VI.—*The Action of Ammonia on some Tungsten Compounds.*

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WÖHLER, in a paper "Ueber Amidverbindungen des Wolframs" (*Annalen*, **73**, 190), described the results of the action of ammonia on tungstic anhydride and tungsten chloride. In the former case, he found that when tungstic anhydride was heated to dull redness in a stream of dry ammonia, it was converted into a black compound, whilst water condensed in the cool part of the tube. The compound at a higher temperature yielded metallic tungsten. The analysis gave results which varied between the numbers 87·65 and 88·47 for the percentage of tungsten present, and a nitrogen determination gave 7·15 per cent. The compound also contained a small quantity of hydrogen, 0·2 per cent. From these data he concluded that the compound might be regarded as a mixture of nitride, amide, and oxide of tungsten, and he named the compound tungsten nitretamid-oxide. The formula with the modern atomic weight for tungsten is $4\text{WN}_2, \text{W}_2(\text{NH}_2)_2, 2\text{WO}_2 = \text{W}_8\text{N}_{10}\text{H}_4\text{O}_4$.

The action of ammonia on tungsten chloride, however, gave a nitrogen compound containing no oxygen. The percentage of tungsten in this varied between 86·76 and 90·80, and a determination of the percentage of nitrogen in the specimen containing the highest percentage of tungsten was found to be 8·24. From these results he concluded that two compounds were formed, represented by the formulæ $2\text{WN}_2 + \text{W}(\text{NH}_2)_2$ (W, per cent. 86·58) and $2\text{WN} + \text{W}(\text{NH}_2)_2$ (W, per cent. 90·44). The latter, it will be seen, is produced from the compound $2\text{WN}_2, \text{W}(\text{NH}_2)_2$ by the removal of one molecule of nitrogen. It could also be obtained by heating the former compound in a current of hydrogen, when ammonia was formed. It is to be noted that the theoretical percentage of nitrogen in the latter compound should be 8·92, and that Wöhler obtained only 8·24 per cent. No determination of the amount of nitrogen or of hydrogen present in the former compound appears to have been made. In a later communication (*Annalen*, **105**, 258) he records the fact that when the chlorides of tungsten are heated with ammonium chloride similar black compounds are produced, which may be either the above-mentioned compounds or a nitride of the metal. No analyses of the compound prepared by this reaction are given.

It seemed of interest to compare these results with the action of

ammonia on the oxychlorides, and also to endeavour to obtain the compounds in a purer state.

Roscoe's work on the tungsten-derivatives has given to chemists a means of preparing the oxychlorides of tungsten, and the present note is to record the results which were obtained by substituting these for the hexachloride and also a re-examination of some of the compounds obtained by Wöhler.

Action of Ammonia on Ignited Tungstic Anhydride.

A current of dry ammonia was passed over a layer of tungstic anhydride heated to dull redness. Water condensed at the further end of the tube, and the pale yellow tungstic anhydride was converted into a black, amorphous product. After allowing the tube to cool, a current of dry air was drawn through it, to ensure the removal of any residual ammonia.

The compound was analysed by ignition in air, until the black colour was entirely destroyed and the weight became constant. The addition of a few drops of nitric acid helped the final oxidation of the tungsten, which was then strongly heated in order to destroy any compound with nitric acid which might be formed.

The results obtaining by noticing the decrease of weight in the tungstic anhydride after treatment with ammonia gave also a set of results which agreed with the determination of the percentage of tungsten obtained by the analysis of the compound. The mean of several experiments gave 85.26 for the percentage of tungsten in the compound, a determination of the nitrogen by Dumas' method showed that 0.3845 gram yielded 24.5 c.c. at 12.5° and 747 mm. = 7.4 per cent. N.

	Theory.	Found.
Tungsten.....	84.6	85.26
Nitrogen.....	7.6	7.4
Hydrogen	0.27	0.27
Oxygen.....	7.3	7.07

The formula with which these numbers best agree is $W_5N_6H_3O_5$, which indicates that the removal of the oxygen had not been so complete as in the experiments described by Wöhler.

The Action of Ammonium Chloride on Tungstic Anhydride.

When tungstic anhydride is mixed with ammonium chloride, and the mixture heated in a hard glass tube or small crucible, a black product is formed. After repeatedly reheating with fresh ammonium chloride the weight becomes constant. Different preparations, how-

ever, vary in the amount of tungsten they contain between the limits 83.9 and 81.0, the average of several experiments being 82.4 per cent. The amount of nitrogen in these products is much smaller than in the compound formed by the action of the ammonia. A compound containing 83.9 per cent. of tungsten having 6.7 per cent. of nitrogen, and that with 81.0 per cent. only 5.7 per cent. of nitrogen.

	Highest.	Lowest.	Mean.	Theory for WN_2, WO_3 .
Tungsten....	83.9	81.0	82.4	82.8
Nitrogen....	6.7	5.7	6.2	6.4

It will be noticed that an increase in the percentage of tungsten is accompanied by a rise in the amount of nitrogen, as if the tungstic anhydride, WO_3 (W per cent. 79.3), was being converted into a nitride, say WN_2 , whose percentage composition is W = 86.8, N = 13.2.

The Action of Ammonia on Tungsten Oxychloride, WO_2Cl_2 .

The oxychloride was prepared by Roscoe's method, and the ammonia, carefully dried, was passed into the tube in which the oxychloride was condensed, so as to prevent decomposition by contact with the moisture in the air. The reaction takes place without the application of heat, and white fumes of ammonium chloride are formed in the further part of the tube. The product, which is semicrystalline and of a dull, dark brown colour, was purified from ammonium chloride by gently heating the tube in a current of dry hydrogen. The analysis of several specimens prepared in this way yielded a percentage of tungsten varying between 84.5 and 85.6, with an average of 85.09. The product differed from the foregoing in not evolving ammonia on heating with soda-lime, and two determinations of the amount of nitrogen present only yielded a few cubic centimetres of gas. It seems, therefore, that, in this case, the ammonia removes chlorine from the molecule, and leaves the dioxide (W per cent. = 85.18) in a semicrystalline form. This result was partially confirmed by observing that a permanent gas was formed during the reaction.

It is interesting to note that the action of ammonia on this oxychloride of tungsten, WO_2Cl_2 , is similar to that which I have previously shown to take place when dry ammonia is allowed to act upon chromyl dichloride, CrO_2Cl_2 (Trans., 1886, 49, 367).

Action of Ammonia on the Red Oxychloride, $WOCl_4$.

This compound, which, on account of its unstable character, was only prepared in small quantity, is also rapidly attacked by dry

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ammonia in the cold. A small quantity (0.2318 gram) of the black compound formed gave 0.2066 gram tungstic anhydride, from which it is seen that 88.9 per cent. of tungsten is present in the product. This was the highest percentage of tungsten in any of the products examined. The quantity formed did not permit of a nitrogen determination being made. If the remainder is chiefly nitrogen, it approaches in composition to a nitride of the formula W_2N_3 , in which the percentage of tungsten is 89.5.

The Action of Ammonia on Tungsten Hexachloride.

Dry ammonia rapidly attacks the hexachloride in the cold, yielding white fumes of ammonium chloride and a black powder having a semi-metallic lustre. The latter can be freed from ammonium chloride by washing with water. It is insoluble in nitric acid, dilute sulphuric acid, and soda. When fused with soda, it gave off ammonia and was converted into sodium tungstate. It is oxidised by aqua regia to tungstic acid. Strong hot sulphuric acid converts it into ammonia and tungstic acid. When heated in the air it glows, and is converted into yellow tungstic anhydride. The oxidation to tungstic anhydride in the air was sometimes accompanied by a slight smell of ammonia, but when the substance had been well washed with water, or heated in a current of dry hydrogen until all the ammonium chloride had been volatilised, it did not give off ammonia when heated in this way. The percentage of tungsten, as determined by the ignition of the black compound to tungstic anhydride in the air, gave results varying between 87.3 and 92.8 per cent. The average of all the determinations gave 90.05 for the percentage of tungsten. It will be noticed that the lowest result obtained was slightly higher than the lowest determination by Wöhler. The decomposition of the compound by hot and strong sulphuric acid suggested Kjeldahl's method for estimating the nitrogen in this substance. Two determinations with different samples gave 10.57 for the amount of nitrogen present.

These results agree with those required by the formula W_2N_3 .

	Found.	Calculated for W_2N_3 .
Tungsten.....	90.05	89.8
Nitrogen.....	10.57	10.2

The somewhat high result for the nitrogen constant may be due to the fact that the compound seems to have the property of condensing ammonia upon its surface. Wöhler determined the percentage of nitrogen in a specimen containing 90.8 per cent. of tungsten to be 8.24, and by assuming that hydrogen was also present arrived at the

formula $2WN, W(NH_2)_2$. The amount of tungsten in other specimens was less than this, the minimum obtained by him being 86.76. To account for this low result, he assumed that the difference was due to an increase in the nitrogen to 12.8 per cent., and that a second compound of the composition $2WN_2, W(NH_2)_2$ was therefore produced when the conditions were slightly modified.

Finely divided metallic tungsten, after heating to redness in a current of dry hydrogen, underwent no alteration in weight when heated in a current of dry ammonia. No action was observed when dry ammonia gas was passed over the heated blue oxide. A black compound is produced when a solution of tungstic acid in aqueous ammonia is evaporated to dryness and the product gently heated in a covered crucible; water is given off, and the black crystalline product on heating in the air is converted into yellow crystalline tungstic anhydride. The acid salt is said to form the blue oxide on ignition in a closed vessel, but the compound does not appear to have been very carefully examined.