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**REACTIONS OF MOLYBDENUM, TUNGSTEN, AND URANIUM
HEXAFLUORIDES WITH NITROGEN COMPOUNDS**

I. NITROUS AND NITRIC OXIDES¹

by

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1. The reactions of MoF_6 , WF_6 and UF_6 with liquid and gaseous nitrogen dioxide will be the subject of later papers in this series.

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SUMMARY

Nitrosylium hexafluoromolybdate (V) and nitrosylium hexafluorouranate (V) have been prepared and characterized. These compounds were prepared by the reaction of nitric oxide with the respective hexafluoride. Nitric oxide did not react with tungsten hexafluoride. Nitrous oxide was found to be unreactive toward molybdenum, tungsten and uranium hexafluorides.

INTRODUCTION

The reactivity of gaseous uranium hexafluoride toward certain of the nitrogen oxides was first established at the Oak Ridge Gaseous Diffusion Plant. Nitric oxide and nitrogen dioxide were observed to form solids by reaction with gaseous uranium hexafluoride while nitrous oxide did not react. A more extensive study was made subsequently in our laboratory to define reaction stoichiometry and to characterize the solid reaction products. The reactions of nitrogen oxides with molybdenum and tungsten hexafluorides were also investigated to determine whether analogous compounds would be formed.

Nitrous oxide was found to be unreactive with gaseous molybdenum, tungsten, and uranium hexafluorides at 25 and 60°C. Nitric oxide did not react with gaseous or liquid tungsten hexafluoride at 25 and 60°C. but did react rapidly with gaseous molybdenum hexafluoride and uranium hexafluoride at 25°C. to form complexes formulated as NOMoF_6 and NOUF_6 , which suggests that they are nitrosylium salts.

The properties and structure of nitrosyl compounds have been reviewed by Moeller.^{2,3} More recently, nitrosyl complex fluorides of vanadium, niobium, tantalum,⁴ gold, phosphorus, germanium and tin⁵ have been obtained by the reaction of the metal fluoride or oxide either directly with nitrosyl fluoride or with nitrosyl chloride in bromine trifluoride. Nitrosylium hexafluoroiridate (IV) has been prepared by the reaction of nitric oxide with iridium hexafluoride.⁶

EXPERIMENTAL

Equipment and Materials.—A conventional vacuum system was used for experimental manipulations. Pressure was measured by means of a Taylor Instrument Company absolute

2. T. Moeller, J. Chem. Educ., 23, 441 (1946).

3. T. Moeller, ibid., p. 542.

4. H. C. Clark and H. J. Emeleus, J. Chem. Soc., 190 (1958).

5. A. A. Woolf, ibid., 1053 (1950).

6. P. L. Robinson and G. J. Westland, ibid., 4481 (1956).

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pressure transmitter in conjunction with a mercury manometer. The gas phase reactions were produced in a glass apparatus consisting essentially of two one-liter bulbs connected by a 10-mm. stopcock. All reaction equipment was exposed to fluorine or chlorine trifluoride before use to minimize consumption of the hexafluorides. The glass bulbs were filled with the individual reactants and brought to the desired temperature in a thermostated oven. The contents were then reacted by opening the stopcock between the bulbs. The other reactions were carried out in nickel reactors. The products of the reaction were handled in a dry box.

The molybdenum and tungsten hexafluorides were obtained commercially from the Harshaw Chemical Company, the uranium hexafluoride being available in this laboratory. The hexafluorides were purified from inerts by evacuation at -78°C . and from hydrogen fluoride by discarding volatile fractions until the theoretical vapor pressures were attained. Nitrous oxide and nitric oxide were obtained from the Matheson Company; purification was accomplished by distilling from a -78°C . to a -196°C . trap to remove nitrogen dioxide. The material in the low temperature trap was then pumped to remove inerts.

Nitrous Oxide Reaction with Molybdenum Hexafluoride, Tungsten Hexafluoride, Uranium Hexafluoride. - Nitrous oxide was allowed to remain in contact with the hexafluorides at 100 mm. Hg. pressure of each component at 25 or 60°C . for times ranging from 4 to 24 hours. No solid products of reaction were observed. The initial pressure in the reactor remained unchanged in each case, indicating that there was no reaction.

Nitrosylium Hexafluorouranate (V). - The compound was prepared by reacting nitric oxide with gaseous or solid uranium hexafluoride at 25 and 60°C . Table I shows some typical preparations of nitrosylium hexafluorouranate (V) by the reaction of excess nitric oxide with solid uranium hexafluoride at 60°C . Yields were calculated on the basis of uranium hexafluoride used.

Table I

TYPICAL PREPARATIONS OF NITROSYLIUM HEXAFLUOROURANATE (V)

<u>UF₆</u> <u>(grams)</u>	<u>NO</u> <u>(grams)</u>	<u>NOUF₆</u> <u>(grams)</u>	<u>Yield</u> <u>(percent)</u>
13.990	2.360	15.070	99.26
13.665	1.283	14.760	99.53
14.829	1.924	15.958	99.16
16.268	1.587	17.566	99.50
24.454	2.630	26.524	99.95

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Nitrosylium hexafluorouranate (V) is a whitish-green solid (vapor pressure < 1 mm. Hg at 25°C.) which reacts with water to form nitric oxide, nitric and hydrofluoric acids, and equal molar quantities of uranium tetrafluoride and uranyl fluoride. The reaction with water is characteristic of a nitrosylium salt.⁶

The salt reacts with acetone, methanol and trichloroethylene to liberate nitrogen dioxide gas and form brownish-black solid products, but it is insoluble in and inert towards carbon tetrachloride, trichlorotrifluoroethane (Freon-113), nitrogen dioxide and monochlorobenzene. The solid density, as determined by volume displacement in carbon tetrachloride, is 4.30 ± 0.05 g./cc.⁷ Nitrosylium hexafluorouranate (V) has a pseudo-cubic x-ray diffraction pattern with $a_0 = 5.1789 \text{ \AA}$.⁸ and gives a weak but well-defined infrared absorption band⁸ at 2333 cm^{-1} which is characteristic of the NO^+ ion.⁹ A representative analysis is shown below.

Anal. Calcd. for NOUF_6 : U, 62.31; F, 29.84; NO, 7.85. Hydrolysis: U(IV), 31.15; U(VI), 31.15. Found: U, 62.36; F, 29.72; NO, 7.38. Hydrolysis: U(IV), 31.40; U(VI), 31.27.

Nitrosylium Hexafluoromolybdate (V). - This salt was formed by reacting nitric oxide with gaseous or liquid molybdenum hexafluoride at 25 and 60°C. The conversion of molybdenum hexafluoride to nitrosylium hexafluoromolybdate is rapid and quantitative. Table II shows some typical preparations of nitrosylium hexafluoromolybdate (V) by reaction of excess nitric oxide with liquid molybdenum hexafluoride at 60°C. Yields were calculated on the basis of molybdenum hexafluoride used.

Table II

TYPICAL PREPARATIONS OF NITROSYLIUM HEXAFLUOROMOLYBDATE (V)

<u>MoF₆</u> <u>(grams)</u>	<u>NO</u> <u>(grams)</u>	<u>NOMoF₆</u> <u>(grams)</u>	<u>Yield</u> <u>(percent)</u>
3.765	0.715	4.285	99.58
7.007	1.612	7.900	98.65
10.439	1.9770	11.894	99.79
14.725	3.400	16.825	99.97

7. At the 95 percent confidence level.

8. F. J. Musil, P. R. Ogle, and K. E. Beu, Powder X-Ray Diffraction and Related Data on NOUF_6 and NOMoF_6 , Goodyear Atomic Corp., December 31, 1958. (GAT-T-553,/ Rev. 1) Official Use Only

9. D. J. Miller and D. Watson, J. Chem. Soc., 1369 (1957).

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The compound is a rusty-orange solid (vapor pressure < 1 mm. Hg at $25^{\circ}\text{C}.$) which rapidly turns purple on exposure to the atmosphere. Hydrolysis of the solid gives nitric oxide, nitric acid, hydrofluoric acid, and a soluble molybdenum compound. Reaction occurs in acetone, methanol, and trichloroethylene to give solid products and nitrogen dioxide gas; the compound is unreactive with and insoluble in carbon tetrachloride. The solid density is 3.04 ± 0.08 g./cc.⁷ as determined by volume displacement in carbon tetrachloride. Nitrosylium hexafluoromolybdate (V) has a pseudo-cubic x-ray diffraction pattern with $a_0 = 5.0797 \text{ \AA}$ ⁸ and gives a weak but well-defined absorption band⁸ at 2331 cm^{-1} which is characteristic of the NO^+ ion.⁹ A representative analysis is shown below.

Anal. Calcd. for NOMoF_6 : Mo, 39.98; F, 47.51; NO, 12.51. Found: Mo, 39.63; F, 47.40; NO, 12.06.

Nitric Oxide Reaction with Tungsten Hexafluoride. - Nitric oxide was allowed to remain in contact with gaseous and liquid tungsten hexafluoride at 25 and $60^{\circ}\text{C}.$ for times ranging from 4 to 48 hours. No reaction occurred and the individual components were recovered unchanged. The failure of nitric oxide to react with tungsten hexafluoride was unexpected since nitrosyl complex fluorides of all the group VB elements have been prepared.⁴ The inertness of tungsten hexafluoride to nitric oxide suggests the possibility of separating tungsten hexafluoride from mixtures with either uranium hexafluoride, or molybdenum hexafluoride, or both.

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