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**REACTIONS OF MOLYBDENUM, TUNGSTEN AND URANIUM HEXAFLUORIDES WITH
NITROGEN COMPOUNDS. III. NITROGEN DIOXIDE AND NITROGEN OXYHALIDES***

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SUMMARY

Reaction between gaseous nitrogen dioxide and gaseous uranium hexafluoride results in the formation of the nitrylium salt NO_2UF_6 . Under similar conditions no reaction occurs between nitrogen dioxide and molybdenum and tungsten hexafluorides. Reaction between nitrosyl and nitryl fluorides and the three hexafluorides results in solid compounds of the composition $\text{NO}_x\text{F} \cdot \text{MF}_6$, where x is 1 or 2 and M represents Mo, W, or U. Reaction between gaseous or liquid nitrosyl chloride and molybdenum and uranium hexafluorides

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results in the formation of the nitrosylium salts NOMoF_6 and NOUF_6 , and chlorine. Tungsten hexafluoride was found not to react with nitrosyl chloride.

The conditions and stoichiometry of the reactions are described. The nitrylium salt NO_2UF_6 is characterized and some of its physical and chemical properties are described. The $\text{NO}_x\text{F} \cdot \text{MF}_6$ compounds are characterized and some physical properties are described. Evidence for the presence of NO_x^+ and MF_7^- ions in these compounds is given. The nitrosylium salts, NOMoF_6 and NOUF_6 , have been characterized previously.

INTRODUCTION

The study of the action of various nitrogen-containing compounds on the hexafluorides of molybdenum, tungsten and uranium has continued in this laboratory. The action of nitrous oxide, nitric oxide and liquid dinitrogen tetroxide has been reported previously^{1,2}. It was found that reaction between nitric oxide and the hexafluorides of molybdenum and uranium resulted in the formation of nitrosylium salts of pentavalent molybdenum and uranium (NOMoF_6 and NOUF_6). Tungsten hexafluoride did not react with nitric oxide. The preparation of analogous salts containing the nitrylium ion was attempted by reacting the hexafluorides with liquid dinitrogen tetroxide; however, only nitrosylium salts were formed in liquid dinitrogen tetroxide. With uranium hexafluoride the same salt (NOUF_6) was obtained as with nitric oxide, while nitrosylium oxyfluoride salts of hexavalent molybdenum and tungsten (NOMoOF_5 and NOWOF_5) were obtained.

In the present investigation the reactions of the hexafluorides with gaseous nitrogen dioxide (NO_2), nitrosyl fluoride (NOF), nitryl fluoride (NO_2F), and gaseous and liquid nitrosyl chloride (NOCl) were studied. The reactions with gaseous nitrogen dioxide were studied in a further attempt to prepare nitrylium salts. The reactions with nitrosyl fluoride, nitryl fluoride and nitrosyl chloride were investigated to determine whether complex formation occurred.

No reaction between molybdenum and tungsten hexafluorides and gaseous nitrogen dioxide at 25° and 60°C. was found to occur. However, under the same conditions, reaction between uranium hexafluoride and nitrogen dioxide resulted in the formation of a solid which has been characterized as a nitrylium salt of pentavalent uranium (NO_2UF_6). Nitrosyl and nitryl fluorides were found to form 1:1 addition compounds with the three hexafluorides. The infrared spectra of these addition compounds indicate that the ionic forms $\text{NO}_2^+ [\text{MF}_7]^-$ or $\text{NO}^+ [\text{MF}_7]^-$ make a contribution to the structure of the solids. The behavior of nitrosyl chloride with the hexafluorides was found to be similar to that of nitric oxide. Reaction occurred with molybdenum and uranium hexafluorides to form the respective nitrosylium salt and chlorine gas. Tungsten hexafluoride was unreactive with nitrosyl chloride under the experimental conditions employed.

*M = Mo, W, or U.

EXPERIMENTAL

EQUIPMENT AND REAGENTS

The procedure and equipment used in this study have been described in earlier reports^{1,2}. All reaction products were handled in a dry box with a nitrogen atmosphere.

Purification of the hexafluorides and nitrogen dioxide was described previously^{1,2}. Nitrosyl fluoride was prepared by allowing gaseous fluorine to mix by diffusion with a slight excess of pure gaseous nitric oxide for 16 hours at 25°C. and a total pressure of approximately 1 atmosphere. A slight excess of fluorine was added to react with the remaining nitric oxide. The excess fluorine was removed by evacuation of the mixture at -196°C. Preparation and storage of the nitrosyl fluoride was most satisfactory when the reaction was performed in nickel equipment. The nitrosyl fluoride contained approximately 1 mole percent of nitryl fluoride, apparently as a result of reaction with the small amount of oxygen in the fluorine.

Nitryl fluoride was prepared by allowing a slight excess (over stoichiometric) of fluorine to mix by diffusion with pure nitrogen dioxide for 16 hours at 25°C. and a total pressure of approximately 1 atmosphere. The gases were condensed into a reactor and were heated at approximately 200°C. for 15 minutes. Excess fluorine was removed by evacuating the frozen product at -196°C. The nitryl fluoride was stored in a nickel container.

Nitrosyl chloride, obtained from the Matheson Company, was further purified by low temperature fractionation to remove nitrogen dioxide and chlorine.

REACTION WITH NITROGEN DIOXIDE

Two 1-liter glass bulbs joined by a 10-mm. stopcock were connected to the vacuum system. This apparatus was dried by flaming and also by treatment for 30 minutes several times with chlorine trifluoride at a pressure of 25 to 50 mm. Hg. The desired hexafluoride gas was added to one glass bulb and the nitrogen dioxide to the other at an equal pressure, and then the stopcock between them was opened. The gases were allowed to mix by diffusion at 25°C. for periods up to 16 hours. The reactions were run at low pressures of nitrogen dioxide to decrease the amount of the dinitrogen tetroxide (N_2O_4) species.

Molybdenum and Tungsten Hexafluorides

No visible change was seen and no decrease in pressure was observed during runs at pressures of 10, 20, and 50 mm. Hg. At a pressure of 100 mm. Hg a slight white film was formed on the glass wall in a period of 16 hours. This was attributed to reaction with the N_2O_4 species which is present in about 15 percent concentration at 100 mm. Hg pressure. Similar runs in an infrared cell held at 60°C. to decrease the concentration of the N_2O_4 species, showed no reaction.

Uranium Hexafluoride

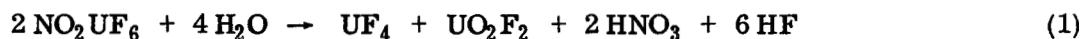
Gaseous uranium hexafluoride and nitrogen dioxide were found to react instantaneously at 25°C. at partial pressures below 100 mm. Hg to form a solid. This solid was characterized as nitrylium hexafluorouranate (V), NO_2UF_6 , by chemical analysis.

Anal. Calc. for NO_2UF_6 : U, 59.80; F, 28.64; N, 3.52. Hydrolysis: U(IV), 29.90

Found: U, 59.95; F, 28.57; N, 3.52. Hydrolysis: U(IV), 26.46

Nitrylium hexafluorouranate (V) is a yellowish-white solid having no vapor pressure at 25°C. It is soluble in anhydrous hydrogen fluoride (approximately 0.2 g./g. HF) and insoluble in carbon tetrachloride. The solid density, as determined by volume displacement in carbon tetrachloride, is 3.90 ± 0.09 g./cc.* Nitrylium hexafluorouranate (V) gives a characteristic X-ray diffraction pattern which has not been indexed as yet. It has a strong, sharp infrared absorption band at 2386 cm.^{-1} which is characteristic of the NO_2^+ ion, and a strong broad band with its center at 495 cm.^{-1} which is attributed to the UF_6^- ion.

Nitrylium hexafluorouranate (V) undergoes relatively slow hydrolysis in air and rapid hydrolysis with excess water according to the equation



The reaction with water is characteristic of pentavalent uranium³ and the NO_2^+ ion⁴. Nitrylium hexafluorouranate (V) is unaffected chemically by treatment with liquid chlorine trifluoride at 60° to 90°C. for one hour. However, the compound dissolved in anhydrous hydrogen fluoride has been completely converted to uranium hexafluoride by reaction at 25°C. with chlorine trifluoride at a ClF_3 -to- NO_2UF_6 mole ratio of 3. Nitrylium hexafluorouranate (V) is approximately 90 percent reduced to uranium tetrafluoride with hydrogen at 300° to 350°C. It is completely converted to nitrosylium hexafluorouranate (V) by reaction with liquid or gaseous dinitrogen tetroxide at 25°C. according to the over-all equation



Dinitrogen pentoxide was observed, by infrared analysis of the gas phase, as an intermediate in this reaction.

REACTION WITH NITROSYL FLUORIDE

Weighed amounts of nitrosyl fluoride and the desired hexafluoride were condensed at -196°C. into a tared prefluorinated nickel or fluorothene reactor. The reactor was allowed to warm up to room temperature for about 1 hour, after which the excess of either

*At the 95% confidence level.

component was removed from the solid reaction product by evacuation. Evacuation was continued until a constant vapor pressure was obtained. The vapor was examined by infrared analysis to determine the constituents present. Also, the infrared spectrum of the solid was determined by preparing the sample in an infrared gas cell. The composition of the solid was obtained by chemical analysis.

Molybdenum Hexafluoride

A white solid with a vapor pressure of 3.5 mm. Hg at 21.5°C. was obtained. The vapor over the solid consisted of approximately equal molar quantities of molybdenum hexafluoride and nitrosyl fluoride. Chemical analysis of the solid indicated the composition to be $\text{NOF} \cdot \text{MoF}_6$. The infrared absorption spectrum of $\text{NOF} \cdot \text{MoF}_6$ contains bands of NOF and MoF_6 , and bands at 2328 and 636 cm.^{-1} which are attributed to the presence of NO^+ and MoF_7^- ions, respectively, in the solid.

Anal. Calc. for NOMoF_7 : Mo, 37.05; F, 51.36; N, 5.41

Found: Mo, 35.89; F, 51.92; N, 5.83

Tungsten Hexafluoride

A white solid with a vapor pressure <1 mm. Hg at 25°C. was obtained. The vapor over the solid consists of approximately equal molar quantities of tungsten hexafluoride and nitrosyl fluoride. Chemical analysis established the composition $\text{NOF} \cdot \text{WF}_6$. The compound $\text{NOF} \cdot \text{WF}_6$ was found to contain infrared absorption bands at 2330 and 2327 cm.^{-1} , and 620 cm.^{-1} which are attributed to NO^+ and WF_7^- ions, respectively, as well as bands of NOF and WF_6 .

Anal. Calc. for NOWF_7 : W, 53.00; F, 38.34; N, 4.04

Found: W, 53.41; F, 36.70; N, 3.50

Uranium Hexafluoride

A greenish-yellow solid with a vapor pressure <1 mm. Hg at 25°C. was obtained by reaction of NOF with UF_6 . The vapor over the solid consists of approximately equal molar quantities of uranium hexafluoride and nitrosyl fluoride. Composition of the compound is $\text{NOF} \cdot \text{UF}_6$, as determined by chemical analysis. The compound $\text{NOF} \cdot \text{UF}_6$ had infrared absorption bands at 2320 and 2318 cm.^{-1} , and 549 to 510 cm.^{-1} which are attributed to NO^+ and UF_7^- ions, respectively as well as bands of NOF and UF_6 .

Anal. Calc. for NOUF_7 : U, 59.36; F, 33.16; N, 3.49

Found: U, 58.98; F, 29.66; N, 3.58

REACTION WITH NITRYL FLUORIDE

The procedure described previously for the reactions with nitrosyl fluoride was followed here for reaction with nitryl fluoride.

Molybdenum Hexafluoride

A white solid with a vapor pressure of 90 mm. Hg at 25°C. and 18 mm. Hg at 0°C. was obtained. The vapor consists of approximately equal molar quantities of molybdenum hexafluoride and nitryl fluoride. Chemical analysis has established the composition $\text{NO}_2\text{F} \cdot \text{MoF}_6$. The compound $\text{NO}_2\text{F} \cdot \text{MoF}_6$ has infrared absorption bands at 2374 and 627 cm.^{-1} which are attributed to NO_2^+ and MoF_7^- ions, respectively, and bands of NO_2F and MoF_6 .

Anal. Calc. for NO_2MoF_7 : Mo, 34.90; F, 48.27; N, 5.10

Found: Mo, 35.06; F, 45.95; N, 4.45

Tungsten Hexafluoride

A white solid with a vapor pressure of 1.3 mm. Hg at 25°C. was obtained. The vapor consists of approximately equal molar quantities of tungsten hexafluoride and nitryl fluoride. The composition of the solid is $\text{NO}_2\text{F} \cdot \text{WF}_6$. This compound has infrared absorption bands at 2377 and 620 cm.^{-1} which are attributed to NO_2^+ and WF_7^- ions, respectively, and bands of NO_2F and WF_6 .

Anal. Calc. for NO_2WF_7 : W, 50.69; F, 36.65; N, 3.86

Found: W, 49.10; F, 36.37; N, 4.47

Uranium Hexafluoride

A greenish-white solid with a vapor pressure of 11.6 mm. Hg at 25.7°C. was obtained. The vapor consists of approximately equal molar quantities of uranium hexafluoride and nitryl fluoride. The composition of the solid is $\text{NO}_2\text{F} \cdot \text{UF}_6$. This compound has an infrared absorption band at 2374 cm.^{-1} which is indicative of the NO_2^+ ion, and bands of NO_2F and UF_6 .

Anal. Calc. for NO_2UF_7 : U, 57.07; F, 31.89; N, 3.36

Found: U, 57.23; F, 28.51; N, 3.64

REACTION WITH NITROSYL CHLORIDE

The procedure described under "Reaction with Nitrogen Dioxide" was followed for the

reaction between nitrosyl chloride gas and the hexafluoride gases. The procedure described under "Reaction with Nitrosyl Fluoride" was followed for the reaction between liquid nitrosyl chloride and the hexafluorides. However, the analyses of the gaseous products of the reaction were made by mass spectrometry rather than by infrared methods.

Molybdenum Hexafluoride

Reaction occurred instantaneously with either gaseous or liquid nitrosyl chloride to form NOMoF_6 and chlorine gas. The nitrosylium hexafluoromolybdate (V) has been characterized previously.

Tungsten Hexafluoride

No reaction between tungsten hexafluoride and liquid or gaseous nitrosyl chloride was observed at temperatures as high as 60°C .

Uranium Hexafluoride

Reaction occurred instantaneously with gaseous or liquid nitrosyl chloride to give solid NOUF_6 and chlorine gas. The nitrosylium hexafluorouranate (V) has been characterized earlier.

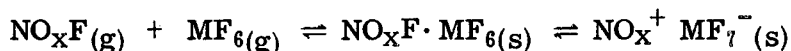
DISCUSSION

REACTION WITH NITROGEN DIOXIDE

Molybdenum and tungsten hexafluorides do not react with nitrogen dioxide. Uranium hexafluoride reacts with nitrogen dioxide to form NO_2UF_6 , which was shown by infrared and chemical evidence to be a salt of pentavalent uranium. Reaction apparently takes place simply by electron transfer from NO_2 to UF_6 . We have no explanation for the lack of reactivity of molybdenum and tungsten with nitrogen dioxide since similar pentavalent compounds of the alkali metals are known⁵, i. e., NaMoF_6 , KMoF_6 , NaWF_6 , and KWF_6 .

REACTION WITH NITROSYL AND NITRYL FLUORIDES

All the hexafluorides were found to form 1:1 addition compounds with both nitrosyl and nitryl fluorides. The information we have obtained supports the following equation:



where x has the value 1 or 2, and M represents Mo, W, or U. Thus, the solid 1:1 addition compound is in equilibrium with the gases NO_xF and MF_6 . Also, the solid structure

is apparently composed of an ionic form $[\text{NO}_x^+ \text{MF}_7^-]$ and a lattice form $[\text{NO}_x\text{F} \cdot \text{MF}_6]$ where the identity of the NO_xF and the MF_6 are retained. The contribution of the ionic form to the structure of the solid is shown by the extra infrared absorption bands which cannot be attributed to NO_xF and MF_6 . The contribution of the lattice form $[\text{NO}_x\text{F} \cdot \text{MF}_6]$ to the structure of the solids is indicated by dissociation of the solid, and infrared absorption bands of NO_xF and MF_6 which do not change appreciably when the vapor over the solid is rapidly removed by evacuation. Further infrared work on the solids at lower temperatures where they are nonvolatile is necessary to determine the degree of contribution of the lattice form to the structure.

REACTION WITH NITROSYL CHLORIDE

Reaction of molybdenum and uranium hexafluorides occurs with gaseous or liquid nitrosyl chloride to form nitrosylium salts and to liberate chlorine. The hexafluoromolybdate (V) or hexafluorouranate (V) ions apparently have a greater attraction for the odd electron on nitric oxide than does chlorine. Since tungsten hexafluoride does not react with nitric oxide, a lack of reactivity with nitrosyl chloride is expected and is found.

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