527. *Studies on the Behaviour of Halides of the Transition Metals with Ammonia. Part II.* The Reaction of Titanium Tetrachloride with Ammonia.*

By G. W. A. Fowles and F. H. Pollard.

The reaction between titanium tetrachloride and ammonia has been investigated tensimetrically at temperatures between −36° and −63°, and explained by the formation of amidochlorides, *e.g.*, $Ti(NH_2)_3Cl$. Thermal decomposition of the products in vacuum at 350° gave TiNCl.

An improved apparatus is described for the study of reactions in liquid ammonia.

THE reaction of titanium tetrachloride with ammonia was first studied by Rose (*Pogg. Ann.*, 1829, **16**, 57) and Persoz (*Ann. Chim. Phys.*, 1830, [ii], **44**, 321) who reported the formation of yellow compounds, $TiCl_4,4NH_3$ and $TiCl_4,6NH_3$, respectively. When the latter compound was left in a desiccator over calcium chloride, it became colourless with the loss of two molecules of ammonia, and, after extraction of this material with liquid ammonia, another colourless substance was obtained which was thought to be the amide, $Ti(NH_2)_4$ (Rosenheim and Schutte, *Z. anorg. Chem.*, 1901, **26**, 245; Blix, *Ber.*, 1903, **36**, 4228). Stahler (*Ber.*, 1905, **38**, 2619), however, observed that the initial hexammoniate

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* Part I, *J.*, 1952, 4938.

was hydrolysed under the conditions used by the former workers, yielding a mixture of titanium hydroxide and ammonium chloride with a similar overall titanium content. He also reported a complex, $TiCl_4,8NH_3$, which on extraction with liquid ammonia gave a dark yellow amide, $Ti(NH_2)_4$.

The work of Blix and of Stahler was repeated by Ruff and Eisner (*Ber.*, 1908, **41**, 2250), who were unable to obtain a completely chlorine-free substance even on prolonged washing with liquid ammonia. When the washed product was thermally decomposed at 300° in vacuum, a blue-black substance was formed, which Ruff claimed to be impure titanium nitrogen chloride, TiNCl, but his analytical results suggest that the product was contaminated with an appreciable amount of hydrolysed material. This would be expected, since the washed product was transferred to a porcelain boat for the decomposition, without any precautions to exclude moisture.

More recently, Brager (*Acta Physicochim. U.R.S.S.*, 1939, **10**, 887) has made a thorough *X*-ray study of the thermal decomposition of the $TiCl_4,4NH_3$ complex (which is formed at room temperature). He found that, at 200°, the complex changed from its initial deep yellow to a greyish-green colour, without alteration in composition. A greenish-brown substance, having a variable composition, was formed at 300°, changing to TiNCl at 350°. Prolonged heating above 400° gave the nitride, TiN, and chlorine.

Since the nature of the complexes which are formed initially has not been previously investigated, we have (*a*) produced materials of maximum ammonolysis, and (*b*) investigated the $TiCl_4$–NH_3 system tensimetrically. (*a*) The products would be expected to show the greatest ammonolysis at high reaction temperatures, and after prolonged washing with liquid ammonia to remove any ammonium chloride which was formed. (Ammonium chloride is very soluble, and the titanium complex insoluble, in liquid ammonia.) The reaction has therefore been carried out at the boiling point of liquid ammonia (—33·5°) and at room temperature (in a Carius tube), and the product extracted with liquid ammonia. (*b*) Our tensimetric studies were made at reaction temperatures of —36° and —63°, followed by the thermal decomposition of the product *in vacuo* to a temperature of 350°.

EXPERIMENTAL

Titanium tetrachloride was obtained in ampoules from British Drug Houses and condensed under vacuum into thin-walled bulbs (Found : Ti, 25·20; Cl, 74·7. Calc. for $TiCl_4$: Ti, 25·25; Cl, 74·75%). Ammonia was purified as described in Part I (*loc. cit.*).

Reaction between Ammonia and Titanium Tetrachloride.—The reaction at —63° and —36° has been followed by a method similar to that described for the niobium pentachloride–ammonia reaction (Part I, *loc. cit.*). The resulting pressure–composition values are plotted in Fig. 1, curves (*a*) and (*b*) respectively. Both curves are perfectly reproducible in their general shape. After the removal of excess of ammonia at the reaction temperature, the complex remaining had an overall composition corresponding to $TiCl_4,8NH_3$.

Thermal Decomposition of $TiCl_4,8NH_3$.—This complex appeared to be the same no matter what the original reaction temperature was, being a very pale yellow, easily hydrolysed substance, which decomposed liberating ammonia when heated over the temperature range —30° to 300°. In order to investigate the possibility of stable intermediate complexes, the initial compound was heated for 2 hr. at 20°-intervals up to 220°, any gases liberated being trapped in a bulb cooled in liquid oxygen, and their nature (ammonia in every case) and amount determined. A typical variation of composition with temperature is shown in Fig. 2.

The colour of the complex deepens as ammonia is removed, becoming orange-yellow when the composition $TiCl_4,2NH_3$ is reached at 180°. On further heating, the product changed to a brick-red, apparently homogeneous substance at 240°, and to a dark green material at 300°. During these heatings, a sublimate appeared on the cooler part of the stem of the reaction bulb, varying in colour from deep red near the hot bulb to yellow in the coolest part. These colours remained if the bulb was allowed to cool to room temperature. No gas pressure was recorded on the manometer during these decompositions, although traces of titanium tetrachloride were found in the tap grease, and could be condensed over into the calibrated bulb.

While the red compound formed at 240° was hydrolysed quite easily, the greenish-black substance was hydrolysed only slowly in water but decomposed readily in concentrated nitric acid. The red compound is evidently a mixture, its analysis (Ti, 39·85; N, 15·2; Cl, 44·2%) corresponding to the ratio $Ti_1N_{1\cdot33}Cl_{1\cdot50}$. The greenish-black material gave analyses corresponding to ratios varying from $Ti_1N_{1\cdot34}Cl_{1\cdot41}$ (after 2 hr.' heating at 300°) to $Ti_1N_{0\cdot97}Cl_{1\cdot04}$ (after 2 hr.' heating at 350°), the total percentage in every analysis being between 99 and 100.

Samples of all these compounds were found to be slightly diamagnetic, thus precluding the possibility of any lower valency state for titanium.

Reaction of Ammonia with Titanium Tetrachloride at −33·5° (*b. p. of ammonia*), *followed by Washing with Liquid Ammonia.*—Several workers have devised an apparatus with which it is possible to achieve some measure of filtration with solutions in liquid ammonia, among whom may be mentioned Schwarz and Schenk (*Ber.*, 1930, **63**, 296) and Thomas and Pugh (*J.*, 1931, 60) : both were concerned with the ammonolysis of germanium compounds. The simple apparatus of Thomas and Pugh needed rebuilding after each experiment, and decomposition studies were not possible. Schwarz and Schenk, on the other hand, designed an intricate system in which many operations would become extremely tedious, if not impossible : a severely modified and simplified version of this apparatus was used in our experiment, the final form being shown in Fig. 3. Reaction vessel *D* contained a sintered glass filter *M* of porosity 3. The ammonia was stored in *B* and could be transferred to any other part of the apparatus by condensation, while *E* was a jointed bulb containing sodium to be used for purifying the ammonia, which was then used again and again for washing. Safety valves, *H*, *I*, *J*, and *K*, in the form of manometer bubblers, were provided in those parts of the apparatus where excessive pressures of ammonia might develop.

FIG. 1.

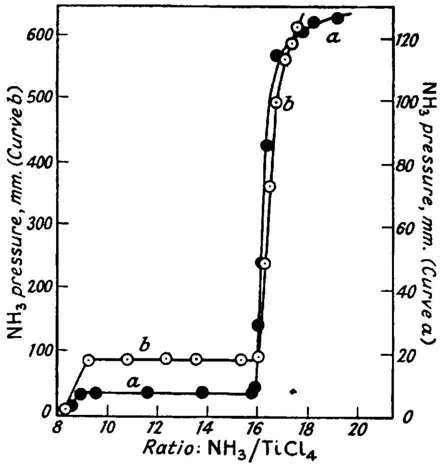
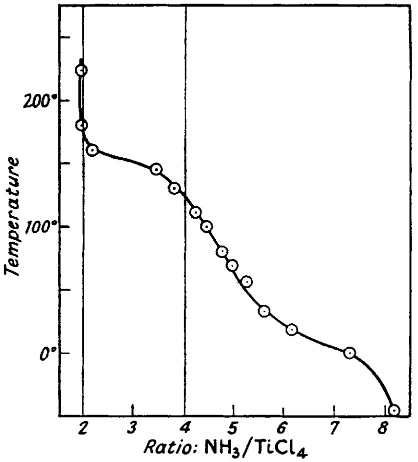


FIG. 2.



Method of using the Apparatus.—Liquid ammonia from the cylinder was placed in trap *A*, and sodium added until a permanent blue colour was observed. The ammonia was allowed to evaporate through bubbler *H*, until all the air in the apparatus had been displaced, final traces being removed by surrounding *A* with a cold bath (−35° to −40°), closing tap 1, and evacuating the storage vessel with the pump. The ammonia was then condensed into *B* by means of a solid carbon dioxide bath. Freezing out with liquid oxygen was avoided, since *A* cracked on a number of occasions.

n-Pentane, which had been carefully dried ($MgSO_4$), was condensed into *C*. A sealed bulb of titanium tetrachloride was placed in a jointed tube, together with a glass-encased ball bearing, and, when air had been removed by the pump, was broken magnetically. The titanium chloride was then condensed on to the pentane in *C*, and a clear solution obtained by warming to room temperature. Ammonia was condensed into *D* from *B* until the filter *M* was covered, and then the pentane solution was run over from *C* into *D* by opening tap 2 (the vapour pressure of the pentane solution being sufficient to push the solution over). A further layer of ammonia was condensed on the titanium tetrachloride solution layer, and the whole allowed to warm to −33·5°. After 2 hr., the ammonia and pentane were pumped away, and a further quantity of ammonia was condensed in the reaction vessel and allowed to boil gently. The solution was agitated magnetically—a glass-encased steel ball being previously placed on the filter. The liquid ammonia was filtered over into *E* (evacuated and surrounded by a solid carbon dioxide bath) by opening tap 3, undue evaporation of the ammonia being prevented by surrounding the tubing from *D* to *E* with asbestos string. The purified ammonia was then condensed back into the storage vessel *B* by way of the glass-wool filter *G* and tap 4. Further quantities of ammonia were condensed on to the reaction products and again filtered off, the process being repeated until the washings were free from ammonium chloride, as shown when no further hydrogen was liberated in *E* ($NH_4Cl + Na = NaCl + NH_3 + \frac{1}{2}H_2$). The product was then allowed to warm to room temperature, and pumped hard with the high-vacuum pump for 1 hr. to remove any absorbed ammonia. A stream of nitrogen (purified in the usual way over P_2O_5 and heated Cu) was flushed through the filter, escaping by way of bubbler *J*, and the reaction vessel was removed and the product shaken into a weighed jointed tube for analysis.

Samples of the deep yellow product remaining after twelve washes were analysed (see Table 1), the total percentage in every case being between 96 and 97. The ratios varied between $Ti_1N_{3\cdot42}Cl_{1\cdot20}$ and $Ti_1N_{3\cdot11}Cl_{1\cdot03}$, the majority of the analyses approaching the second ratio. Since the precautions taken eliminate the possibility of hydrolysis of the product with consequent oxide contamination, the persistent 3—4% deficiency in the total analysis may be assumed to be hydrogen, giving the substance an empirical formula $Ti_1N_3Cl_1H_{4-6}$.

FIG. 3.

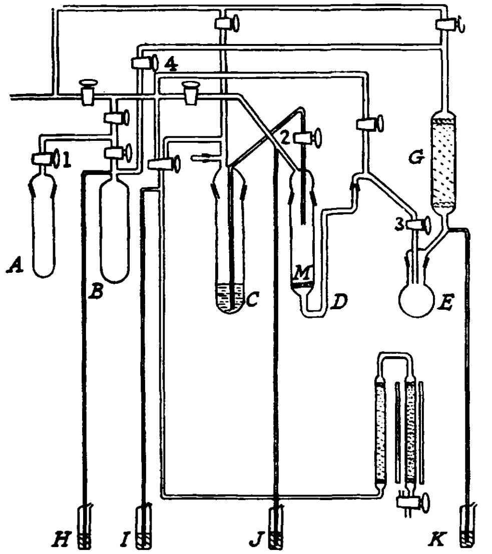
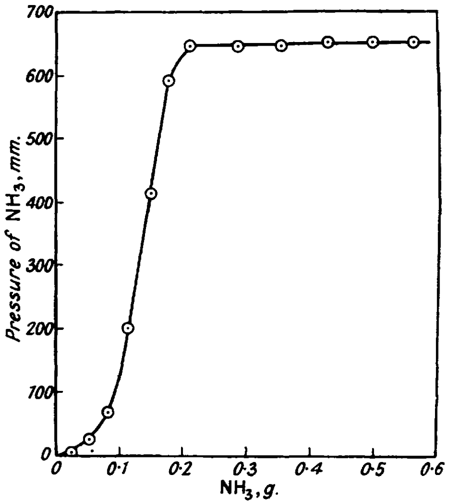


FIG. 4.



Reaction in Sealed Carius Tubes, followed by Washing with Liquid Ammonia.—Even extensive washing of the low-temperature reaction product failed to replace the last chlorine atom, so in an attempt to achieve complete ammonolysis, titanium tetrachloride and ammonia were condensed into a Carius tube, sealed off, and allowed to react at room temperature. After 5 days, the tube was cooled to −33°, and its tip scored and hot-spotted. A length of Polythene tubing was quickly slipped over the Carius tube, whose contents were then poured rapidly into the filter vessel. Hydrolysis during this transference was reduced to a minimum by passing a steady stream of dried nitrogen through the filter vessel. After excess of ammonia had evaporated away, the pale yellow product was pumped hard and washed with liquid ammonia in the usual way. The deep yellow material produced in this way appeared to be identical

TABLE 1. *Typical analyses for the washed product from the* $TiCl_4$–NH_3 *reaction.*

No.	Ti, %	N, %	Cl, %	Total, %	Ratio Ti : N : Cl
1	33·4	33·4	29·7	96·5	1 : 3·42 : 1·20
2	34·3	33·9	28·9	97·1	1 : 3·38 : 1·12
3	35·9	32·7	27·4	96·0	1 : 3·11 : 1·03
4	35·0	33·1	28·3	96·4	1 : 3·23 : 1·09

with the low-temperature washed product in both appearance and composition (Table 2), and in no experiment did the Ti : Cl ratio exceed 1 : 1.

TABLE 2. *Typical analyses for the washed product* (*Carius tube*).

No.	Ti, %	N, %	Cl, %	Total, %	Ratio Ti : N : Cl
1	34·0	31·4	29·7	95·1	1 : 3·16 : 1·18
2	34·0	32·7	29·0	95·7	1 : 3·28 : 1·15

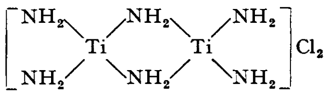
Tensimetric Study of the Washed Product.—A weighed sample (0·303 g.) was placed in the reaction bulb, a known excess of ammonia condensed on it, and a tensimetric curve (Fig. 4) obtained in the usual way.

Thermal Decomposition of the Washed Product.—When heated *in vacuo*, the product liberated almost 2 mol. of ammonia between 100° and 220°, becoming very deep red-brown. When heated to 380° for 2 hr., the product became black, and liberated a small amount of ammonia—making 2 mol. in all. Only a very small amount of yellow sublimate formed on the cooler part of the tube. Analysis of the black sample gave the following figures : Ti, 47·8; N, 14·6; Cl, 35·9%, corresponding to Ti : N : Cl = 1 : 1·04 : 1·01.

DISCUSSION

The substance obtained by washing with liquid ammonia had an empirical formula $Ti_1N_3Cl_1H_{4-6}$, irrespective of whether the initial reaction was carried out at −33·5° or room temperature, and is no doubt the amidochloride $Ti(NH_2)_3Cl$. The pressure–composition curve for the system NH_3–$Ti(NH_2)_3Cl$ (Fig. 4) has no univariant portion, and it is evident that the titanium complex does not take up ammonia to form an ammoniate, and that no ammonium chloride is present. Since all the added ammonia is exactly given up, no further reaction has taken place.

Complex structures of the type (I) could be suggested for the washed product, but they


(I)

seem less likely since the tetrachlorides of silicon and germanium are known to give simple amides or imides when ammonolysed. Stannic chloride, moreover, is reported by Schwarz and Jeanmaire (*Ber.*, 1932, **65**, 1443) to give the analogous amidochloride, $Sn(NH_2)_3Cl$.

The thermal decomposition of the titanium amidochloride may be represented by the equation $Ti(NH_2)_3Cl = TiNCl + 2NH_3$. Our tensimetric study might be expected to show the existence of a mixture of such an amidochloride with ammonium chloride, though the reaction might not go to completion until the ammonium chloride was removed by washing with ammonia. The pressure–composition curves (Fig. 1) show three sections, as with those obtained for the ammonium chloride–ammonia reaction (Part I, *loc. cit.*), and it is evident that 16 molecules of ammonia initially react with one of titanium tetrachloride, $TiCl_4 + 16NH_3 = TiCl_4,16NH_3$, 8 being removed by a univariant process leaving $TiCl_4,8NH_3$. The pressure of this univariant step corresponds to the dissociation of ammonium chloride triammoniate, suggesting the formation of $2\frac{2}{3}$ moles of ammonium chloride, *i.e.*, the initial reaction is represented by the stoicheiometric equation :

$$3TiCl_4 + 48NH_3 = 2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2,8NH_3 + 8NH_4Cl,3NH_3$$

so that the product contains two amidochlorides. The ammonium chloride loses its ammonia in a vacuum at the reaction temperature, leaving a mixture of ammonium chloride and amidochlorides, with the overall composition $TiCl_4,8NH_3$ [*i.e.*, $2Ti(NH_2)_3Cl + Ti(NH_2)_2Cl_2,8NH_3 + 8NH_4Cl$]. When this mixture is heated to 180° *in vacuo*, its composition changes to $TiCl_4,2NH_3$ (*i.e.*, without loss of hydrogen chloride), so it is not possible to account for the presence of $2\frac{2}{3}$ moles of ammonium chloride at this stage.

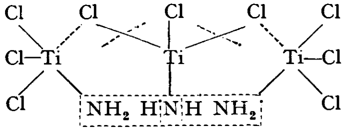
The two possibilities are : (1) The ammonium chloride present reacts with the product on heating, liberating ammonia. (2) The length of the univariant portion of the tensimetric curve is not proportional to the amount of ammonium chloride present. The first possibility is perhaps the more likely. The ammonium chloride initially formed will be taken into solution by the excess of ammonia present, and an equilibrium position reached. It is not possible to prove the existence of this equilibrium tensimetrically, since the amount of ammonia needed to produce a measurable shift would be considerable, and the experimental error involved would be of similar significance. When excess of ammonia is removed, an intimate mixture of ammonium chloride and the amidochlorides exists, which might react on heating according to the equations :

$$\text{(i)}\quad Ti(NH_2)_3Cl + NH_4Cl = Ti(NH_2)_2Cl_2 + 2NH_3$$

$$\text{(ii)}\quad Ti(NH_2)_2Cl_2 + NH_4Cl = Ti(NH_2)Cl_3 + 2NH_3$$

$$\text{(iii)}\quad Ti(NH_2)Cl_3 + NH_4Cl = TiCl_4 + 2NH_3$$

The thermal decomposition of the $TiCl_4,8NH_3$ complex is shown in Fig. 2, and since the general shape of this curve is reproducible under very varied conditions, the inflexion in the slope suggests the intermediate existence of $TiCl_4,4NH_3$. The ammonia held by amidochloride $Ti(NH_2)_2Cl_2$, by weak ion–dipole forces, would be easily lost, the amidochlorides then reacting with the ammonium chloride. Since $Ti(NH_2)_3Cl$ has been shown not to lose ammonia below 90°, it probably reacts with the ammonium chloride before it can split out ammonia, leaving the mixture $Ti(NH_2)_2Cl_2 + 2NH_4Cl$, with the overall composition $TiCl_4,4NH_3$. On continued heating, $Ti(NH_2)Cl_3$ is formed (see reaction ii), so the limiting composition obtained at 180° is the mixture $Ti(NH_2)Cl_3 + NH_4Cl$. When the temperature is raised still further, the amidochloride may react either with the ammonium chloride (see reaction iii), giving titanium chloride and ammonia (which react immediately outside the hot zone), or with other amidochloride molecules: $3Ti(NH_2)Cl_3 = 2TiCl_4 + 2NH_3 + TiNCl$, *i.e.*, (II). Both of these reactions are equally probable at high temperatures, and would no doubt take place simultaneously.



(II)

In such a complicated system, it is difficult, from phase-rule considerations, to see how a univariant step is obtained which is not a direct measure of the amount of ammonium chloride present, unless some mixed-crystal formation takes place, giving rise to equilibria of the type $Ti(NH_2)_nCl_{4-n},nNH_4Cl,yNH_3 = Ti(NH_2)_nCl_{4-n},nNH_4Cl + yNH_3$. Under these conditions, the complex could contain any quantity of ammonium chloride up to the maximum of $2\frac{2}{3}$ moles. Since $Ti(NH_2)_3Cl$ is formed on washing, it seems more likely that at least some of this will be present in the unwashed product.

A discussion of this reaction cannot be concluded without mentioning the chance of complex-ion formation. Anions of the type $[Ti(NH_2)_xCl_{6-x}]^{--}$ are not unlikely, and Schmitz-DuMont (*Angew. Chem.*, 1950, **62**, 560), for instance, has found titanium alkoxides to react with a solution of potassium in liquid ammonia, forming the salt $K_2[Ti(OR)_4(NH_2)_2]$. Such ions would, however, be expected to be soluble in liquid ammonia, whereas the titanium complex is a solid, insoluble in all the usual solvents, and so probably has a polymeric nature. Any amidochlorides present will, therefore, almost certainly not be monomeric.

TiNCl is produced on decomposition *in vacuo* at 350°, but in view of Brager's excellent *X*-ray study (*loc. cit.*), thermal decomposition of this substance was not studied in detail.

A discussion of the replacement of chlorine atoms by amido-groups, along the lines of Wardlaw's alcoholysis studies (*J.*, 1950, 3450), is reserved until a subsequent paper, when the study of the behaviour of the Group IVA metal tetrachlorides with ammonia will be completed.

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