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,
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ACTION OF AMMONIA GAS UPON WOLFRAMYL CHLORIDE.

BY EDGAR F. SMITH AND OWEN L. SHINN.

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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 in the action of ammonia upon wolframyl chloride, WO_2Cl_2, it seemed to us to be worth the while to develop as much light upon the reaction as possible. Hence it was followed with the results that will appear later.

Preparation of Wolframyl Chloride, WO_2Cl_2.—We experienced no difficulty in getting this derivative by the direct action of dry chlorine upon the dioxide of the metal. It is true that slight amounts of tungsten oxytetrachloride were formed simultaneously, but these were quite easily and quickly eliminated by exposing the WO_2Cl_2 to a very gentle heat in an atmosphere of carbon dioxide. The resublimed product was employed by us in the experiments which were made.

Wolframyl Chloride and Ammonia.—The wolframyl chloride was placed in porcelain boats and these introduced into a hard glass tube through which a brisk current of dry ammonia gas was conducted. It will be recalled that the moment the gas came in contact, at the ordinary temperature, with the molybdenyl chloride, the latter at once assumed a deep black color, clouds of ammonium chloride, water, and much heat were evolved. With wolframyl chloride and ammonia there was no visible sign of action. The chloride remained unaltered even after the gas had passed over it for an hour. We thus observe here a marked difference in the conduct of these two similarly constituted chlorides, MoO_2Cl_2, and WO_2Cl_2, towards ammonia, the first being exceedingly reactive, while the second was absolutely inert, at least at the ordinary temperature. Upon applying heat to wolframyl chloride while exposed to the ammonia vapor, a slow change began. Fumes of ammonium chloride were evolved, and in time the entire mass became black in color. It was not until an intense heat was applied that the product became uniform in appearance. When ammonium chloride ceased to be formed the boat and contents were allowed to cool in ammonia. The metallic mass was allowed to stand over sulphuric acid during the night in order that any adhering ammonia might be absorbed. Portions of it were also examined for chlorine, but this was not found.

Tungsten Determination.—The material was evaporated several times to dryness in a porcelain crucible with moderately concentrated nitric acid. The residue was then heated for a period of fifteen minutes with the direct flame. The tungstic acid was bright yellow in color and free from lower oxides.

	WO_3.	W, per cent.
(*a*) 0.1025 gram substance gave	0.1106 gram	= 85.75
(*b*) 0.1028 " " "	0.1108 "	= 85.49

Nitrogen Determination.—The estimations were made by igniting the substance with soda lime.

	N.	N, per cent.
(*a*) 0.1054 gram substance gave	0.00744 gram	= 7.06
(*b*) 0.1009 " " "	0.00665 "	= 6.60

Hydrogen Determination.—0.1609 gram substance gave 0.0028 gram water, equal to 0.193 per cent.

The preceding percentages led to the empirical formula, $W_4N_4O_4H_2$, which could also be graphically written so as to indicate the presence of broken down wolframyl amide nuclei, just as was done by Smith and Lenher in their discussion of the constitution of the products obtained from molybdenyl chloride and ammonia.

Our tungsten derivative is jet black in color, and it is insoluble in water. Hydrochloric acid is without action upon it. Concentrated nitric acid oxidizes it very rapidly with the evolution of sparks. Dilute alkalies do not alter it, but fusion with caustic potash liberates ammonia gas. When introduced into an aqueous solution of silver nitrate it causes the separation of crystals of metallic silver. This behavior we assume to be indicative of the presence of metallic tungsten in the compound, for it has already been observed that metallic tungsten, like metallic molybdenum,[1] precipitates silver quantitatively from its salt solutions. Hoping that we might perhaps obtain direct evidence of the presence of the group WO_2 (which we believe to be present) if we dissolved our product in sulphuric acid and then titrated with potassium permanganate, we made this attempt. We heated the black material with sulphuric acid (sp. gr. 1.8) in sealed tubes for several days at temperatures ranging from 180°–250°, but it was unaltered. We must therefore be satisfied to represent our reaction product as we have already represented it, and abstain from any graphic formulation as was

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[1] *Ztschr. anorg. Chem.*, 1, 360.

done with the molybdenum derivative, although by analogy we might deduce a similar structure. We tried the action of ammonia upon wolframyl chloride suspended in ether (it is not soluble in this menstruum), and also in chloroform, but obtained green colored decomposition products.

Our experiments demonstrate: (1) that wolframyl chloride behaves very differently from molybdenyl chloride at the ordinary temperature when exposed in an atmosphere of ammonia; (2) that the reaction product is not a true amide, but in all probability a union of disintegrated amide molecules; and (3) that metallic tungsten is present in the product.

UNIVERSITY OF PENNSYLVANIA,
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DETERMINATION OF ORGANIC MATTER BY MOIST OXIDATION.

BY H. HEIDENHAIN.

ANY chemist who has carried out combustions by the ordinary dry process knows how much time is required, and what care must be observed, to obtain results of practical value. In technical work, where time is limited, the combustion process is resorted to only when nothing else will give the desired result.

Many attempts have been made to shorten and simplify the general process of organic elementary analysis, but for carbon and hydrogen we have, as yet, no process which accomplishes what the Kjeldahl method does for nitrogen.

I have tried to solve this problem by employing a wet method in place of the ordinary dry one. The advantages of a wet process are evident. First, the trouble of preparing the copper oxide, or substitute, would be saved. Besides this, it would not be necessary to have the substance in the dry condition, and finally, much simpler apparatus could be used. Instead of the combustion tube and the combustion furnace, a simple burner and a flask may be used.

I am sorry to say that, at the present time, the methods of combustion by the wet process have not been improved so much that all substances can be determined. What has been