20. *The Ammonolysis of Hexahalogenotitanates.*

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

The ammonolysis of several hexachlorotitanates (M_2TiCl_6, where M = NH_4, NH_3Me, K) and diammonium hexabromotitanate has been studied; in each case two titanium–halogen bonds are ammonolysed. The thermal decomposition of the products has been examined.

Halides of most of the transition metals in their highest valency state are ammonolysed in liquid ammonia,[1,2] and the ammonobasic metal halides formed can often be isolated because they are insoluble in liquid ammonia. This insolubility is probably due to the highly polymeric nature of the compounds. They dissolve, however, in highly concentrated solutions of ammonium halides, and in view of recent ion-exchange experiments with solutions of titanium(IV) iodide in liquid ammonia,[2] and by analogy with acids $H_2[Ti(OH)_nCl_{6-n}]$ formed in aqueous systems,[3] it seems likely that the solution is brought about through the formation of ammono-acids, *e.g.*:

$$TiX(NH_2)_3 + NH_4X \text{ (excess)} \longrightarrow (NH_4)_2[TiX_3(NH_2)_3]$$

To obtain further support for this idea, we have examined the ammonolysis of several hexahalogenotitanates.

The hexachlorotitanates dissolve almost completely, and the hexabromotitanate completely, in ammonia; ammonolysis undoubtedly occurs, giving a soluble complex, and information on the extent of this ammonolysis is provided by tensimetric experiments (cf. Table 1 and Figs. 1a, 2a, and 3a). This tensimetric procedure can give only an average value for the number of metal–chlorine bonds ammonolysed when the product is insoluble in ammonia, and hence polymeric, but gives a truer picture for the hexahalogenotitanates where the products are largely soluble. Considering the ammonolysis of the diammonium hexachloro- and hexabromo-titanates, we observe that four mols. of ammonium halide are present. There are two possible explanations, namely:

$$\text{(i)}\ (NH_4)_2TiX_6 \longrightarrow (NH_4)_2[TiX_2(NH_2)_4] + 4NH_4X$$

$$\text{(ii)}\ (NH_4)_2TiX_6 \longrightarrow \begin{array}{c}(NH_4)_2[TiX_4(NH_2)_2] + 2NH_4X\\ \downarrow\\ TiX_2(NH_2)_2 + 4NH_4X\end{array}$$

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[1] Fowles and Nicholls, *J.*, 1958, 1687.

[2] Fowles and Nicholls, *J.*, 1959, 990.

[3] Rumpf, *Ann. Chim.* (*France*), 1937, **8**, 456.

TABLE 1.

Halide	Solubility (%) with excess of ammonia	Insoluble product, washed with ammonia	Mol. ratio NH_4X/Ti detected tensimetrically
$TiCl_4$	5	$TiCl(NH_2)_3$	2·7
$(NH_4)_2TiCl_6$	90	$TiCl(NH_2)_3 + TiCl_2(NH_2)_2$	4·0
K_2TiCl_6	70	,, ,,	2·0
$(NH_3Me)_2TiCl_6$	90	,, ,,	—
$TiBr_4$	70	$TiBr(NH_2)_3 + TiBr_2(NH_2)_2$	2·7
$(NH_4)_2TiBr_6$	100	—	4·0
TiI_4	100	—	2·5

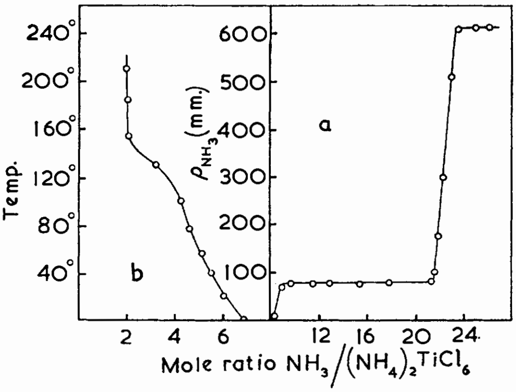
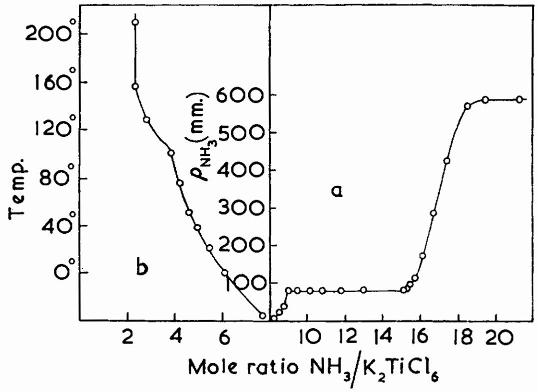


FIG. 1. *The* NH_3–$(NH_4)_2TiCl_6$ *system.*
(a) *Tensimetric plot.*
(b) *Thermal decomposition.*

FIG. 2. *The* NH_3–K_2TiCl_6 *system.*
(a) *Tensimetric plot.*
(b) *Thermal decomposition.*



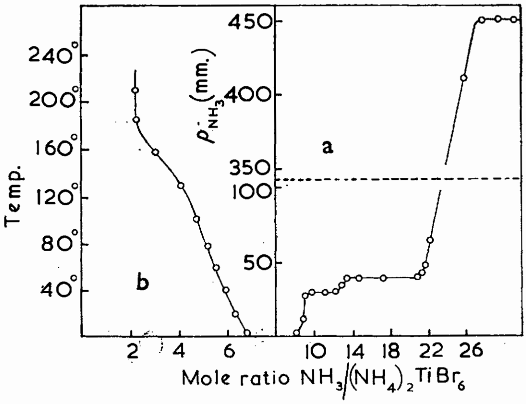


FIG. 3. *The* NH_3–$(NH_4)_2TiBr_6$ *system.*
(a) *Tensimetric plot.*
(b) *Thermal decomposition.*

In scheme (i), four mols. of ammonium halide are produced, the complex is stable under the conditions of the tensimetric runs, and the four mols. of ammonium halide form the appropriate ammoniates. In scheme (ii), only two titanium–halogen bonds are ammonolysed, but breakdown of the complex (in the absence of excess of ammonia) leads to the formation of four mols. of ammonium halide.

The complex is unlikely to remain intact under the tensimetric conditions, because it certainly does not in the analogous reactions of titanium(IV) bromide and iodide with ammonia, where although the solutions contain complex anions, virtually all the ammonium halide is detected tensimetrically. Under scheme (ii) we get a consistent explanation whereby a soluble complex is formed with excess of ammonia; when the ammonia is removed the complex breaks down into the ammonobasic titanium(IV) halide and ammonium halide. Hence under the tensimetric conditions we should expect to find four mols. and two mols. of ammonium halide produced by the ammonolysis of the diammonium and dipotassium salts respectively.

Although two titanium–chlorine bonds are ammonolysed in both hexachlorotitanates, a further reaction will occur with the potassium salt because potassium chloride has only a moderate solubility in liquid ammonia and will be precipitated:

$$\begin{aligned} K_2TiCl_6 &\xrightarrow{NH_3} K_2[TiCl_4(NH_2)_2] + 2NH_4Cl \\ &\longrightarrow (NH_4)_2[TiCl_4(NH_2)_2] + 2KCl \end{aligned}$$

This removal of ammonium chloride is unlikely to result in further ammonolysis of the complex ion because the acidity of the solution (*i.e.*, concentration of NH_4^+) is unchanged.

The small residue remaining on filtration of the solution formed by diammonium hexachlorotitanate had a composition corresponding to a mixture of $TiCl_2(NH_2)_2,2NH_3$ and $TiCl(NH_2)_3$; this is presumably a polymer of variable composition, in which the Ti : Cl ratio can be lowered close to 1 : 1 by prolonged washing with ammonia. A similar residue is obtained from the dipotassium salt, except that it is somewhat contaminated with potassium chloride.

The reaction of bismethylammonium hexachlorotitanate with ammonia is essentially the same as that of the other hexachloro-salts, except that there is also interaction between ammonia and the methylammonium ion:

$$(NH_3Me)X + NH_3Me \longrightarrow (NH_4)X + NH_2Me$$

This reaction goes almost to completion in the presence of excess of ammonia. Direct evidence for this displacement comes from the work of Aida[4] who from Raman spectra measurements showed free methylamine to be present in solutions of methylamine hydrochloride in liquid ammonia. A similar displacement of one amine from amine hydrochloride and bisalkylammonium hexachlorozirconates by another amine has been reported recently.[5]

Removal of excess of ammonia at −36° from products formed in the tensimetric experiments leaves ammonolytic mixtures with the overall compositions of octa-ammoniates:

$$(NH_4)_2TiX_6,8NH_3 \equiv TiX_2(NH_2)_2,4NH_3 + 4NH_4X$$

$$K_2TiCl_6,8NH_3 \equiv TiCl_2(NH_2)_2,4NH_3 + 2NH_4Cl + 2KCl$$

When the mixtures are heated *in vacuo* ammonia is lost and examination of the thermal decomposition curves (Figs. 1b, 2b, and 3b) suggests a modest stability for mixtures with the overall composition $M_2TiX_6,4NH_3$.

The decomposition above 130° is in every case of a more fundamental nature. Thus

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[4] Aida, *Sci. Reports Res. Inst. Tohôku Univ.*, 1956, Ser. A, **8**, **441**.

[5] Drake and Fowles, *J. Inorg. Nuclear Chem.*, in the press.

the products from the diammonium hexabromotitanate(IV)–ammonia reaction decompose between 130° and 210° to produce a red sublimate of the simple adduct $TiBr_4,2NH_3$ (this has been previously obtained from the titanium(IV) bromide–ammonia system under similar conditions), and ammonium bromide also sublimes, leaving finally a residue of composition approaching TiNBr. It seems that the ammonobasic titanium(IV) bromide, $TiBr_2(NH_2)_2$, may either decompose [cf. reactions (*a*) and (*b*)] or interact with ammonium bromide [cf. reactions (*c*) and (*d*)], both probably occurring simultaneously:

$$\left.\begin{array}{ll}(a) & TiBr_2(NH_2)_2 \longrightarrow TiBr_2(NH) + NH_3 \\ (b) & TiBr_2(NH) \longrightarrow TiNBr + HBr\end{array}\right\} \longrightarrow NH_4Br$$

$$(c)\ TiBr_2(NH_2)_2 + NH_4Br \longrightarrow TiBr_3(NH_2) + 2NH_3$$

$$(d)\ TiBr_3(NH_2) + NH_4Br \longrightarrow TiBr_4 + 2NH_3 \longrightarrow TiBr_4,2NH_3$$

The diammoniate of titanium(IV) bromide is formed on the cooler part of the wall of the reaction vessel through recombination of ammonia and the bromide; some ammonium bromide is formed by a similar process, and some sublimes directly from the reaction mixture.

Both hexachlorotitanate–ammonia products decompose analogously, although the residue from the dipotassium salt contains the involatile potassium chloride. The yellow sublimate is probably the diammoniate $TiCl_4,2NH_3$, since this has previously been reported by Antler and Laubengayer[6] to be a product of the gas-phase reaction of titanium(IV) chloride and ammonia.

The transient blue colour formed by solutions of some of the residues on hydrolysis in dilute sulphuric acid indicates that there is a little reduction of titanium to the tervalent state; this is not perhaps surprising in view of the reducing conditions.

EXPERIMENTAL

Materials.—The preparation of the hexahalogenotitanates is described elsewhere.[7] Liquid ammonia was dried over sodium.

Analysis.—Gravimetric methods were used to determine titanium (as dioxide), chlorine (as silver chloride), and bromine (as silver bromide). Potassium was determined by difference. Nitrogen was determined as ammonia. Unless otherwise stated, all products were hydrolysed with dilute sulphuric acid before analysis, and colourless solutions were formed.

Reactions and Tensimetric Studies.—Since all reactants and products were readily hydrolysed, studies were made under rigorously anhydrous conditions in the usual type of all-glass closed-vacuum system.[8]

(a) *Solubility studies in liquid ammonia.* (i) Diammonium hexachlorotitanate dissolved almost completely in excess of liquid ammonia to give a yellow solution. A little yellow solid remained on filtration, and this was washed several times, kept *in vacuo* for several hours at room temperature, and then analysed (Found: Ti : Cl : N = 1·00 : 1·65 : 3·58). A mixture of yellow and white solids was obtained by evaporation of the filtrate, and this was hydrolysed *in situ* and analysed. Table 2 shows the analytical results expressed in the form of N : Cl ratios; the soluble portion is assumed to be a mixture of some ammonobasic titanium(IV) chloride with ammonium chloride, and the N : Cl ratio is obtained from the nitrogen and chlorine still unaccounted for after allowing for that associated with the titanium. This ratio should be 1 : 1 (*i.e.*, NH_4Cl).

TABLE 2. *Analysis of the soluble portion.*

Run	N : Cl ratio if Ti present as			
no.	$Ti(NH_2)_4$	$TiCl(NH_2)_3$	$TiCl_2(NH_2)_2,2NH_3$	$TiCl_3(NH_2),2NH_3$
1	1·00 : 0·67	1·00 : 0·97	1·00 : 0·96	1·00 : 1·52
2	1·00 : 0·73	1·00 : 1·03	1·00 : 1·04	1·00 : 1·58

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[6] Antler and Laubengayer, *J. Amer. Chem. Soc.*, 1955, **77**, 5250.
[7] Fowles and Nicholls, *J. Inorg. Nuclear Chem.*, in the press.
[8] Fowles and Pollard, *J.*, 1953, 2588.

(ii) *Triaminochloridotitanium*(IV), prepared by Fowles and Pollard's method[8] [Found: Ti, 35·7; N, 32·2. $TiCl(NH_2)_3$ requires Ti, 36·4; N, 32·0%], partly dissolved in a solution of ammonium chloride in ammonia, the solubility increasing with the concentration of ammonium chloride. The solubility was far less than that of $VCl(NH_2)_3$ (in $NH_4Cl–NH_3$), and appreciably less than that of $TiBr(NH_2)_3$ (in $NH_4Br–NH_3$).

(iii) Dipotassium hexachlorotitanate largely dissolved to a yellow solution. The residue left on filtration continued to dissolve when washed with ammonia, but the filtrate became colourless after three washings, although it still deposited a white solid on evaporation. The residue of 15 washings with 50 ml. of ammonia was analysed after it had been heated *in vacuo* at 40° for some hours (Found: Ti, 28·6; Cl, 23·6; NH_2, 40·0; K, 7·8%; corresponding to Ti : Cl : N : K = 1·00 : 1·89 : 2·46 : 0·33, or 0·33KCl + Ti : Cl : N = 1·00 : 1·56 : 2·46). The soluble product contained almost all the original potassium (Found: Ti, 9·78; Cl, 46·6; NH_3, 14·1; K, 29·5%; corresponding to Ti : Cl : N : K = 1·00 : 6·44 : 3·84 : 3·70, or 3·70KCl + Ti : Cl : N = 1·00 : 2·74 : 3·84).

(iv) Bismethylammonium hexachlorotitanate resembled the potassium salt in its solubility. Twelve washings left an orange-yellow residue (0·16 g.) (Found: Ti, 26·3; Cl, 33·0; N, 32·6%; corresponding to Ti : Cl : N = 1·00 : 1·69 : 4·24). As excess of ammonia was removed from the filtrate, the last drops smelled strongly of methylamine; the orange-pink residue (0·854 g.) was analysed (Found: Ti, 10·3; Cl, 51·5; N, 29·2%; corresponding to Ti : Cl : N = 1·00 : 6·74 : 9·66). On the assumption that the difference in the total from 100% is due to either H (from ammonia), or H and CH_3 (from methylamine), it can be calculated that more than 90% of the original methylamine had been expelled by ammonia.

(v) Diammonium hexabromotitanate was entirely soluble in excess of ammonia, giving a yellow solution; the pale yellow heterogeneous solid obtained from the filtrate was analysed (Found: Ti, 7·09; Br, 69·6; NH_3, 21·1%; corresponding to Ti : Br : N = 1·00 : 5·88 : 8·38).

(b) *Tensimetric studies.* These were carried out at −36°, and the product thermally decomposed in the usual way.[8] Results obtained for the systems of ammonia with diammonium and dipotassium hexachlorotitanates, and diammonium hexabromotitanate, are illustrated in Figs. 1, 2, and 3 respectively. In view of the liberation of methylamine from the ammonia–bismethylammonium hexachlorotitanate reaction, this system was not examined tensimetrically.

With both of the hexachlorotitanates, the products changed from pale yellow at −36° (overall composition $M_2TiCl_6,8NH_3$) to orange at 100° (overall composition $M_2TiCl_6,4NH_3$). When the products were heated above 130° a yellow sublimate started to be formed, and above 160° a substantial white sublimate was formed in addition. The compositions given in Figs. 1b, 2b, and 3b include any sublimed material. The residue from the diammonium salt reaction, which was red-brown after being heated to 210°, had an analysis corresponding to Ti : Cl : N = 1·00 : 1·52 : 1·01. The residue from the dipotassium salt reaction became black when heated above 200°; samples were taken for analysis from reaction products heated to 210° and 360° [Found (for the 210° product): Ti, 17·1; Cl, 47·0; N, 3·36; K, 32·5%; corresponding to 2·34KCl + Ti : Cl : N = 1·00 : 1·38 : 0·67. Found (for the 360° product): Ti, 15·5; Cl, 46·8; N, 2·94; K, 34·8%; corresponding to 2·75KCl + Ti : Cl : N = 1·00 : 1·33 : 0·65]. These residues, which contained all the potassium originally introduced as K_2TiCl_6, dissolved in dilute sulphuric acid to give pale-blue solutions which rapidly became colourless.

In the thermal decomposition of the products from the $NH_3–(NH_4)_2TiBr_6$ reaction, a bright red sublimate appeared at 155°, and a copious white sublimate formed at 180° [Found, for mixed sublimate (0·47 g.): Ti, 6·27; Br, 81·4; N, 10·5%; corresponding to Ti : Br : N = 1·00 : 7·78 : 5·73 (approximately $TiBr_4,2NH_3$ + 3·73NH_4Br]. The black residue (0·039 g.) remaining at 210° dissolved in dilute sulphuric acid with the formation of a rapidly fading blue colour (Found: Ti, 29·8; Br, 61·7; N, 8·9%; corresponding to Ti : Br : N = 1·00 : 1·24 : 1·02).

SOUTHAMPTON UNIVERSITY.

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