the reaction bed for 15 min. at −112°. The ozonide was extracted from the insoluble hydroxide with about 10 ml. of liquid ammonia. In order to precipitate the ozonide, the ammonia solution then was added to about 20 ml. of fluoroform maintained at −112°. The resulting red solid was washed several times with fluoroform to remove the excess ammonia. This method resulted in 5–10% conversions, based on the lithium hydroxide charged.

Calculation of Degree of Ammoniation of Lithium Ozonide.—After fluoroform had been distilled from the solid ozonide at −126°, the temperature was raised to −78° to allow the ammonia to distil. Some ammonia came off very quickly, but the remainder distilled at a slow steady rate. No oxygen was evolved while the first amount of ammonia was removed. The oxygen that was evolved in the second process was separated from the ammonia, transferred into a calibrated volume, and measured. The solid residue was analyzed for Li^+, NO_3^-, and NO_2^-.

The Li^+ was determined by flame photometry; Li^+ standards having the same acidity as the sample were used.

TABLE II

SPECIES FOUND IN THE DECOMPOSITION OF LITHIUM OZONIDE TETRAAMMONIATE

Specie	Amount, mmoles or g.-atoms
O_2	5.25
NH_3	34.65
NO_3^-	4.22
NO_2^-	0.44
Li^+	9.42

The nitrite was determined colorimetrically by means of the sulfanilic acid and α-naphthylamine method. The total nitrate and nitrite was found by means of the standard DeVarda method; the nitrate was calculated by difference.

The total nitrogen was calculated from the amounts of the various species given in Table II. The ratio of NH_3 to Li^+ was found to be 4.17. A repeat run gave a ratio of 4.32.

CONTRIBUTION FROM THE GOODYEAR ATOMIC CORPORATION,
PORTSMOUTH, OHIO

Hexafluorides of Molybdenum, Tungsten, and Uranium. I. Reactions with Nitrous and Nitric Oxides[1,2]

BY J. R. GEICHMAN, E. A. SMITH, S. S. TROND, AND P. R. OGLE

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Reaction of nitric oxide with molybdenum and uranium hexafluorides gives the solid ionic compounds $NO^+[MoF_6]^-$ and $NO^+[UF_6]^-$. These same compounds result when molybdenum and uranium pentafluorides are allowed to react with nitrosyl fluoride. No reaction occurs between nitric oxide and tungsten hexafluoride, while nitrous oxide does not react with tungsten, molybdenum, or uranium hexafluorides.

Introduction

The properties and structure of nitrosyl compounds have been reviewed by Moeller.[3,4] Recently, nitrosyl complex fluorides of vanadium, niobium, tantalum,[5] gold, phosphorus, germanium, and tin[6] have been obtained by the reaction of the metal fluoride or oxide either directly with nitrosyl fluoride or with nitrosyl chloride in bromine trifluoride. Also, nitrosyl hexafluoroiridate(IV) has been prepared by the reaction of nitric oxide with iridium hexafluoride.[7] In this reaction, the formation of nitrosyl fluoride and iridium tetrafluoride was not detected. Simple electron transfer from nitric oxide to the hexafluoride was postulated as the mechanism of reaction.

An investigation was carried out in this Laboratory to characterize the reactions of the gaseous hexafluorides of molybdenum, tungsten, and uranium with nitrous and nitric oxides. The absorption spectra of the solids produced in these reactions were determined using samples prepared in the infrared gas cell. Work also was done to determine the mechanism of the reactions.

Experimental

Equipment, Procedure, and Materials.—A metal vacuum system was used for experimental manipulations. Pres-

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[1] This work was performed under Contract AT-(33-2)-1 with the U.S. Atomic Energy Commission.

[2] Presented in part at the 136th National Meeting of the American Chemical Society in Atlantic City, N. J., on September 17, 1959.

[3] T. Moeller, *J. Chem. Educ.*, **23**, 441 (1956).

[4] T. Moeller, *ibid.*, **23**, 542 (1956).

[5] H. C. Clark and H. J. Emeléus, *J. Chem. Soc.*, 190 (1958).

[6] A. A. Woolf, *ibid.*, 1053 (1950).

[7] P. L. Robinson and G. J. Westland, *ibid.*, 4481 (1956).

sure was measured by means of a Taylor Instrument Co. absolute pressure transmitter used in conjunction with a mercury manometer or a bronze Bourdon tube gage.

The gas-phase reactions were produced either in a glass apparatus essentially consisting of two 1-l. bulbs connected by a 10-mm. stopcock, or in a metal apparatus made of two 1-l. metal reactors joined by a large aperture valve. Other reactions were carried out in flanged nickel vessels sealed with Teflon or aluminum gaskets, and in fluorothene tubes. All reaction equipment was exposed to fluorine or chlorine trifluoride before use. Reactors were heated in a thermostatically controlled oven. Solid products of reaction were removed, sampled, and stored in a nitrogen atmosphere drybox.

Three Perkin-Elmer infrared spectrometers were used for obtaining the spectral data over the range 5000 to 450 cm.$^{-1}$. A Model 112 single-beam, double-pass instrument with a lithium fluoride prism was used in the 5000–1700-cm.$^{-1}$ range. The sample section of this instrument was covered completely with a Plexiglass enclosure which was purged with dry nitrogen to eliminate atmospheric water and carbon dioxide absorption bands from the spectra. A Model 21-A double-beam instrument calibrated linearly in wave length from 2–15 μ was used with a sodium chloride prism in the 1700–650-cm.$^{-1}$ range. A Model 13 double-beam, constant I_0 instrument was used with a potassium bromide prism in the 650–450-cm.$^{-1}$ range. The Models 112 and 13 instruments were calibrated in reciprocal centimeters by a method described by Downie, *et al.*[8] This method of calibration provides measurement accuracy to within about one wave number. The Model 21-A is specified by the manufacturer to be accurate to ± 0.015-μ wave length over its entire range and it was used without modification. Optical materials used for the gas absorption cell windows included calcium fluoride and silver chloride to cover the spectral range studied and to provide adequate corrosion resistance to the reactants and the reaction products.

Attempts to obtain the infrared absorption spectra of $NOMoF_6$ and $NOUF_6$ by the use of conventional techniques for solids did not succeed. Incorporation of the samples in potassium bromide, Nujol, or fluorocarbon oil failed since the solids either reacted or were decomposed by exposure to the atmosphere. To prevent exposure to the atmosphere, the spectra of the solids finally were obtained by preparing them within a 10-cm. gas infrared absorption cell by gas-phase reaction, which deposits a layer of the solid product over the interior surfaces. An infrared absorption spectrum then may be obtained of the solids on the windows, the gas reaction products, and the unreacted gas components. The spectrum of the non-volatile solid products may be obtained separately after evacuating the cell. After the infrared study the solid can be removed from the infrared cell in a drybox for subsequent X-ray and chemical analyses.

Molybdenum and tungsten hexafluorides were obtained commercially from the Harshaw Chemical Co.; the uranium hexafluoride was available in this Laboratory. The hexafluorides were purified by evacuation at −78° and by discarding volatile fractions at 25° until the theoretical vapor pressures were attained. Infrared analyses revealed that hydrogen fluoride or metal oxyfluorides were not present in these hexafluorides after purification. Nitrous and nitric oxide were obtained from the Matheson Co. Purification was accomplished by low temperature distillation. A trace ($<0.1\%$) of nitrous oxide remained as the only infrared-detectable impurity in the nitric oxide. Nitrosyl fluoride was prepared by allowing fluorine to mix by diffusion with a stoichiometric excess of nitric oxide at 25° and a total pressure of approximately 1 atm. After 16 hr. a small amount of fluorine was added to react with the excess nitric oxide. The remaining fluorine was removed by cooling the mixture to −196° and pumping off volatile components. Preparation and storage of nitrosyl fluoride in nickel equipment was most favorable. The nitrosyl fluoride contained approximately 1 mole % of nitryl fluoride, apparently resulting from a small amount of oxygen in the fluorine. Molybdenum pentafluoride was prepared by the reaction of molybdenum hexafluoride and carbon monoxide, while uranium pentafluoride was prepared by the reaction of uranium hexafluoride and anhydrous hydrogen chloride.[9]

Reaction of Nitrous Oxide with Molybdenum, Tungsten, and Uranium Hexafluorides.—An equimolar gaseous mixture of N_2O and the appropriate hexafluoride was held at a total pressure of 200 mm. and a temperature of either 25 or 60°. The contact times were varied from 4–24 hr. No solid products of reaction were observed. The initial pressure in the reactor did not change in each case, indicating no reaction. Also, the infrared spectra of nitrous oxide mixed with the individual hexafluorides remained unaltered.

Reaction of Nitric Oxide with Molybdenum, Tungsten, and Uranium Hexafluorides.—Excess nitric oxide was found to react rapidly, if not instantaneously, with gaseous molybdenum or uranium hexafluorides at temperatures from 25–60°. The reaction is not as rapid when liquid molybdenum hexafluoride and solid uranium hexafluorides are used.

A small amount of heat is evolved in the reaction. However, if excess nitric oxide and either gaseous or liquid tungsten hexafluoride are mixed at 25 and 60° for times ranging from 4–48 hr., the individual components may be recovered unchanged.

Nitrosyl Hexafluoromolybdate(V).—Molybdenum hexafluoride (14.725 g., 0.0701 mole) was condensed into an evacuated nickel reactor with nitric oxide (3.400 g., 0.1133 mole) at −196°. The mixture was heated for 16 hr. at 60°, after which all volatile gases were evacuated. A rusty orange non-volatile (vapor pressure <1 mm.) solid identified as $NOMoF_6$ (16.825 g., 0.0701 mole) by chemical analysis was obtained.

Anal. Calcd. for $NOMoF_6$: Mo, 39.98; F, 47.51; N, 5.84. Found: Mo, 39.63; F, 47.40; N, 5.63.

The solid melts at approximately 190° to a dark blue liquid with the apparent liberation of a colorless gas.[10] The solid density is 3.04 ± 0.08 g./cc.[11] as determined by volume displacement in carbon tetrachloride. Nitrosyl hexafluoromolybdate(V) has a pseudo-cubic X-ray diffrac-

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[8] A. R. Downie, M. C. Magoon, T. Pursell, and B. Crawford, *J. Opt. Soc. Am.*, **43**, 194 (1943).

[9] P. R. Ogle and E. A. Smith, Goodyear Atomic Corp., unpublished work.

[10] The melting point was determined in a closed tube; the gas is presumably nitrosyl fluoride.

[11] At the 95% confidence level.

tion pattern with $a_0 = 5.080$ Å.[12] The compound rapidly turns purple on exposure to the atmosphere. Hydrolysis of the compound in the absence of air gives nitric oxide, nitric acid, hydrofluoric acid,[13] and a water-soluble molybdenum compound not identified by X-ray diffraction analysis from the diffraction patterns available. The reaction with water to produce nitric oxide is characteristic of the NO^+ ion.[7] When the compound is added to acetone, methanol, and trichloroethylene in the air it gives dark-colored solid products and nitrogen dioxide gas. The $NOMoF_6$ is inert and insoluble in carbon tetrachloride. In liquid dinitrogen tetroxide at 25° the rusty orange-colored $NOMoF_6$ liberates nitrosyl fluoride and gives a white solid of the empirical composition NO_2MoF_5.

Anal. Calcd. for NO_2MoF_5: Mo, 40.49; F, 40.49; N, 5.91. Found: Mo, 40.26; F, 38.67; N, 6.21.

Nitrosyl Hexafluorouranate(V).—Uranium hexafluoride (24.454 g., 0.0694 mole) was condensed into an evacuated nickel reactor with nitric oxide (2.630 g., 0.0874 mole) at −196°. The components were left in contact for 2 hr. at 25° and then all volatile gases were evacuated. The reaction yielded 26.534 g. of a greenish white non-volatile (vapor pressure <1 mm.) solid (0.0694 mole as $NOUF_6$). The compound with excess water in the absence of air forms nitric oxide, nitric acid, hydrofluoric acid,[13] and equal molar quantities of insoluble uranium tetrafluoride and a soluble hexavalent uranium salt (presumably uranyl fluoride). The reaction with water is characteristic of the NO^+ ion[7] and pentavalent uranium.[14] When heated, the solid appears to decompose gradually above 200° to give a colorless gas, with melting occurring at approximately 350° to a green liquid.[10] When the salt is added to acetone, methanol, and trichloroethylene in air it liberates nitrogen dioxide and forms brownish black solid products. It is insoluble in, and inert toward, carbon tetrachloride, trichlorotrifluoroethane (Freon-113), liquid dinitrogen tetroxide, and monochlorobenzene. The solid density, as determined by volume displacement in carbon tetrachloride, is 4.30 ± 0.05 g./cc.[11] Nitrosyl hexafluorouranate(V) has a pseudo-cubic X-ray diffraction pattern with $a_0 = 5.179$ Å.[12]

Anal. Calcd. for $NOUF_6$: U, 62.31; F, 29.84; N, 3.66; hydrolysis: U(IV), 31.15; U(VI), 31.15. Found: U, 62.36; F, 29.72; N, 3.45; hydrolysis: U(IV), 31.40; U(VI), 31.27.

Infrared Study.—Nitrosyl hexafluoromolybdate(V) and hexafluorouranate(V) were prepared in a 10-cm. infrared gas absorption cell with silver chloride windows by the reaction between nitric oxide and the hexafluoride. The desired component at a pressure of 25 mm. was admitted, followed by an excess of the other reactant. Rapid reaction was indicated by the instantaneous disappearance of the infrared absorption band characteristic of the component not in excess and the instantaneous appearance of bands characteristic of the solid reaction product.

After reaction, the cell was evacuated to a pressure of 5 μ and the solid spectrum was recorded. Nitrosyl hexafluoromolybdate(V)[15] has a sharp absorption band at 2331 cm.$^{-1}$ and a broad intense band with an absorption maximum at 615 cm.$^{-1}$ (see Fig. 1). Nitrosyl hexafluorouranate(V)[15] has a sharp absorption band at 2333 cm.$^{-1}$ and a broad intense band split into two absorption maxima at 551 and 509 cm.$^{-1}$. The spectrum looks very similar in general appearance to that of Fig. 1 except for a small shoulder on the low field side of the 551-cm.$^{-1}$ peak (*i.e.*, 509-cm. peak). $NOMoF_6$ and $NOUF_6$ are slightly volatile, as evidenced by a decrease in the intensity of infrared spectra when they are continuously evacuated at 5 μ for long periods of time.

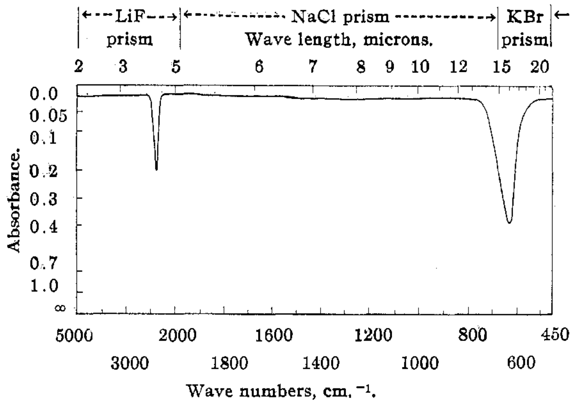

Fig. 1.—Infrared spectrum of nitrosyl hexafluoromolybdate ($NOMoF_6$).

The formation of a small amount of nitrosyl fluoride (NOF) in the reaction was indicated by the immediate appearance of an absorption band at 1845 cm.$^{-1}$. If excess nitric oxide was used this band only slowly disappeared, while if excess hexafluoride was present the band rapidly disappeared and other bands appeared in the spectrum. These bands are due to $NOF \cdot MoF_6$ and $NOF \cdot UF_6$; they disappear upon evacuation of the cell.[16]

Further investigation was required to account for the presence of nitrosyl fluoride in the reaction. Nitrosyl fluoride has been observed when nitric oxide is placed in an infrared cell containing silver chloride windows which have been pretreated with fluorine. Silver difluoride apparently is formed as a film on the cell windows. This then reacts with nitric oxide to give nitrosyl fluoride. No nitrosyl fluoride was formed when nitric oxide was placed in a cell with fluorine-treated calcium fluoride windows.

To preclude formation of nitrosyl fluoride from this source, the reactions with excess nitric oxide were repeated with calcium fluoride windows. Nitrosyl fluoride was still observed. The amount may be exceedingly small since the infrared sensitivity for nitrosyl fluoride is very great. No quantitative estimate of the concentration was made.

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[12] F. J. Musil, P. R. Ogle, and K. E. Beu, "Powder X-Ray Diffraction Data on $NOUF_6$ and $NOMoF_6$," ASTM X-ray Powder Data File, Cards 11-245, 11-246 (1961) (see also Goodyear Atomic Corp. report GAT-T-553/Rev. 1 by these authors).

[13] Determined by chemical and mass spectrometer analysis of the gaseous and liquid phases.

[14] J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium," McGraw-Hill Book Co., New York, N. Y., 1951, p. 391.

[15] Identified by chemical and X-ray analysis.

[16] J. R. Geichman, P. R. Ogle, and L. R. Swaney, "Reactions of Molybdenum, Tungsten and Uranium Hexafluorides with Nitrogen Compounds. III. Nitrogen Dioxide and Nitrogen Oxyhalides," Goodyear Atomic Corp., January 27, 1961 (GAT-T-809), to be published.

Discussion

The presence of nitrosyl fluoride suggests that the reaction of the hexafluoride with nitric oxide proceeds through the intermediate formation of nitrosyl fluoride and the metal pentafluoride, the nitrosyl fluoride then reacting quite rapidly with the metal pentafluoride to form the ionic nitrosyl salt. However, the pentafluoride intermediate was not detected by the infrared work. The amount of pentafluorides produced may not be enough to cause observable absorption and their absorption bands will be overlapped by the $NOMoF_6$ and $NOUF_6$ absorption bands.[9]

As a test of this possible reaction sequence the reaction of nitrosyl fluoride with the metal pentafluoride was carried out. Molybdenum pentafluoride (0.180 g., 0.94 mmole), when allowed to react with excess gaseous nitrosyl fluoride for 16 hr. at 25°, gave $NOMoF_6$ (0.205 g., 0.85 mmole).[15] Uranium pentafluoride (0.472 g., 1.41 mmoles), when allowed to react with excess gaseous nitrosyl fluoride for 16 hr. at 25°, gave $NOUF_6$ (0.535 g., 1.40 mmoles).[15] When these reactions were repeated in an infrared gas cell the spectra of the solids formed were identical with those of the solids formed when nitric oxide reacts with the hexafluorides.

The reaction of nitric oxide with either molybdenum or uranium hexafluoride to form an ionic nitrosyl salt is consistent with the following reaction sequence, where M represents either Mo or U

$$\mathrm{NO(g)} + \mathrm{MF_6(g)} \longrightarrow \mathrm{NOF(g)} + \mathrm{MF_5(s)} \qquad (1)$$

$$\mathrm{NOF(g)} + \mathrm{MF_5(s)} \longrightarrow \mathrm{NO^+[MF_6]^-(s)} \qquad (2)$$

Characterization of the solid products of the reaction as nitrosyl salts of pentavalent molybdenum and uranium is established by their infrared absorption spectra. The sharp bands at about 2330 cm.$^{-1}$ belong to the absorption of the nitrosyl ion (NO^+). Compounds containing NO^+ ions have been reported in the literature. Angus and Leckie[17] assigned a Raman frequency of 2340 cm.$^{-1}$ to the NO^+ ion in nitrosyl sulfuric acid ($NOHSO_4$). Gerding and Houtgraaf[18] have made similar observations with $NOAlCl_4$ and $NOClO_4$, assigning the NO^+ ion Raman frequencies of 2236 and 2313 cm.$^{-1}$, respectively. Millen and Watson[19] reported that the NO^+ infrared absorption occurs at 2240 for dinitrogen tetroxide dissolved in HNO_3, and at 2275 and 2238 cm.$^{-1}$ for $NOHSO_4$ and $NOAlCl_4$, respectively. Other workers[20] have found that the NO^+ ion gives infrared absorption bands in the range 2100 to 2350 cm.$^{-1}$.

A further test of the infrared absorption characteristic of the NO^+ ion was made. Nitric oxide gas contained in a glass infrared gas cell in the Model 21-A spectrometer was exposed to a microwave beam (2400 to 2500 Mc.).[21] Some of the neutral NO gas molecules were excited to the NO^+ gaseous ion state as evidenced by an infrared absorption band obtained at 2332 cm.$^{-1}$. This absorption band disappeared from the spectrum when the generator was turned off.

The large shift from 1876 cm.$^{-1}$ for neutral NO to 2331 cm.$^{-1}$ for $NOMoF_6$ and to 2333 cm.$^{-1}$ for $NOUF_6$ can be explained on the basis of a completely ionized NO^+ group in the solid. This information is in agreement with published data[22-24] that such a shift is consistent with the removal of one electron from the antibonding orbital of the nitric oxide. Removal of such an electron would result in a decreased internuclear distance, which increases the bond strength and, hence, would cause the shift in the direction observed. In addition to the NO^+ absorption band, the only other absorption bands observed for these compounds fall in the range of 615 to 509 cm.$^{-1}$. Broad intense unresolved bands are observed in this region for both $NOMoF_6$ and $NOUF_6$. The absorption at 615 cm.$^{-1}$ in $NOMoF_6$ is associated with the MoF_6^- ion. Peacock and Sharp have assigned the infrared absorption at 623 cm.$^{-1}$ in potassium hexafluoromolybdate(V) to the ν_3 vibration of the MoF_6^- ion.[25] The two absorption maxima at 550 and 509 cm.$^{-1}$ in $NOUF_6$ are attributed to the ν_3 vibration of the UF_6^- ion. These absorption maxima represent a shift to lower wave numbers of 73 and 114 cm.$^{-1}$, respectively, from the intense band of neutral gaseous uranium hexafluoride at 623

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(17) W. R. Angus and A. H. Leckie, *Proc. Roy. Soc.* (London), **A149**, 327 (1935).

(18) H. Gerding and H. Houtgraaf, *Rec. trav. chim.*, **72**, 21 (1953).

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

(20) R. W. Sprague, A. B. Garrett, and H. H. Sisler, *J. Am. Chem. Soc.*, **82**, 1059 (1960).

(21) Microwave energy was obtained with a Model CMD-4 Raytheon microtherm and a 3-in. director. The unit was operated at about 30% of its maximum power output of 125 watts.

(22) J. Lewis, R. J. Irving, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **7**, 32 (1958).

(23) A. F. Wells, "Structural Inorganic Chemistry," Oxford, Clarendon Press, 1950, pp. 468–470.

(24) Y. K. Syrkin and M. E. Dyatkina, "Structure of Molecules," Interscience Publishers, New York, N. Y., 1950, pp. 154–156.

(25) R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

cm.$^{-1}$ (ν_3) according to the assignment of Burke, *et al.*[26]

Further evidence that these solids are ionic compounds is provided by their X-ray diffraction data. Musil, *et al.*,[12] have shown that the solids have pseudo-cubic crystal structures. Although the structures of these compounds have not been fully elucidated due to lack of single crystal X-ray data, it has been clearly demonstrated that the gross geometrical arrangement involves an NO^+ ion in the center of a cube with MF_6^- ions at the corners.

The failure of nitric oxide to react with tungsten hexafluoride to form $NOWF_6$ was unexpected, especially since the pentavalent complex fluorotungstates of sodium and potassium already have been prepared.[27] The potassium salt (KWF_6) has an infrared absorption band at 594 cm.$^{-1}$ attributed to ν_3 vibration of the WF_6^- ion.[25] Also, nitrosyl pentavalent complex fluorides of all of the group V-B elements have been prepared.[5] We have no explanation for the lack of reactivity of tungsten hexafluoride with nitric oxide.

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[26] T. G. Burke, D. F. Smith, and A. H. Nielsen, *J. Chem. Phys.*, **20**, 447 (1952).

[27] G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 4212 (1957).

CONTRIBUTION FROM REACTOR CHEMISTRY DIVISION,
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Phase Equilibria in the System Chromium(II) Fluoride–Chromium(III) Fluoride

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An investigation of the CrF_2–CrF_3 system established the existence of a single chromium(II,III) fluoride covering the solid solution range $CrF_{2.40}$ to $CrF_{2.45}$. There are two invariant points, the eutectic at 831 ± 5° containing 14 mole % CrF_3 and the peritectic at 997 ± 5° containing 29 mole % CrF_3. CrF_3 forms a solid solution containing 10 mole % CrF_2. Melting points of the components CrF_2 and CrF_3, both previously reported to be 1100°, were determined to be 894 ± 6° and 1404 ± 20°, respectively. Because classical procedures yielded mixed products, new methods of synthesizing CrF_2 were sought. Five new procedures are reported: (1) disproportionation of CrF_3 at 1100°, (2) pyrolysis of $(NH_4)_3CrF_6$, (3) reduction of CrF_3 with Cr^0 at 1100°, (4) reduction of $CrCl_3$ with molten SnF_2, and (5) oxidation of Cr^0 with a molten fluoride of a more noble metal, SnF_2, PbF_2, CuF_2, CdF_2, or BiF_3. $(NH_4)_3CrF_6$ for the preparation of CrF_3 and CrF_2 has been synthesized by the reaction of molten NH_4HF_2 with $CrF_3 \cdot 3H_2O$, CrO_3, or $(NH_4)_2Cr_2O_7$. The compound chromium(II,III) fluoride, previously unreported, was encountered when the disproportionation of CrF_3 was incomplete, when CrF_3 was partially reduced by hydrogen, and when CrF_2 was oxidized by HF or SnF_2. The compound forms green, translucent crystals that are biaxial (−) with refractive indices $N_\alpha = 1.518$ and $N_\gamma = 1.534$.

Introduction

Extensive studies at the Oak Ridge National Laboratory[2] of the corrosion of chromium alloy containers by molten fluorides have depended on a source of pure, anhydrous CrF_2. New methods for synthesizing CrF_2 were investigated when the necessary large quantities could not be obtained readily in sufficient purity by the usual procedures. In the course of this investigation, chromium(II,III) fluoride, a compound previously unreported, was encountered and studied. Interest in this compound stimulated a complete study of the CrF_2–CrF_3 system.

Chromium(II) fluoride is known only in the form of the anhydrous salt. It first was reported

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[1] Operated by Union Carbide Corporation for the U. S. Atomic Energy Commission.

[2] (a) Molten-Salt Reactor Program Quarterly Progress Report for Period Ending January 31, 1958, U. S. Atomic Energy Commission ORNL-2474, pp. 104–111; (b) R. B. Evans III, J. H. DeVan, and G. M. Watson, "Self-Diffusion of Chromium in Nickel-Base Alloys," U. S. Atomic Energy Commission ORNL-2982, Jan. 20, 1961.