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GOOD YEAR

Mo W U

HEXAFLUORIDES OF MOLYBDENUM, TUNGSTEN AND URANIUM.
III. REACTIONS WITH NITROGEN DIOXIDE AND NITROGEN OXYHALIDES^{1,2}

by

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ABSTRACT

Reaction between gaseous nitrogen dioxide and gaseous uranium hexafluoride gave NO_2UF_6 . The same compound resulted when uranium pentafluoride and nitryl fluoride reacted. Reaction between nitrosyl and nitryl fluorides and the three hexafluorides results in solid compounds of the composition $\text{NO}_x\text{F} \cdot \text{MF}_6$. Reaction between nitrosyl chloride and molybdenum and uranium hexafluorides formed the nitrosylium salts NOMoF_6 and NOUF_6 , and liberated chlorine.

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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 and gaseous dinitrogen tetroxide has been reported previously.^{5,9} 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.

EXPERIMENTAL

MATERIALS

The procedure, equipment, and methods of purification of the hexafluorides, nitrogen dioxide, and nitrosyl fluoride have been described in earlier reports.^{5,6}

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 15°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.

5. Geichman, J. R., Smith, E. A., Trond, S. S. and Ogle, P. R. 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.
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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° or 60°C at partial pressures below 40 mm Hg to form a solid. This solid was characterized as nitrylium hexafluorouranate (V), NO_2UF_6 , by chemical and infrared analysis. Study of the reaction in an infrared gas cell showed as an initial product nitryl fluoride, which then rapidly disappears. After evacuation, the infrared spectrum of the solid in the gas cell gave an absorption band at 2386 cm^{-1} which is characteristic of the NO_2^+ ion⁷ and a strong broad band with its center at 495 cm^{-1} which is attributed to the UF_6^- ion (see Figure 1).

The presence of nitryl fluoride suggests that the reaction proceeds by the formation of nitryl fluoride and uranium pentafluoride which then combine. Excess gaseous nitryl fluoride was mixed with uranium pentafluoride (0.375 g, 1.12 millimoles) for 16 hours at 25°C to determine the reaction. NO_2UF_6 (0.455 g, 1.14 millimoles), identified by x-ray analysis, was produced in this reaction. The infrared spectrum of the product of this reaction was the same as that produced by reacting the NO_2 with uranium hexafluoride.

7. Teraneski, R. and Decius, J. C. J. Chem. Phys. **22**, 896 (1954)

FIG. 1. INFRARED SPECTRUM OF NITRYLIUM HEXAFLUOROURANATE (NO_2UF_6)

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.⁸ Nitrylium hexafluorouranate (V) gives a characteristic x-ray diffraction powder pattern which is unindexed.⁹

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 uranium¹⁰ and the NO_2^+ ion.¹¹ 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

REACTION WITH NITROSYL AND NITRYL FLUORIDES

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

8. At the 95% confidence level.

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10. Katz, J.J. and Rabinowitch, E. The Chemistry of Uranium. New York, McGraw-Hill Book Co., 1951. p.391

11. Robinson, P. L. and Westland, G. J. J. Chem Soc., 4481 (1956)

either component was removed from the solid reaction product by evacuation. Evacuation was continued until a constant vapor pressure was obtained. Chemical analysis showed that nitrosyl and nitryl fluorides form 1:1 addition compounds with the three hexafluorides.

Examination of the vapor over the solid (by infrared analysis) showed that it consisted of approximately equal molar quantities of the starting components. Also, the infrared spectrum of the solid was determined by preparing the sample in an infrared gas cell. The infrared absorption spectra of the solid compounds $\text{NO}_x\text{F} \cdot \text{MF}_6$ showed bands of NO_xF and MF_6 and bands which are attributed to the presence of NO_x^+ and MF_7^- ions. The bands characteristic of these ions, and other physical properties of the solids, are given in Table I.

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 and Nitryl Fluorides" 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 and infrared methods.

Molybdenum and Uranium Hexafluorides - Reaction of the hexafluorides occurred rapidly with either gaseous or liquid nitrosyl chloride to form respectively the solids NOMoF_6 or NOUF_6 and chlorine gas. Nitrosyl fluoride was looked for as an intermediate in the reaction but was not observed.

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

DISCUSSION

REACTION WITH NITROGEN DIOXIDE

This investigation suggested that reaction between nitrogen dioxide and uranium hexafluoride occurs first by the formation of nitryl fluoride and uranium pentafluoride which then

Table I

PHYSICAL PROPERTIES OF $\text{NO}_x\text{F} \cdot \text{MF}_6$ SOLID COMPOUNDS

Compound	Wave Numbers (cm^{-1})			Color	Vapor Pressure at 20°C (mm. Hg)	Analyses (%)		
	NO^+	MF_7^-	NO_2^+			Element	Calc. for	Found
$\text{NOF} \cdot \text{MoF}_6$	2328	636		white	3	Mo	37.05	35.89
						F	51.36	51.92
						N	5.41	5.83
$\text{NOF} \cdot \text{WF}_6$	2327 2330	620		white	< 1	W	53.00	53.41
						F	38.34	36.70
						N	4.04	3.50
$\text{NOF} \cdot \text{UF}_6$	2320 2318	549-610		greenish- yellow	< 1	U	59.36	58.98
						F	33.16	29.66
						N	3.49	3.58
$\text{NO}_2\text{F} \cdot \text{MoF}_6$		627	2374	white	53	Mo	34.90	35.06
						F	48.27	45.95
						N	5.10	4.45
$\text{NO}_2\text{F} \cdot \text{WF}_6$		620	2377	white	6	W	50.69	49.10
						F	36.65	36.37
						N	3.86	4.47
$\text{NO}_2\text{F} \cdot \text{UF}_6$		12	2374	greenish- white	7.5	U	57.07	57.23
						F	31.89	28.51
						N	3.36	3.64

12. The band expected for the UF_7^- ion is in the region where it would be masked by bands of NO_2F .

form the nitrylium salt. The lack of reactivity of molybdenum with nitrogen dioxide is unexpected since similar pentavalent compounds are known, i.e., NaMoF_6 , KMoF_6 ,¹³ and NOMoF_6 .⁵ Since tungsten hexafluoride does not react with nitric oxide,⁵ the inertness of nitrogen dioxide was anticipated.

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 identities of the NO_xF and the MF_6 are retained. The contribution of the ionic form to the structure of the solids is shown by 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 the dissociation pressure of the solids, and the intensity of the infrared absorption of NO_xF and MF_6 which does not change appreciably when the vapor over the solid is rapidly removed by evacuation. Similarly, Addison and Hathaway concluded from the infrared absorption spectrum of solid $\text{Cu}(\text{NO}_3)_2 \cdot \text{N}_2\text{O}_4$ that the ionic form $\text{NO}^+ \text{Cu}(\text{NO}_3)_3^-$ made a contribution to the structure of that solid.¹⁴

REACTION WITH NITROSYL CHLORIDE

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

13. Hargreaves, G. B. and Peacock, R. D. J. Chem. Soc., 4212 (1957)

14. Addison, C. C. and Hathaway, B. J. J. Chem. Soc., 1468 (1960)

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