840. *Studies on the Behaviour of Halides of the Transition Metals with Ammonia. Part III.* The Reaction of Zirconium and Thorium Tetrachlorides with Ammonia.*

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

The reaction of zirconium and thorium tetrachlorides with ammonia has been studied tensimetrically at −36° and −44°. Whereas zirconium tetrachloride gives an amidochloride, $ZrNH_2Cl_3$, thorium tetrachloride forms only an addition complex which dissociates into its constituents *in vacuo* at 200°. The mechanism of the reaction of ammonia with the Group IVA tetrachlorides is discussed and compared with the mechanisms proposed in recent analogous ' alcoholysis " studies.

Zirconium tetrachloride has been reported to give a number of complexes with ammonia, $ZrCl_4,xNH_3$, where $x = 8$, 6, 4, 3, and 2, although their nature has not been studied systematically (Paykull, *Ber.*, 1873, **6**, 1467; Mathews, *J. Amer. Chem. Soc.*, 1898, **20**, 82; Stahler and Denk, *Ber.*, 1905, **38**, 2611). By thermal decomposition of such complexes, Bruère and Chauvenet (*Compt. rend.*, 1918, **167**, 201) produced a nitride, Zr_3N_2.

The tetrabromide of zirconium is said to form a tetra-ammoniate (Mathews, *J. Amer. Chem., Soc.*, 1898, **20**, 840) and a deca-ammoniate (Stahler and Denk, *loc. cit.*). Young (*J. Amer. Chem. Soc.*, 1935, **57**, 1195) suggested that the di-imide, $Zr(NH)_2$, was formed when potassamide was added to a solution of zirconium tetrabromide in liquid ammonia, and the potassium salt of this imide was obtained by Bowerman and Fernelius (*ibid.*, 1939, **61**, 121) by the addition of potassium metal to its liquid ammonia solution.

With thorium tetrachloride, Mathews (*loc. cit.*, p. 824) and Stahler and Denk (*loc. cit.*) obtained ammoniates corresponding to those formed by zirconium tetrachloride. Chauvenet

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* Part II, *J.*, 1953, 2588.

(*Compt. rend.*, 1910, **151**, 387), however, found that thorium tetrachloride gave two series of compounds with ammonia: (i) With liquid ammonia, a series of simple addition ammoniates were formed, which decomposed *in vacuo*, leaving a complex $ThCl_4,4NH_3$ at 15°. (ii) With gaseous ammonia, another series of complexes resulted, which, unlike the preceding type, were stable to moisture. Chauvenet unfortunately gives neither analytical nor tensimetric data to support his formulæ, and the subsequent thermochemical information he quotes is accordingly of little value.

A tensimetric investigation of the thorium tetrabromide–ammonia reaction at 0° (Young, *J. Amer. Chem. Soc.*, 1935, **57**, 997) shows the existence of a number of ammoniates, $ThBr_4,xNH_3$, where $x = 20$, 14, 10 and possibly 8; but it is evident from these pressure–composition curves that no ammonium bromide is present, since there is no univariant portion corresponding to the known equilibrium $NH_4Br,3NH_3 \rightleftharpoons NH_4Br + 3NH_3$.

In this paper we report the results of a tensimetric investigation of the reaction of liquid ammonia with zirconium and thorium tetrachlorides, thus completing our studies on the ammonolysis of the Group IVA chlorides.

EXPERIMENTAL

Zirconium tetrachloride was prepared by the action of chlorine on zirconium at 330°. Thorium tetrachloride was made in a similar way from thorium at 800°, a quartz tube being used for this preparation, and both halides were purified by sublimation. Analysis confirmed the purity of the products (Found: Zr, 39·0; Cl, 60·1. Calc. for $ZrCl_4$: Zr, 39·1; Cl, 60·9%. Found: Th, 63·0; Cl, 37·6. Calc. for $ThCl_4$: Th, 62·1, Cl, 37·9%). The purification of ammonia was described in Part I (*J.*, 1952, 4938).

FIG. 1.

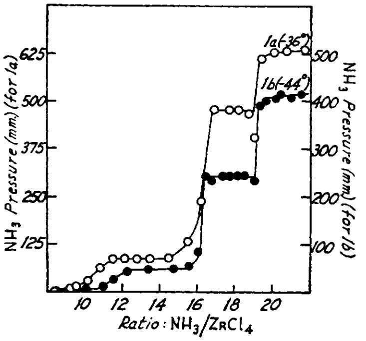
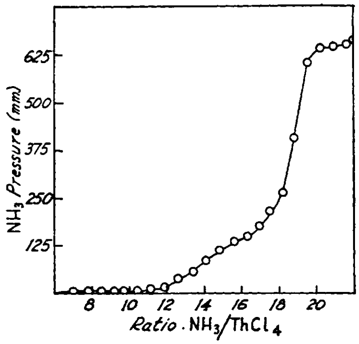


FIG. 2.



Tensimetric Studies.—(i) *Zirconium tetrachloride–ammonia reaction.* Equilibrium pressure–composition curves which were obtained at −44° and −36° in the usual way (Part I, *loc. cit.*) are produced in Fig. 1. These pressures were only fully attained after several days, particularly over the composition range 19—16 moles of ammonia per mole of $ZrCl_4$. The system was assumed to be in equilibrium when no further pressure increase resulted after 24 hr. The complex remaining after the excess of ammonia had been removed (at the reaction temperature) by pumping with a high-vacuum pump for 12 hr., had an overall composition closely approximating to $ZrCl_4,8NH_3$.

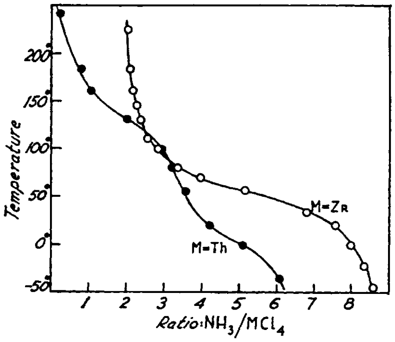
(ii) *Thorium tetrachloride–ammonia reaction.* This reaction was investigated at −36° only; the curve obtained is given in Fig. 2. The product remaining after the removal of excess of ammonia (at −36°) was shown by analysis to be $ThCl_4,6NH_3$.

Thermal Decomposition of $ZrCl_4,8NH_3$ *and* $ThCl_4,6NH_3$.—These complexes were decomposed *in vacuo* in a similar manner to that described for $NbCl_5,9NH_3$ (Part I, *loc. cit.*), and the resultant composition curves are shown in Fig. 3. These curves were fully reproducible in their general shape, no matter what quantity of material was used, and irrespective of the time for which it was decomposed at any given temperature.

$ZrCl_4,8NH_3$ decomposes when heated in this way, giving off ammonia (identified by analysis and density) until $ZrCl_4,2NH_3$ remained at 180°. This complex was further heated above 200°, and a white sublimate, shown by analysis to be ammonium chloride, appeared on the cooler parts of the vessel walls. No further gases were liberated until 350°, whereat a huge white sublimate formed, which consisted essentially of zirconium tetrachloride, with a slight contamination of ammonium compounds. The small quantity of compound remaining unsublimed gave an analysis corresponding to Zr : N : Cl = 1 : 1·4 : 1·8, but only a small quantity of the complex was available, so these figures are only approximate. This substance was very reactive, taking fire when hydrolysed in the presence of air. The substance formed initially, and all products of subsequent decompositions up to 400°, were white, but when heated to 800° *in vacuo* gave a black material containing zirconium and nitrogen, but no chlorine. No quantitative analysis of this black material was carried out since the very small amount available was somewhat contaminated with white hydrolysis products formed when the 350° product was transferred to a quartz tube for further heating.

Only ammonia was evolved when $ThCl_4,6NH_3$ was heated *in vacuo*, and at temperatures above 200° the complex was completely decomposed into ammonia and thorium tetrachloride, and no ammonium chloride was formed. If, however, ammonia was allowed to remain in contact with the thorium tetrachloride at temperatures above 200° rather than trapped out immediately in liquid oxygen, a reaction occurred slowly, and ammonium chloride sublimed on to the cooler walls of the reaction bulb.

FIG. 3.



DISCUSSION

In our investigations, zirconium tetrachloride was found to take up 19 moles of ammonia initially. The tensimetric curves shown in Fig. 1 have a univariant step corresponding to the equilibrium $ZrCl_4,19NH_3 \rightleftharpoons ZrCl_4,16NH_3 + 3NH_3$, and calculation of the dissociation energy from the equilibrium pressures at −44° and −36° shows it to be approximately 9·0 kcal./mole—a typical value for ammonia molecules bound by weak ion–dipole forces. Over the composition range 16—12 moles of ammonia per mole of zirconium tetrachloride, the curves closely approximate to univariancy, although the pressure is not completely constant at the ends of this range. This part of the curve is most likely composite, being due largely to the ammonium chloride triammoniate equilibrium, together with some desorption of ammonia. It is suggested that 3 moles of ammonia are present as $NH_4Cl,3NH_3$, so one mole of ammonium chloride is formed in the initial reaction. Further ammonia which is lost by a bivariant process until $ZrCl_4,8NH_3$ remains is probably of the "zeolitic" type.

The zirconium tetrachloride–ammonia reaction is thus represented by the equations :

(i) $ZrCl_4 + 19NH_3 \longrightarrow ZrNH_2Cl_3,14NH_3 + NH_4Cl,3NH_3$

(ii) $ZrNH_2Cl_3,14NH_3 \rightleftharpoons ZrNH_2Cl_3,11NH_3 + 3NH_3$ (9·0 kcal.)

(iii*a*) $NH_4Cl,3NH_3 \rightleftharpoons NH_4Cl + 3NH_3$

(iii*b*) $ZrNH_2Cl_3,11NH_3 \longrightarrow ZrNH_2Cl_3,6NH_3 + 5NH_3$ (bivariant)

i.e., $ZrCl_4,8NH_3$ corresponds to $ZrNH_2Cl_3,6NH_3 + NH_4Cl$.

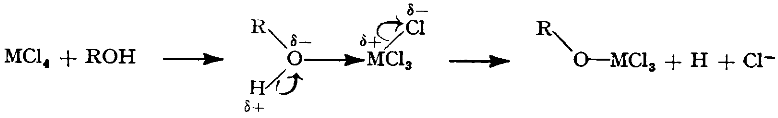
Fig. 3, which shows the thermal breakdown of $ZrCl_4,8NH_3$, is a smooth curve, and there is no evidence for the existence of ammoniates intermediate between this and $ZrCl_4,2NH_3$ which is formed at 180°. This decomposition may be due to the reaction

$$ZrNH_2Cl_3,6NH_3\ (+\ NH_4Cl) \longrightarrow ZrNH_2Cl_3 + 6NH_3\ (+\ NH_4Cl)$$

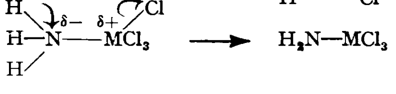
the ammonium chloride then subliming away above 200°. The complex $ZrCl_4,2NH_3$ resembles the analogous titanium compound (Part II, *loc. cit.*), breaking down when heated further to liberate zirconium tetrachloride. This zirconium tetrachloride might be formed at any temperature between 200° and 350°, but remains in the reaction bulb until its sublimation temperature (~330°) is reached. The nature of subsequent thermal decomposition is speculative in view of the small amount of material remaining at this stage, but it is significant that the black substance obtained at 800° is chlorine-free and is therefore probably a nitride.

The pressure–composition curve for the thorium tetrachloride–ammonia reaction (Fig. 2) contains no univariant portion corresponding to the dissociation of ammonium chloride triammoniate, so evidently ammonolysis has not taken place. The bivariant section, in which the pressure falls continuously while the composition changes from 20 to 10 moles of ammonia per mole of thorium tetrachloride, represents the desorption of ammonia. Four further moles of ammonia are then lost, the pressure remaining almost constant around 5·5 mm.; *i.e.*, $ThCl_4,10NH_3 \rightleftharpoons ThCl_4,6NH_3 + 4NH_3$. The curve (Fig. 3) obtained for the thermal decomposition of the hexa-ammoniate into its components shows two very distinct parts, indicating the intermediate existence of $ThCl_4,3NH_3$, but there is no evidence for other ammoniates and it seems likely that those reported by Chauvenet (*loc. cit.*) are mixtures rather than distinct compounds. The complexes he obtained with gaseous ammonia are no doubt a mixture of ammonium chloride with some amidochloride, *i.e.*, in agreement with the observed reaction of thorium tetrachloride with ammonia above 200° to give ammonium chloride.

The results of our studies on the ammonolysis of the Group IVA halides may be summarised by saying that, with liquid ammonia, titanium and zirconium tetrachloride form the amidochlorides $Ti(NH_2)_3Cl$ and $Zr(NH_2)Cl_3$, and thorium tetrachloride gives the hexa-ammoniate $ThCl_4,6NH_3$. Now silicon tetrachloride is known to undergo complete ammonolysis to the amide, $Si(NH_2)_4$ (Emeléus, *Chem. and Ind.*, 1937, 813), so the degree of ammonolysis obviously decreases regularly down the series of halides, $SiCl_4$, $TiCl_4$, $ZrCl_4$, $ThCl_4$. Hydrolysis assumes the same order of reactivity, and Wardlaw and his co-workers (*J.*, 1950, 3452) found a similar degree of replacement when they investigated the analogous alcoholysis of these halides. In his reaction mechanism, Wardlaw suggests the initial co-ordination of an alcohol molecule through the " lone pair " of the oxygen atom, followed by the splitting off of a proton and a chloride ion :

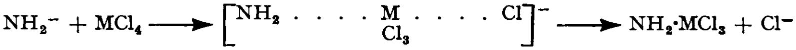


It seems reasonable to suggest a parallel mechanism for ammonolysis, in view of the known tendency for the ammonia molecule to co-ordinate to halides, and particularly since the subsequent splitting out of hydrogen chloride would be facilitated in liquid ammonia, which is a good ionising solvent :



This replacement of chlorine atoms by amino-groups should at first sight take place most readily when the M–Cl bond possesses pronounced ionic character, but calculation of the percentage ionic character for the Group IVA halides shows it to increase regularly from silicon to thorium tetrachloride. When the radius of the metal atom is taken into consideration, however, the specific surface intensity charge (which determines the co-ordination energy available for the ionisation of the M–Cl and N–H bonds) is in the reverse order. The elimination of hydrogen chloride is therefore expected to occur most easily with silicon tetrachloride, and least readily with thorium tetrachloride.

A possible alternative mechanism is that in which an amide ion reacts with a halide molecule :

(i) 

$$NH_2^- + MCl_4 \longrightarrow \left[NH_2 \cdots\cdots \underset{Cl_3}{M} \cdots\cdots Cl\right]^- \longrightarrow NH_2{\cdot}MCl_3 + Cl^-$$

followed by further replacement in the same way. This mechanism is supported by the increased ammonolysis resulting when amide ions (as KNH_2) are added to the solution, although the variation of the reaction temperature (which determines the degree of auto-ionisation of ammonia) has no apparent effect.

These mechanisms are very similar, since both involve the ionisation of the M–Cl bond. In Wardlaw's scheme, an ammonia molecule co-ordinates initially, followed by the ionisation of the M–Cl and N–H bonds, whereas in the alternative mechanism an amide ion co-ordinates and then transfers its charge to the chlorine atom, which splits off as an ion.

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