VOL. XV. FEBRUARY, 1893. NO. 2.
Issued July 11, 1893.

THE JOURNAL

OF THE

AMERICAN CHEMICAL SOCIETY.

THE ACTION OF AMMONIA GAS UPON MOLYBDENYL CHLORIDE.

BY EDGAR F. SMITH AND VICTOR LENHER.

Received May 26.

IN 1857, Tuttle (*Annalen*, **101**, 285) studied the action of ammonia upon molybdenum trioxide and molybdenum chloride ($MoCl_4$). In the case of the trioxide the temperature at which the reaction was made approached a red heat. The resulting product was in part black in color and possessed metallic luster. Its analysis revealed the pressure of nitrogen, hydrogen, and molybdenum. The quantity of the latter constituent equaled 92.9 per cent. Upon conducting the experiment at more elevated temperatures the product was found to contain 77.9 per cent. and seventy-three per cent. of molybdenum, while the hydrogen content did not exceed 0.18 per cent. The results consequently were not constant.

On exposing molybdenum chloride to the action of ammonia gas, at a temperature just sufficient to volatilize the ammonium chloride which arose in the reaction, Tuttle obtained a black, metallic, sintered mass. It was found to contain 82.83 per cent. of molybdenum and was assumed to have the composition expressed by the formula: $Mo_2N_2 + Mo(NH_2)_2$, analogous to a compound of tungsten obtained in a similar manner by Wöhler (*Annalen* **73**, 190).

Several years after the publication of the preceding investigation Uhrlaub presented an inaugural thesis entitled " Die Verbindungen einiger Metalle mit Stickstoff" (Göttingen, 1859), from which we collate the following interesting facts.

In the action of ammonia gas in the cold upon molybdenum chloride much heat was evolved and a black colored product resulted; its analysis showed the presence of 76.457 per cent. of molybdenum, 23.134 per cent. of nitrogen and 0.677 per cent. of hydrogen. In subsequent experiments Uhrlaub employed a more intense heat, thus hoping to estimate the slight hydrogen content, but this element continued to show itself in his various products, until on raising the tube in which the reaction took place to an intense red heat he obtained a compound that on careful analysis gave a composition which may be expressed by the formula Mo_3N_2. In other words a molybdenum nitride had been formed by action upon the chloride of the metal with ammonia gas at a high temperature.

When Uhrlaub tried the action of ammonia upon molybdic acid at a gentle heat he obtained "pseudomorphosen," as he designates them, bluish-black in color. Several were prepared: they varied much in composition. Uhrlaub attributes this variation to the different degrees of heat employed and to the length of time during which the heated molybdenum trioxide was exposed to the action of the gas.

The preceding facts indicate that the action of ammonia gas either upon the trioxide or chloride is not as simple as might be presumed. An amide that might well be expected in either case appears not to have been obtained either by Tuttle or Uhrlaub[1]. We hoped to reach this result by the action of ammonia gas upon molybdenyl chloride in accordance with the equation:

$$MoO_2Cl_2 + 4NH_3 = MoO_2(NH_2)_2 + 2NH_4Cl.$$

It will be noticed that we apply the term molybdenyl chloride to the compound generally called molybdenum dioxychloride. Our assumption of molybdenyl is based upon the terms sulphuryl, chromyl, etc., applied to compounds possessing a constitution similar to that of the dioxychloride of molybdenum, MoO_2Cl_2, SO_2Cl_2, CrO_2Cl_2.

---

[1] The primary object of these chemists seems to have been the preparation of molybdenum nitrides.

Preparation of Molybdenyl Chloride.—Of the various methods proposed for the formation of this derivative of molybdenum we discovered that the action of dry chlorine on the dioxide of the metal yielded by far the most satisfactory product, both as to purity and quantity. The molybdenyl chloride forms at a very gentle heat quite rapidly and sublimes in feathery crystals. Schulze (*J. prakt. Chem.*, **29** (N. F.) 440) in discussing the action of molybdic acid upon metallic chlorides proposes this procedure for the object we had in view, but we failed to meet with success in our application of the method; the yield was not very abundant.

The crystalline molybdenyl chloride prepared, as just described, was introduced into porcelain boats and these placed in tubes of hard glass, through which we conducted a brisk current of well dried ammonia gas. The molybdenyl chloride immediately assumed a deep black color, much heat was evolved and copious fumes of ammonium chloride vapor were carried out of the tube. Considerable moisture also collected upon the anterior portion of the combustion tube. At last, heat sufficient to expel any ammonium chloride retained by the compound was applied; but this was not done for a longer period than half an hour. The boat and contents were cooled in ammonia gas. The product of the reaction was placed over sulphuric acid to absorb any retained gas; a portion of it was also washed with water and the aqueous solution examined for chlorine, but this was not found present. In general appearance the product was metallic and black in color. Analyses were made of different preparations. The molybdenum content was determined by oxidizing weighed portions of material with dilute nitric acid, evaporating carefully to dryness, finally applying a gentle heat for a period of fifteen minutes.

The hydrogen was estimated by burning the substance in a current of oxygen, and collecting the water that was produced in a weighed calcium chloride tube.

The nitrogen estimations were three in number; one of them was carried out by the method of Dumas, while the other two were made by the soda-lime process.

The oxygen was obtained by difference.

Our analytical results may be tabulated as follows:

	Substance taken.	MoO_3 found.	Mo per cent.
1	0.1047 gram	0.1156 gram	73.65
2	0.1006 "	0.1108 "	73.42
3	0.1004 "	0.1110 "	73.70
4	0.1028 "	0.1113 "	73.47
5	0.1017 "	0.1126 "	73.80

The mean molybdenum percentage of these five determinations is 73.61 per cent.

Hydrogen determination:

Substance taken.	Water found.	H per cent.
0.2088 gram	0.0082 gram	0.43

Nitrogen determination:

	Substance taken.	Pt found.	N per cent.
1	0.1510 gram	0.0643 gram	6.05
2	0.1529 "	0.0642 "	5.96

The nitrogen found by the Dumas method equaled 6.00 per cent. and the mean of the three nitrogen estimations was also 6.00 per cent.

Two-thirds of this nitrogen content were expelled when our compound was exposed to the action of hydrogen at the highest temperature attainable with a good combustion furnace. Taking the mean of our analyses as a basis for calculation,

	Per cent.
Molybdenum	73.60
Nitrogen	6.00
Hydrogen	0.43
Oxygen (by difference)	19.96

We deduce $Mo_5O_8N_3H_3$ as the most probable empirical formula, which may be variously written to express the enigmatical constitution of this compound. Thus it might be $MoO(NH)_2.MoONH.3MoO_2$, or $4MoO_2.Mo(NH)_3$, which may be correctly termed tetra-molybdenyl molybdenimide.

Our compound is stable in the air. Hydrochloric acid does not affect it. Nitric acid of sp. gr. 1.42 causes it to burn very energetically. Dilute alkalies attack it very sluggishly. It liberates ammonia when fused with caustic potash, when heated in a current of oxygen it is slowly oxidized. Heated in nitrogen gas the black compound loses water and assumes a reddish color. The analysis of this product indicates that it probably was molybdenum dioxide mixed with a very small amount of nitride; at least traces of nitrogen were found upon examination. Another interesting observation was that when the black product was introduced into an aqueous solution of silver nitrate, crystals of metallic silver gradually appeared over the surface of the molybdenum compound.

We obtained our first product several times, but care must be exercised and the same conditions, noted by us, strictly observed if success in its formation is desired.

An examination of Uhrlaub's analytical results will show that one of his products approaches very closely the compound we have just described. He speaks of it as a black "pseudomorph" with the composition

	Per cent.
Molybdenum	73.55
Nitrogen	5.58
Hydrogen	0.54
Oxygen	20.30

The formula deduced from these figures differs from that presented by us, and what is more, if we understand Uhrlaub correctly, his compounds prepared from ammonia gas and molybdenum trioxide were all "blau-schwarz" in color, and were not acted upon in the cold by nitric acid (see his dissertation pp. 13, 14, 17). However, it is evident that the product we obtained by the action of ammonia gas upon molybdenyl chloride is not the amide we had in view. Thinking that perhaps the heat we applied to drive out the final traces of occluded ammonium chloride may have been sufficient to alter the composition of the product formed at first we allowed the ammonia to act upon the molybdenyl chloride at the ordinary temperature, and when there was no further evolution of ammonium chloride and the boat had become perfectly cold[1], we introduced carbon dioxide, applying a very gentle heat at the same time, but we failed to achieve our aim. Nitrogen, when substituted for carbon dioxide, gave no better result. We next dissolved molybdenyl chloride in the purest ether we could get and conducted ammonia gas into this solution. We

[1] Portions of the product removed at this stage and shaken with cold water decomposed into a mixture of blue and brown colored masses. The possibility of removing the ammonium chloride in this manner was therefore excluded.

obtained decomposition products. A closer examination of the behavior of the molybdenyl chloride towards ether revealed the fact that the moment the two came in contact a slight hissing sound was perceptible and the ether at once imparted a strong acid reaction to blue litmus. The same was observed when pure chloroform was employed as a solvent.

If molybdenyl chloride be gradually heated in an ammonia atmosphere until the tube of hard glass becomes bright red in color, and the gas action continued for the period of an hour, the resulting product will be an amorphous, metallic, black mass. Subjected to analysis, it gave results as appended:

Molybdenum Determination:

Substance taken.	MoO_3 found.	Mo. per cent.
0.1042 gram	0.1061 gram	67.87

Nitrogen Determination.—0.1025 gram substance burned with soda lime gave 7 per cent. nitrogen.

Hydrogen Determination.—0.1012 gram substance ignited in a current of oxygen gave 0.0109 gram of water equal to 1.19 per cent. hydrogen.

	Per cent.
Molybdenum	67.87
Nitrogen	7.00
Hydrogen	1.19
Oxygen (by diff.)	23.94

The empirical formula deduced from these figures is $Mo_7O_{14}N_5H_{10}$, which can also be written:

$$4MoO_2.2MoO_2(NH_2)_2.MoO_2NH_2.$$

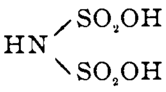
Dilute alkalies have no effect upon this compound; but it liberates ammonia when fused with caustic potash. It is converted into molybdenum trioxide very energetically, with evolution of sparks, when brought in contact with cold nitric acid.

Other products were obtained by us. Their analyses lead us to the conclusion that with us, as with Uhrlaub, the composition of the derivative depended wholly upon the length of time during which the gas acted upon the molybdenyl chloride, and upon the degree of heat employed in the experiment. It seems highly improbable to us that the amide, $MoO_2(NH_2)_2$, molybdenyl amide, can be prepared after the fashion pursued by us, for it is quite certain that the heat of the reaction evolved in the first contact of the ammonia with the molybdenyl chloride exercises a very potent influence upon the composition of the product.

When we recall the action of ammonia gas upon sulphur trioxide and sulphuryl hydroxychloride resulting in the formation of compounds of the following constitutions:

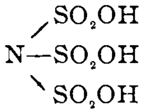
$H_2N.SO_2.OH$

Amido sulphuric acid



$$HN\begin{cases}SO_2OH\\SO_2OH\end{cases}$$

Imido sulphuric acid



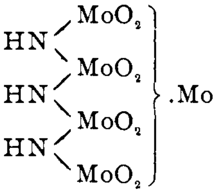
$$N\begin{cases}SO_2OH\\SO_2OH\\SO_2OH\end{cases}$$

Nitril-sulphuric acid

the question that obtrudes itself is, are not these products and their methods of formation types of the processes and results that have occurred not only in our studies described in this paper, but also in the studies of Tuttle and of Uhrlaub?[1] Are not their products, as well as our own, only residues of amido, imido and nitrilo-molybdic acids? Above we have written for our first product the constitutional formulas,

$MoO(NH)_2.MoONH.3MoO_2$, and $4MoO_2.Mo(NH)_3$,

but after considering the sulphur types we would express our empirical formula $Mo_5O_8N_3H_3$ differently as follows:



$$\left.\begin{matrix}HN\begin{cases}MoO_2\\MoO_2\end{cases}\\HN\begin{cases}\\MoO_2\end{cases}\\HN\begin{cases}\\MoO_2\end{cases}\end{matrix}\right\}.Mo$$

We have here several broken down molybdenyl amide nuclei in conjunction, not chemically combined, with metallic molybdenum. Reviewing the behavior of the product which we thus graphically represent we may be allowed to emphasize the fact that when it was brought in contact with an aqueous argentic nitrate solution metallic silver was precipitated, and this we know from an observation of Smith (*Ztschr. anorg. Chem.*, **1**, 360) is a property of metallic molybdenum. Further, it will be

---

[1] At least in so far as the action of ammonia gas upon molybdenum trioxide was concerned.

recalled that when our product was heated in an atmosphere of nitrogen it left a reddish colored compound that, upon analysis, approximated the requirements of molybdenum dioxide, and that traces of nitrogen were also detected in it. All these experimental facts find expression in our graphic representation above.

The second product obtained by us was even more active when introduced into a silver nitrate solution, throwing out metal quite rapidly, proving in our opinion the presence in it of even a greater quantity of metallic molybdenum than is contained in the first body. Similar reduced molybdenyl amide nuclei, mixed with metallic molybdenum, could also be constructed for our second compound and be in harmony with the observed deportment of this body if it were necessary.

UNIVERSITY OF PENNSYLVANIA,
MAY 16, 1893.

ACTION OF AMMONIA GAS UPON WOLFRAMYL CHLORIDE.

BY EDGAR F. SMITH AND OWEN L. SHINN.

Received May 26, 1893.

THE results obtained by Smith and Lenher in their investigation of the action of ammonia gas upon molybdenyl chloride suggested the idea of making similar research with tungsten, chiefly for the sake of comparison. It will be recalled that Wöhler (*Annalen*, **73**, 190) carried out a careful investigation on the behavior of ammonia toward both tungsten trioxide and tungsten chloride. He succeeding in preparing by the first process the compound $3WN_2 + W_2N_2H_4 + 2WO_2$, and by the second. the compounds $2WN_2 + WN_2H_4$ and $W_2N_2 + WN_2H_4$. These experiments did not yield either a simple nitride. or an amide. They were, however, the patterns for the later investigations of Tuttle and those of Uhrlaub, although their final results were in reality not what they had hoped to get. The attempts of Smith and Lenher were not any more fruitful, when we remember that they sought to prepare molybdenyl amide, $MoO_2(NH_2)_2$. While a like result was naturally to be expected