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HEXAFLUORIDES OF MOLYBDENUM, TUNGSTEN AND URANIUM.
II. REACTIONS WITH LIQUID AND GASEOUS DINITROGEN TETROXIDE^{1,2}

by

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ABSTRACT

Molybdenum and tungsten hexafluorides form the solids nitrosylium pentafluoroxymolybdate (VI) and-tungstate (VI) respectively. Uranium hexafluoride gives nitrosylium hexafluorouranate (V) $[\text{NOUF}_6]$, the same salt that it forms with nitric oxide.

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INTRODUCTION

The reactions of molybdenum, tungsten and uranium hexafluorides with liquid and gaseous dinitrogen tetroxide were studied to determine whether nitrylium salts analogous to the nitrosylium salts described previously⁵ would be formed. Other workers have prepared nitryl complex fluorides of vanadium, niobium, tantalum,⁶ gold, phosphorus, germanium, and tin⁷ by the action of the metal fluoride or oxide either directly with nitryl fluoride or with dinitrogen tetroxide in bromine trifluoride. Also, Robinson and Westland⁸ made nitrylium hexafluoroiridate (IV) by reacting gaseous dinitrogen tetroxide with iridium hexafluoride. These same workers obtained a heterogeneous product by the reaction of iridium hexafluoride with liquid dinitrogen tetroxide.

EXPERIMENTAL

EQUIPMENT, MATERIALS AND PROCEDURE — A metal vacuum system was used for storage and manipulation of reactants. Flanged nickel vessels with Teflon gaskets were employed for reactors. All equipment was exposed to fluorine before use to minimize reaction with the hexafluorides. The reactors were heated in a thermostatically controlled oven. Purification of the hexafluorides has been described previously.⁵ Dinitrogen tetroxide obtained from the Matheson Company was purified by low temperature distillation.

For reactions with liquid dinitrogen tetroxide, the desired amounts of reactants were added to a tared evacuated reactor by cold trapping, using a liquid nitrogen bath. The reactor was then brought to temperature in the oven. After reaction, the gases and liquids remaining in the reactor were analyzed and then removed by evacuation. Solid products were removed, sampled and stored in a dry box. Reactions with gaseous dinitrogen tetroxide were performed and studied in an infrared gas cell by a technique already described.⁵

5. Geichman, J. R., et al. Hexafluorides of Molybdenum, Tungsten and Uranium. I. Reactions with Nitrous and Nitric Oxides. Goodyear Atomic Corp., Jan. 10, 1962. 12p. (GAT-T-969) Submitted to Inorg. Chem.
6. Clark, H. C. and Emeleus, H. J. J. Chem. Soc., 190 (1958)
7. Woolf, A. A. and Emeleus, H. J. J. Chem. Soc., 1050 (1950)
8. Robinson, P. L. and Westland, G. J. J. Chem. Soc., 4481 (1956)

REACTION WITH EXCESS LIQUID DINITROGEN TETROXIDE – The reactions were studied at 25° and 60°C. The experimental results were the same at both temperatures except that the reaction is accomplished in less time at 60°C.

Uranium Hexafluoride – UF_6 (10.032 g., 0.0285 mole) mixed with liquid dinitrogen tetroxide (4.457 g., 0.0484 mole) at 25°C. liberates a slight amount of heat and slowly gives off oxygen gas for several days. One mole of oxygen is liberated per mole of uranium hexafluoride. The oxygen was identified by the vapor pressure and by mass spectrometer analysis of the reaction mixture at -196°C. The amount of oxygen was determined by the difference in the weight of the reactor before and after evacuation at -196°C. After removal of all volatile constituents at 25°C. a solid identified as NOUF_6 (10.896 g., 0.0285 mole) was obtained.

This reaction was repeated and, after 2 hours, the solid and liquid phases were separated. Infrared analysis of the liquid phase showed the presence of N_2O_5 . Based on a material balance of the solid phase, the UF_6 was nearly 100 percent converted to NOUF_6 . The experimental results indicate that the reaction stoichiometry can be expressed by the following equation:

Decomposition of dinitrogen pentoxide accounts for the slow evolution of oxygen observed.

Molybdenum Hexafluoride – MoF_6 (3.890 g., 0.0185 mole) mixed with liquid dinitrogen tetroxide (5.630 g., 0.0612 mole) at 25°C. slowly evolved oxygen (0.150 g., 0.0094 mole) for 42 days. Infrared analysis of the volatile constituents showed the presence of NO_2F , NOF , N_2O_5 and the excess dinitrogen tetroxide. Upon removal of the volatile components a white solid having the empirical composition NOMoOF_5 (4.442 g., 0.0187 mole) was obtained.

Anal. Calc. for NOMoOF_5 : Mo, 40.49; F, 40.09; N, 5.91.

Found: Mo, 40.79; F, 40.44; N, 5.84.

The following equation gives the over-all stoichiometry for the reaction:

The NOMoOF_5 is a white solid which has a vapor pressure less than 1 mm. Hg at 25°C . and melts at $243 \pm 5^\circ\text{C}$. to a colorless liquid.⁹ The density of the solid was determined (by volume displacement in carbon tetrachloride) to be 2.99 g./cc. The NOMoOF_5 is not soluble in carbon tetrachloride, carbon disulfide, and trichlorotrifluoroethane but dissolves in ethanol to give a colorless solution and in acetone to give a yellow solution. The NOMoOF_5 dissolved in water evolves NO_2 gas, a reaction characteristic of the NO^+ ion.⁸

Tungsten Hexafluoride — WF_6 (6.736 g., 0.0226 mole) mixed with liquid dinitrogen tetroxide (3.803 g., 0.0413 mole) at 25°C . evolved oxygen (0.179 g., 0.0122 mole) for 11 days. Analysis of the remaining volatile constituents showed only NO_2F and the excess dinitrogen tetroxide. However, shortly after the reaction had started, dinitrogen pentoxide was observed in the reaction mixture. Removal of the volatiles left a white solid of the empirical composition $\text{N}_3\text{O}_5\text{W}_2\text{F}_{11}$ (7.892 g., 0.0113 mole). The solid did not decompose under vacuum at 60°C ., although extensive decomposition with the evolution of brown fumes occurred on standing in the dry box. Elemental analyses were performed on the solid immediately after preparation and removal from the reactor.

Anal. Calc. for $\text{N}_3\text{O}_5\text{W}_2\text{F}_{11}$: W, 52.62; F, 29.90; N, 6.01.

Found: W, 52.15; F, 29.30; N, 5.77.

The following equation shows the reaction stoichiometry:

The solid of empirical composition $\text{N}_3\text{O}_5\text{W}_2\text{F}_{11}$, when heated under vacuum, undergoes decomposition according to the equation:

For example, tungsten hexafluoride (12.139 g., 0.0408 mole) and dinitrogen tetroxide (16.0 g., 0.1739 mole) reacted at 60°C . for 16 hours gave, on removal of all volatile constituents at room temperature, 14.333 g. of nonvolatile solid (calculated as $\text{N}_3\text{O}_5\text{W}_2\text{F}_{11}$, 14.254 g.). Without removing the solid from the reactor it was heated at 115°C . for 4

9. The melting point was determined in a sealed glass capillary tube, which was extensively attacked during the determination.

hours. The solid evolved NOF (identified by infrared analysis) and produced 13.441 g. of a solid identified by chemical analysis as NOWOF₅ (theory indicates 13.255 g.).

Anal. Calc for NOWOF₅: W, 56.59; F, 29.24; N, 4.31.

Found: W, 56.40; F, 29.44; N, 4.00.

Decomposition can be accomplished in about one hour at 200°C. but the NOWOF₅ is slightly volatile at this temperature. Combination of reactions 3 and 4 gives reaction 5, which is analogous to that found in the case of molybdenum hexafluoride:

The NOWOF₅ is a white solid with a vapor pressure less than 1 mm. Hg at 25°C.; it melts at $282 \pm 5^\circ\text{C}$. into a colorless liquid.⁹ The density of the solid was determined (by volume displacement in carbon tetrachloride) to be 3.87 g./cc. at 25°C. The NOWOF₅ is insoluble in carbon tetrachloride, carbon disulfide and trichlorotrifluoroethane and dissolves in ethanol and acetone. Its reaction with water to evolve NO₂ is characteristic of the NO⁺ ion.⁸

The compounds NOMoOF₅ and NOWOF₅ are quite similar. They give characteristic X-ray diffraction powder patterns which are nearly identical.¹⁰ The first infrared work on the two solids was done with a Nujol mull. This work showed an absorption band in the solids in the 2320 cm^{-1} region which is characteristic of the NO⁺ ion.¹¹ However, the moisture sensitivity of the compounds left doubt as to the validity of the other bands in the spectra. Thus, the infrared spectra which are reported in this work were obtained from solids prepared in place in an infrared gas cell by the reaction of the gaseous hexafluorides with an excess of gaseous dinitrogen tetroxide at 25°C.

10. Ralston, K. and Musil, F. J. X-Ray Diffraction Data for Nine New Salts Containing Hexafluoro-Uranate (V), -Molybdate (V), or -Tungstate (V) Ions. Goodyear Atomic Corp., Oct. 18, 1960. 22p. (GAT-T-839). [Also submitted to ASTM for X-Ray Diffraction Powder Data Card File, 1961.]

11. Millen, D. J. and Watson, D. J. Chem. Soc., 1369 (1957)

INFRARED STUDIES

Uranium Hexafluoride — Uranium hexafluoride at 20 mm. Hg pressure was reacted at first in an infrared gas cell with dinitrogen tetroxide at 800 mm. Hg pressure.¹² The large excess of N_2O_4 obscured absorption bands of volatile products that might be expected; e.g., NO_3 , N_2O_5 , NOF , NO_2F . After evacuation of the volatile components the solid product of reaction was identified as $NOUF_6$ by its X-ray diffraction pattern and infrared spectrum.⁵ The gas phase reaction apparently proceeds as shown in Equation 1.

The reaction, repeated using dinitrogen tetroxide (40 mm. Hg) pressured to 800 mm. Hg with nitrogen, showed $NOUF_6$, dinitrogen pentoxide and nitryl fluoride. In addition, a small infrared absorption band at 835 cm.^{-1} appeared in the spectrum of the solid. This band is attributed to a uranium oxygen absorption.¹³ These results suggest that a reaction similar to that represented in Equation 6 also occurred to a very minor extent under these experimental conditions.

Molybdenum and Tungsten Hexafluorides — Both of these gaseous hexafluorides react with excess gaseous dinitrogen tetroxide¹⁴ to produce nitryl fluoride and a nitrosylium salt. The nitrosylium salts appear to be similar to the sodium and cesium pentafluoroxymolybdate and -tungstate reported by Hargreaves and Peacock.¹⁵ These reactions can be represented by the equation

where M represents Mo or W.

The solid products of the gas phase reactions were the same as when liquid dinitrogen tetroxide was used. No evidence was found for dinitrogen pentoxide and nitrosyl fluoride in the gas phase reactions. These species were found only when the reaction was carried out in liquid dinitrogen tetroxide.

12. A large pressure of N_2O_4 is needed to decrease the presence of the NO_2 species which can react to form NO_2UF_6 .

13. Jones, L. H. Spectrochim. Acta, 409 (1959)

14. Since NO_2 was found not to react with MoF_6 or WF_6 , the pressure of the N_2O_4 is not critical.

15. Hargreaves, G. B. and Peacock, R. D. J. Chem. Soc., 2170, 4390 (1958)

Nitrosylium Pentafluoroxymolybdate (VI) — This compound was prepared in an infrared gas cell by reacting MoF_6 (20 mm. Hg) with N_2O_4 (800 mm. Hg) at 25°C . The absorption bands of MoF_6 disappeared immediately from the infrared spectrum on addition of the N_2O_4 . Absorption bands at 2323, 1793, 988, 822, 643 cm^{-1} and those characteristic of N_2O_4 were then observed in the infrared spectrum. The absorption bands at 1793 and 822 cm^{-1} were attributed to NO_2F . The infrared spectrum obtained of the solid remaining after the evacuation of the volatile constituents is given in Figure 1. The absorption band at 2323 cm^{-1} is assigned to the NO^+ cation while the bands at 988 and 643 cm^{-1} are attributed to the anion $(\text{MoOF}_5)^-$.

Nitrosylium Pentafluoroxytungstate (VI) — Preparation of the compound and determination of the infrared spectrum were analogous to that for the molybdenum hexafluoride reaction. The infrared spectrum is shown in Figure 2. The absorption band at 2325 cm^{-1} is due to the NO^+ cation, and those at 1005 and 608 cm^{-1} are due to the $(\text{WOF}_5)^-$ anion.

Barradough, et al.,¹⁶ have recently reported metal oxygen band vibrations in the 900 to 1000 cm^{-1} range, and the bands in the above compounds at 988 and 1005 cm^{-1} are considered a similar vibration and are assigned to the metal-oxygen stretching frequency for molybdenum and tungsten respectively. The broad intense and structureless bands at 643 and 608 cm^{-1} respectively for molybdenum and tungsten are due to the metal-fluorine frequency.

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16. Barradough, C. G., Lewis, J. and Nyholm, R. S. J. Chem. Soc., 3552 (1959)

FIG. 1. INFRARED SPECTRUM OF NITROSYLIUM PENTAFLUOROXYMOLYBDATE (NOMoOF₅)

FIG. 2. INFRARED SPECTRUM OF NITROSYLIUM PENTAFLUOROXYTUNGSTATE (NOWOF₅)