450. *The Reaction between Ammonia and Transition-metal Halides. Part VI.*[1] *The Reaction of Ammonia with Tungsten*(VI) *Chloride.*

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Tungsten(VI) chloride reacts with liquid ammonia to give a series of ammoniates, but subsequently undergoes ammonolysis with the formation of various ammonobasic tungsten(VI) chlorides. Compounds of overall composition $WCl_6,4NH_3$ and $WCl_6,6NH_3$, which are formed by passing ammonia gas through a solution of tungsten(VI) chloride in carbon tetrachloride, contain the ammonobasic products $WCl_5(NH_2)$ and $WCl_4(NH_2)_2$, respectively; the thermal decomposition of these compounds is discussed.

The reaction of ammonia with transition-metal halides has been studied in detail in recent years;[1] covalent halides of the metals in their higher-valency states are ammonolysed in liquid ammonia to give an ammonobasic metal halide and the appropriate ammonium halide, *e.g.*, $TiCl_4 \longrightarrow TiCl(NH_2)_3,2NH_3 + 3NH_4Cl$.

Little work has been done on the analogous reactions of the molybdenum and tungsten halides, however, apart from that by Bergström,[2] who cursorily examined the ammonolysis of several halides and reported the formation of ammonobasic metal halides of indefinite composition. Spacu[3] studied the tungsten(VI) chloride–ammonia system tensimetrically at −75°, and then removed associated ammonia at various temperatures up to 0°; except for establishing the formation of a product of overall composition approximating to $WCl_6,6NH_3$, this investigation gave little information about the reaction.

Extending our studies on ammonolysis, we now report on the reaction of tungsten(VI) chloride with liquid ammonia (as investigated by both tensimetric and washing experiments) and with gaseous ammonia (when passed through a solution of the halide in carbon tetrachloride).

EXPERIMENTAL

Materials.—Liquid ammonia (from Imperial Chemical Industries Limited) was dried (Na) before distillation into the apparatus *in vacuo.* Tungsten(VI) chloride was prepared by the action of chlorine on pure tungsten powder (Messrs. Johnson and Matthey) at 600° in a quartz tube; traces of tungsten(VI) oxychlorides were also formed, but were sublimed off *in vacuo*

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[1] Part V, Fowles and Nicholls, *J.*, 1959, 990.

[2] Bergström, *J. Amer. Chem. Soc.*, 1925, **47**, 2317.

[3] Spacu, *Bull. Sect. sci. Acad. Roumaine,* 1940, **22**, 329.

(Found: Cl, 53·4. Calc. for WCl_6: Cl, 53·6%). Carbon tetrachloride ("AnalaR") was dried over, and distilled from, phosphoric oxide immediately before use.

Analyses.—Nitrogen was determined as ammonia by distillation from alkaline solution into hydrochloric acid followed by titration with standard sodium hydroxide (B.D.H. 4·5 indicator). Chlorine was determined potentiometrically by titration with silver nitrate, in a sodium acetate–acetic acid buffered solution, silver–silver chloride and mercurous sulphate electrodes being used. Tungsten was determined by reduction to the tervalent state with lead amalgam, followed by addition of ferric alum and titration with potassium dichromate with sodium diphenylaminesulphonate as indicator; a modified form of Holt and Gray's apparatus[4] was used.

Magnetic-moment Measurements.—These were made at room temperature on a Gouy-type balance, at a field strength of 8000 gauss.

Reactions and Tensimetric Studies.—These were carried out in the usual type of all-glass closed vacuum system,[5,6] with joints and stopcocks lubricated with Silicone grease.

(i) *Passage of ammonia vapour through a solution of tungsten*(VI) *chloride in carbon tetrachloride.* Tungsten(VI) chloride dissolved in carbon tetrachloride to give a red solution, and when ammonia vapour, in a stream of well-dried oxygen-free nitrogen, was passed through the solution, a green precipitate formed, but this became chocolate-brown with excess of ammonia. The green and the brown product were isolated by stopping the reaction at the appropriate stage, filtering *in vacuo*, and washing out any unchanged tungsten(VI) chloride with carbon tetrachloride. The products were analysed after removal of excess of carbon tetrachloride at the pump [Found, for green product: $WCl_6 : NH_3 = 1·00 : 4·20$ (1·00 : 4·35). Found, for brown product: $WCl_6 : NH_3 = 1·00 : 6·04$ (1·00 : 5·95)]. Both products were heated *in vacuo* from room temperature to 200°, and any evolved products were condensed and examined. The results are in Table 1.

TABLE 1. *Thermal decomposition of* $WCl_6,4NH_3$ *and* $WCl_6,6NH_3$.

	$WCl_6,4NH_3$	$WCl_6,6NH_3$
* Gas liberated below 130°	—	1 mole NH_3
* Gas liberated above 130°	1·8 moles HCl	1 mole HCl
NH_4Cl found	2·0 moles	2·84 moles
Analysis of black residue remaining at 200° (W : Cl : N)	1·0 : 2·05 : 1·60	1·0 : 2·18 : 1·82

* The liberated gas was identified by its vapour density and by simple chemical tests.

(ii) *Washing procedure.* Tungsten(VI) chloride largely dissolved in liquid ammonia to give a deep reddish-brown solution, although a small amount of brown solid remained undissolved even on prolonged washing with liquid ammonia. The composition of this residue, which contained about 10% of the original tungsten, varied from experiment to experiment within the limits W : Cl : N = 1·0 : 2·5 : 3·4 and 1·0 : 1·9 : 3·8 although it approached the latter ratio in the majority of cases. The solid was diamagnetic.

When excess of ammonia was evaporated from the filtrate, a heterogeneous solid remained, which after pumping for several hours was hydrolysed *in situ* and analysed. In expressing the results of the analysis of several products (cf. Table 2) we have assumed that the soluble portion is a mixture of ammonium chloride and an ammonobasic tungsten(VI) chloride, so that from the determined tungsten content, the associated nitrogen and chlorine required for each of the more likely compounds can be calculated. The N : Cl ratio for the remaining nitrogen

TABLE 2. *Soluble portion.*

	N : Cl ratio, W being assumed to be present as:	
Run No.	$WCl_3(NH_2)_3$	$WCl_4(NH_2)_2$
1	1·00 : 0·72	1·00 : 0·96
2	1·00 : 0·68	1·00 : 1·11
3	1·00 : 0·65	1·00 : 1·02

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[4] Holt and Gray, *Ind. Eng. Chem., Anal.*, 1940, **12**, 144.
[5] Fowles and Pollard, *J.*, 1953, 4128.
[6] *Idem, J.*, 1953, 2588.

and chlorine (cf. Table 2) should then be 1 : 1, corresponding to ammonium chloride. A tensimetric run on the soluble portion–ammonia system showed the presence of ammonium chloride.

(iii) *Tensimetric experiments.* A known excess of ammonia was condensed on a known weight of the halide at liquid-oxygen temperatures; a very vigorous reaction took place when the reaction vessel was surrounded with a slush bath at −36°, and the vessel was shattered on several occasions. The reaction was made less energetic by using a detachable vessel, and shaking constantly while the contents warmed to −36° during several hours; at −80° an orange product formed, which later became brown. The tensimetric plot subsequently obtained at −36° [(*a*) in Figure] showed two univariant portions with pressures of 40 mm. and 19 mm. which extended over composition ranges of 6 and 2 moles of NH_3/mole of WCl_6, respectively. From this plot it is evident that a bivariant system, probably representing a general desorption of ammonia, is also present.

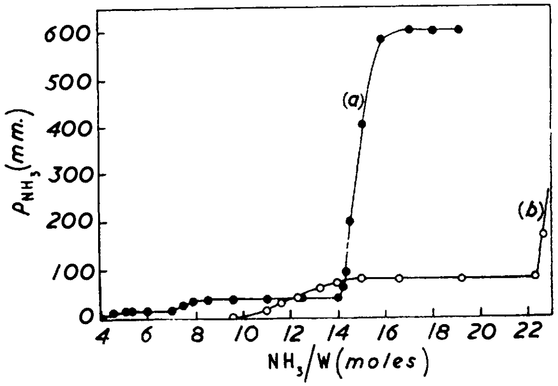

TABLE 3. *Dissociation pressures of the " A " and " B " ammoniates of* WCl_6.

	" A " ammoniate			" B " ammoniate			
Temp.	−38·9°	−22·0°	−11·0°	−64·5°	−49·0°	−38·0°	−28·0:
Press. (mm.)	16·0	56·0	122·0	5·0	19·0	43·0	91·0

The dissociation pressures of these ammoniates (referred to in future as " A " and " B ") were measured over a 30° temperature range (Table 3), and from the integrated form of the van't Hoff equation ΔH values of 8·10 and 8·90 kcal./mole, respectively, were calculated. The tensimetric curves were reproducible (in ten experiments) to within 0·4 mole of NH_3/mole of WCl_6. The overall composition of the solid remaining after removal of excess of ammonia at −36° was $WCl_6,4NH_3$.

Despite constant shaking and slow attainment of the equilibrium temperature (−36°), a violent reaction still occurred in about a quarter of the experiments, and, as with experiments in which the reaction vessel was warmed directly to −36°, the product was heterogeneous and contained white particles. In some eight experiments in which the reaction vessel survived the initial reaction, tensimetric plots were made in the usual way, and in every experiment a new univariant step appeared in the curve. This step occurred at a pressure corresponding to the dissociation $NH_4Cl,3NH_3 \rightleftharpoons NH_4Cl + 3NH_3$, showing that ammonium chloride was now present. The amount of ammonium chloride triammoniate found varied, and was in inverse proportion to the amount of " A " and " B " ammoniate present, showing that these ammoniates disappeared as ammonium chloride was formed. In limiting experiments, in which the " A " and " B " ammoniates were no longer present [(*b*) in Fig.], the univariant portion corresponding to the dissociation of $NH_4Cl,3NH_3$ had a length of about 8 moles of NH_3/mole of WCl_6, showing the presence of 2—3 mol. of ammonium chloride. On removal of excess of ammonia (at −36°) the remaining product had an overall analysis of $WCl_6,9NH_3$.

The compositions of the final products of tensimetric runs were confirmed by direct analysis.

DISCUSSION

Although the two compounds obtained by passing ammonia gas through a solution of tungsten(VI) chloride in carbon tetrachloride had overall compositions approximating to tetra- and hexa-ammoniates, it is unlikely that they are simple adducts, because this implies covalencies of 10 and 12 for the tungsten atom. A covalency of 12 is plainly impossible, but it has been suggested [7] that the tungsten atom achieves a covalency of 10 in such complex anions as $[W(CN)_8(NH_3)_2]^{2-}$. There are three alternatives to considering these products as simple adducts: (1) The covalency may be limited to 8 by considering only two ammonia molecules to be bonded directly to the tungsten atom, with the remaining molecules more loosely held by " secondary bonding," rather like that in the ammoniates formed by the cobaltammine ions; [8] (2) cationic complexes may be formed, *e.g.*, $[WCl_4(NH_3)_4]^{2+}2Cl^-$ and $[WCl_2(NH_3)_6]^{4+}4Cl^-$; (3) ammonolysis has taken place, so that the products are mixtures of ammonobasic tungsten(VI) chlorides and ammonium chloride. The first two suggestions must be ruled out because an uncharged adduct such as $WCl_6,2NH_3$ could hardly attract significantly further ammonia molecules at room temperature, and sexavalent tungsten is too acidic to form cationic complexes.

At room temperature, it is more likely that ammonolysis has taken place, and if, moreover, the tetra- and hexa-ammoniates are formulated as mixtures containing one and two moles of ammonium chloride respectively, then their thermal decomposition *in vacuo* is readily interpreted.

The formation of ammonium chloride at 130° in both decompositions implies that ammonia and hydrogen chloride are being liberated simultaneously and recombining on the cooler parts of the reaction vessel, since pre-formed ammonium chloride would not sublime *in vacuo* below 180—200°.

The tetra-ammoniate would decompose according to the sequence:

$$\begin{tikzcd}
NH_4Cl + WCl_5(NH_2),2NH_3 \arrow[r, "(1)"] & NH_4Cl + WCl_5(NH_2),NH_3 + NH_3 \arrow[d, "(2)"] & \\
NH_4Cl + WCl_2(NH)_2 + 2HCl & NH_4Cl + WCl_4(NH_2)_2 + HCl \arrow[l] & \left.\right\}\text{ recombine giving } NH_4Cl
\end{tikzcd}$$

As soon as reaction (1) has taken place, reaction (2) follows, so that 1 mol. of ammonium chloride is formed, and together with that present initially in the mixture will give a total sublimate of 2 mol. of ammonium chloride at 200°.

The hexa-ammoniate differs from the tetra-ammoniate in liberating 1 mol. of ammonia around 100° and only 1 mol. of hydrogen chloride above 130°, and its thermal decomposition is probably:

$$\begin{tikzcd}
2NH_4Cl + WCl_4(NH_2)_2,2NH_3 \arrow[r] & 2NH_4Cl + WCl_4(NH_2)_2,NH_3 + NH_3 \arrow[d] & \\
 & 2NH_4Cl + WCl_4(NH_2)_2 + NH_3 \arrow[d] & \left.\right\}\text{ recombine giving } NH_4Cl \\
2NH_4Cl + WCl_2(NH)_2 + HCl & 2NH_4Cl + WCl_3(NH_2)(NH) + HCl \arrow[l] &
\end{tikzcd}$$

The final product of either decomposition would be $WCl_2(NH)_2$. Analysis shows that this is certainly the major product, and the rather low nitrogen content is attributed to some side reaction.

The low-temperature reactions with liquid ammonia are essentially of two distinct types, first, those in which only addition ammoniates are formed, and secondly, those in which ammonolysis takes place. The first type of reaction takes place when tungsten(VI) halide and ammonia are allowed to warm slowly to —36°, and on these

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[7] Jakób and Jakób, *Roczniki Chem.*, 1952, **26**, 492.

[8] Spacu and Voichescu, *Z. anorg. Chem.*, 1940, **243**, 268.

occasions the tensimetric curves show only the presence of two simple ammoniates, and the final formation of a tetra-ammoniate when excess of ammonia is removed at the reaction temperature. This tetra-ammoniate is quite different from that obtained in the flow runs, in being steel-blue, rather like tungsten(VI) chloride itself, and in gradually losing some of this ammonia on warming to room temperature and above. It is not perhaps unreasonable to consider this low-temperature product to be a simple adduct in which the tungsten atom achieves a covalency of 10.

This is in agreement with the absence of ammonium chloride triammoniate from the tensimetric plots. Higher ammoniates (" A " and " B ") are also formed, although the ease with which the additional ammonia is removed at $-36°$ and the ΔH values of 8—9 kcal./mole show that the ammonia is very weakly held, as with the higher ammoniates of many metal halides.

In the violent reaction, ammonolysis is indicated by the heterogeneous nature of the product and confirmed by the tensimetric experiments. Moreover, the reaction products now contain smaller amounts of the " A " and " B " ammoniates—in inverse proportion to the amount of ammonium chloride present—showing that the compound which forms these ammoniates disappears as ammonium chloride is formed. The probable explanation is that, although tungsten(VI) chloride initially forms ammoniates (in the tranquil reaction), it subsequently undergoes ammonolysis with considerable violence. The maximum ammonolysis observed in the tensimetric experiments (that when the " A " and " B " ammoniates were no longer present) [cf. Fig. (*b*)] corresponds to an equilibrium position in which 2—3 tungsten–chlorine bonds have been ammonolysed.

When tungsten(VI) chloride is exposed to a large excess of liquid ammonia at its boiling point, then ammonolysis is evidently much more complete. Most of the product is soluble, and analysis of this portion shows it to be a mixture of excess of ammonium chloride and the ammonobasic tungsten(VI) chloride, $WCl_4(NH_2)_2$; the small insoluble portion appears to be a mixture of $WCl_3(NH_2)_3$ and $WCl_2(NH_2)_4$. It seems likely that when $WCl_4(NH_2)_2$ is formed, it is complexed by the ammonium chloride with the formation of a soluble anionic tungsten species such as $[WCl_6(NH_2)_2]^{2-}$, similar to the behaviour in the titanium(VI) iodide–ammonia system.[1] The more highly ammonolysed products remain undissolved, since most of the ammonium chloride is removed in the first washing. The formation of a complex anion in liquid ammonia also explains Bergström's observation that, although the product is entirely soluble in concentrated solutions, an ammonobasic tungsten(IV) chloride is precipitated on dilution, since complex formation would take place most readily in a high concentration of chloride ion. When the liquid ammonia is removed, as in the tensimetric experiments, then the complex anions will be unstable, so that the ammonium chloride is available to form its normal triammoniate. The tungsten-blue colour which developed when the products of the tungsten(VI) chloride–ammonia reaction were placed in acid solution suggests that some reduction might have taken place, but the diamagnetism of the products shows that reduction is in fact insignificant.

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[9] Biltz, *Z. anorg. Chem.*, 1923, **130**, 93.