH_4X}$$

there is almost quantitative formation of $\mathrm{TiBr(NH_2)_3}$ at —36° with slightly less ammonolysis at lower temperatures because of the lower ionisation of the ammonia. Titanium(IV) iodide will be less completely ammonolysed, because ammonium iodide is more soluble in liquid ammonia than is ammonium bromide, and in the tensimetric experiments very concentrated and highly acidic solutions would be formed, reversing the maximum ammonolysis attained in dilute solutions.

This explanation is more satisfactory than postulating that some ammonium iodide remains undetected because it is bound up and unable to form its characteristic ammoniates; this alternative would imply that the complex anion formed in solution partly remains in the solid state. Not only would one expect the complex to be present entirely, or not at all, but it would then be very odd that the full amount of ammonium bromide is found when the complex bromide anion should be even more stable; it is well known that the stability of anionic titanium complexes falls off in the order $\mathrm{F^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$.

We can summarise the main reactions of the titanium(IV) halides with ammonia by saying that, with excess of ammonia, three of the titanium–halogen bonds are ammonolysed, and that some of the ammonium halide will combine with the ammonobasic titanium(IV) halide to form anionic titanium species. As the solution becomes concentrated, so the ammonolysis tends to be reversed, and at the saturation point there is a mixture of ammonobasic titanium(IV) halides. The complex titanium anions break down when the ammonia is removed, and the mixture of ammonium halide and ammonobasic titanium(IV) halides remains:



$$\begin{tikzcd}
\mathrm{TiX_4} \arrow[r] & \cdots\ \mathrm{TiX_2(NH_2)_2 + 2NH_4X} \arrow[r, shift left, "\mathrm{NH_3}"] \arrow[d, shift left] & \mathrm{TiX(NH_2)_3 + 3NH_4X} \arrow[l, shift left] \arrow[d, shift left] \\
 & {[\mathrm{NH_4}]_2[\mathrm{TiX_4(NH_2)_2}]} \arrow[u, shift left] \arrow[r, shift left, "\mathrm{NH_3}"] & {[\mathrm{NH_4}]_2[\mathrm{TiX_3(NH_2)_3}] + \mathrm{NH_4X}} \arrow[l, shift left] \arrow[u, shift left]
\end{tikzcd}$$

With titanium(IV) chloride,[1] only a small amount of the reaction product dissolves in liquid ammonia, and an insoluble ammonobasic titanium(IV) chloride, $\mathrm{TiCl(NH_2)_3}$, remains. Titanium(IV) bromide largely dissolves, however, although some solid remains, which even on exhaustive washing and pumping between washes still has a Ti : Br : N ratio of 1·0 : 1·3 : 3·7. Since the insoluble residue no longer dissolved after four or five washes unless it was first pumped, it seemed that the residue must either be a polymer, which broke down on pumping, or contain trapped titanium(IV) bromide. Some bromide might not have reacted, since the bromide used was in rather large crystals so that the centre could be protected by surface reaction products. Accordingly, the hexa-ammoniate from a flow run was washed with liquid ammonia, and in this case most of it dissolved in only a few washes without intermediate pumping to leave a residue similar to that finally obtained in straight washing runs. Since the hexa-ammoniate would not contain unchanged titanium(IV) bromide, and is unlikely to be highly polymeric (because it is formed from solution), it seems that the pumping effect was indeed a matter of " pulling out " unchanged bromide. The final residue, however, is still high in bromine and particularly in nitrogen content, compared with that expected for $TiBr(NH_2)_3$. Ruff and Eisner,[4,5] who obtained a somewhat similar analysis, suggested a mixture of $2Ti(NH_2)_4,TiBr_4,8NH_3$ and $3Ti(NH)_2,TiBr_4,8NH_3$, and although this is clearly impossible, the non-stoicheiometric composition does imply a mixture. The main component is probably $TiBr(NH_2)_3$, which is soluble only in excess of ammonium bromide, so that the readily soluble ammonium bromide will have been washed away before all the $TiBr(NH_2)_3$ has dissolved. The other likely component is $TiBr_2(NH_2)_2,2NH_3$; on prolonged washing this will gradually become ammonolysed, producing $TiBr(NH_2)_3$ and NH_4Br, much of which will dissolve as the complex $[NH_4]_2[TiBr_3(NH_2)_3]$. The mixture of these two components required to produce the correct Ti : Br ratio will still give a low Ti : N ratio (1 : 3·3), and it is likely that $TiBr_2(NH_2)_2$ is present partly as a tetra-ammoniate, this ammonia of addition being partly lost on pumping.

These observations are in agreement with the tensimetric experiments, and the uptake of almost 2 mol. of ammonia by the insoluble residue around —36° is readily accounted for:

$$2NH_3 + TiBr(NH_2)_3 \longrightarrow TiBr(NH_2)_3,2NH_3;\quad TiBr_2(NH_2)_2,2NH_3 \longrightarrow TiBr_2(NH_2)_2,4NH_3$$

A comment should be made on the tetra-ammoniate, since this gives the titanium atom a co-ordination number of eight; the same behaviour was observed with tin(IV) iodide.[9] Titanium is usually assumed to have a maximum covalency of six, even though a number of apparently octacovalent compounds have been reported.[10] It is perhaps possible that the titanium atom could attain a covalency of eight with the relatively small ammonia molecule, although more probable that the two extra ammonia molecules are held in a " secondary sphere of influence," rather like the ammoniates formed by cobaltammine-type ions.[11]

Although the products formed in the tensimetric studies are similar for both the bromide and the iodide, in that overall compositions $TiX_4,6NH_3$ remain at 60°, the subsequent thermal decompositions differ; iodine is liberated from the iodide product above 70°, and there is no sublimate of $TiI_4,2NH_3$. The decomposition of the bromide product appears to follow the scheme:

$$\begin{array}{lcl}
TiBr_4,8NH_3 = TiBr(NH_2)_3,2NH_3 + 3NH_4Br & & -36^\circ \\
\qquad\qquad\quad \downarrow (1) & & \\
TiBr_4,6NH_3 = TiBr(NH_2)_3 + 3NH_4Br & & 60^\circ \\
\qquad\qquad\quad \downarrow (2) & & \\
TiBr_4,2NH_3 = TiBr_3(NH_2) + NH_4Br & & 150^\circ \\
\qquad\qquad\qquad\quad \downarrow (3) & & \\
\qquad\quad TiBr_4 + 2NH_3 \xrightarrow[(4)]{} TiBr_4,2NH_3 & &
\end{array}$$

Some of these decompositions obviously overlap, and reaction (3) is evidently incomplete because some ammonium bromide sublimes before it can react. The residue of $TiBr_3(NH_2)$ then forms TiNBr, although, as previously mentioned, the latter compound could also arise from reaction (4). From the magnetic susceptibility and chemical properties of the product, it is clear that titanium is still quadrivalent.

The thermal decomposition of the iodide product is more complicated, once the composition $TiI_4,6NH_3$ has been attained. In view of the liberation of iodine, the formation of lower-valency titanium compounds would be expected, and this is in agreement with the formation of a blue-green solution when the unsublimed product is hydrolysed, although the diamagnetism of the product shows that the titanium atom has no unpaired electrons.

---

[10] Trost, *Canad. J. Chem.*, 1952, **30**, 835.

[11] Spacu and Voichesu, *Z. anorg. Chem.*, 1940, **243**, 288.

A possible explanation is that a titanium–iodine bond is thermally broken (with the liberation of iodine), followed by the formation of a titanium–titanium link. The resulting species would then have chemical properties consistent with tervalent titanium, but be diamagnetic. The final product of prolonged heating at 400° contains very little iodine, and appears to be largely a nitride of titanium. A possible decomposition scheme is:

$$\mathrm{TiI(NH_2)_3 + 3NH_4I[or\ TiI_2(NH_2)_2{,}2NH_3 + 2NH_4I] \longrightarrow TiI_2(NH_2)_2 + 2NH_4I \xrightarrow{>70^\circ}}$$

$$\mathrm{[TiI(NH_2)_2]_2 + I_2 + 2NH_4I \xrightarrow{200^\circ} (TiINH)_{\mathit{n}} + NH_3 + 2NH_4I \xrightarrow{400^\circ} TiN}$$

We thank the Esso Petroleum Company for a maintenance grant (to D.N.) and British Titan Products for their interest and financial assistance.

THE UNIVERSITY, SOUTHAMPTON. [*Received, October 6th,* 1958.]