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Reactivity of Transition Metal Fluorides. I. Higher Fluorides of Chromium, Molybdenum, and Tungsten

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Received December 6, 1965

Study of chemical reactions of higher fluorides of chromium, molybdenum, and tungsten with lower fluorides of some non-metallic elements and with a range of other compounds, mostly nonmetal chlorides, has indicated that the higher fluorides of chromium are very much more reactive than the hexafluorides of molybdenum and tungsten. The surprising feature of the study is that tungsten hexafluoride is relatively inert, differing markedly in its chemical reactivity from molybdenum hexafluoride.

Although much work has been published describing the preparation, purification, and physical characterization of volatile fluorides of transition elements in higher oxidation states, relatively little is known of the chemical reactivity of these compounds. Weinstock's reviews of the work done on transition metal hexafluorides^{1,2} support this generalization.

Previously we have described a series of reactions illustrating the reactivity of molybdenum hexafluoride.³ These reactions were of two types, first those designed to indicate the reactivity of molybdenum hexafluoride as an oxidant in reactions with lower fluorides and, second, halogen-exchange reactions involving replacement of fluorine atoms in molybdenum hexafluoride by chlorine. In marked contrast to previous accounts of its reactivity,⁴ molybdenum hexafluoride proved to be only a mild fluorinating agent, but it reacted readily to replace some or all of its fluorine atoms by chlorine.

Prior to this present study it was believed that molybdenum and tungsten hexafluorides were both vigorous fluorinating agents and nearly identical in their chemical behavior.^{4,5} However, when tungsten hexafluoride was added to a series of compounds similar to those used in the molybdenum hexafluoride study, the tungsten compound was found to be surprisingly inert.

At this point it was decided to study the comparative reactivity of the higher fluorides of subgroup VI elements. Chromium hexafluoride has only fairly recently been prepared⁶ and is thermally unstable even at -100° . By comparison with the thermally stable molybdenum and tungsten hexafluorides it would be extremely reactive chemically. Its properties make it quite unsuitable for a study of reactions at room temperature, and therefore, for this work, it was decided to restrict a study of chemical reactivity of chromium fluorides to the pentafluoride.

(1) B. Weinstock, *Rec. Chem. Progr.*, **23**, 23 (1962).(2) B. Weinstock, *Chem. Eng. News*, **42**, No. 28, 86 (1964).(3) T. A. O'Donnell and D. F. Stewart, *J. Inorg. Nucl. Chem.*, **24**, 309 (1962).

(4) A. B. Burg, "Fluorine Chemistry," J. H. Simons, Ed., Vol. I, pp 112-113.

(5) N. V. Sidgwick, "The Chemical Elements and their Compounds," Oxford University Press, London, 1950, p 1034.

(6) O. Glemser, H. Roesky, and K. H. Hellberg, *Angew. Chem.*, **75**, 346 (1963); *Angew. Chem. Intern. Ed. Engl.*, **2**, 266 (1963).

Recently, uranium hexafluoride has been subjected to a series of reactions similar to those studied for chromium pentafluoride and for molybdenum and tungsten hexafluorides. This work enables a comparison of the reactivity of uranium hexafluoride with the higher fluorides of subgroup VI elements and is described in a subsequent paper.⁷

Experimental Section

Apparatus.—Except for those reactions otherwise referred to specifically below, all reactions were carried out in the apparatus shown in Figure 1. This consists essentially of a manifold constructed from 0.25-in. o.d. nickel tubing to which the various components of the vacuum system are joined by vacuum-tight connections. These are compression fittings based on Teflon glands as shown in the inset in Figure 1. These fittings are similar to commercial Swagelok unions and enable connection to be made between metal, glass, or Kel-F components provided each component is fitted with a connecting tube of 0.25-in. o.d. Metal needle valves V (Hoke A 432) are used and these are fitted with the female portion of a compression vacuum connection as in the inset in Figure 1. Reactions are carried out in molded Kel-F tubes A (6×0.75 in.) as supplied by the Argonne National Laboratory. These tubes are normally used with a metal taper plug B and a metal valve fitted through a Teflon O ring. If pressure buildup through formation of gaseous products is anticipated a nickel bulb can be fitted to the Kel-F tube as shown at C.

Volatile reactants such as molybdenum and tungsten hexafluorides were stored in Kel-F tubes. All components were interchangeable because of the demountable vacuum connections. Therefore traps could be disconnected from the manifold for heating or shaking or they could be replaced by other components. This interchangeability allowed the possibility of carrying out several different reactions on the one vacuum system. The manifold was fitted with a nickel bulb D of known volume. By use of this bulb with the Bourdon gauge E known quantities of volatile reactants could be metered into a reaction tube. For accurate pressure measurements an all-metal bellows manometer F could be used as a null-point instrument to measure pressures to 0.1 mm. Involatile reactants were added to Kel-F reaction tubes in a glove box filled with carefully dried air.

On completion of a reaction an optical cell or a trap could be connected to the manifold through a Teflon gland compression fitting at H and a sample of the volatile products removed for spectral, mass-spectrometric, or other examination. After removal of volatile products and excess reactants, the involatile products were removed from the Kel-F trap in a glove box for analyses.

The reactions of molybdenum hexafluoride and tungsten

(7) T. A. O'Donnell, D. F. Stewart, and P. Wilson, *Inorg. Chem.*, **5**, 1438 (1966).

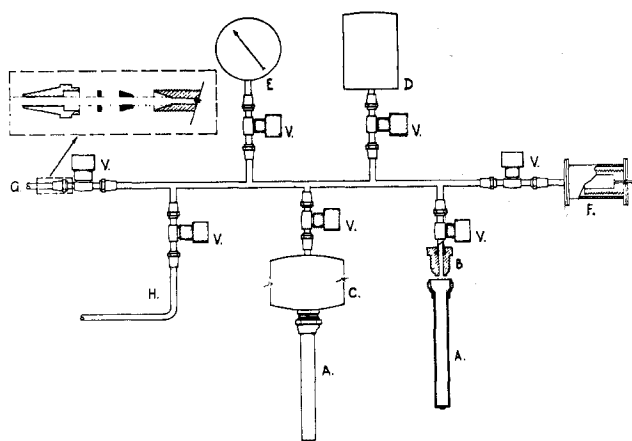


Figure 1.—Apparatus for reactions of volatile fluorides.

hexafluoride with titanium tetrachloride were carried out in glass apparatus to allow separation of the products by fractional sublimation. The products of reaction were separated by sublimation along a horizontal tube with capillary constrictions so that separated samples of the products could be sealed off under vacuum.

Reagents.—Molybdenum hexafluoride and tungsten hexafluoride were prepared by direct fluorination of the metals, as described previously for molybdenum hexafluoride.³ Fluorination of chromium powder produced chromium pentafluoride as described by Edwards,⁸ but modifications were made to the procedure to improve the purity of the product. For fluorination, a 0.5-in. diameter nickel tube fitted with standard cones at the ends and water-cooled for 4 in. of its length at the outlet end was used. The chromium powder, previously heated in hydrogen to 800°, was heated to 300° in fluorine to initiate reaction. Red chromium pentafluoride collected in the water-cooled end of the tube, and after completion of the reaction fluorine was flushed from the tube with dried nitrogen. The nickel tube was then connected to a molded Kel-F trap of the type shown at A in Figure 1. However, in this case the nickel taper plug as shown at B in Figure 1 was replaced by a Kel-F taper plug. The lower part of this Kel-F plug joined the trap through a flare fitting but the upper part of the plug was machined to a B14 socket to accommodate the B14 cone at the end of the nickel reaction tube. The whole system was evacuated, the Kel-F trap was cooled to -196° , and chromium pentafluoride sublimed into the trap.

Phosphorus, arsenic, antimony, and bismuth trifluorides and trichlorides were obtained as described previously.⁸ Carbon, silicon, and titanium tetrachlorides, boron trichloride, phosphorus tribromide, and carbon disulfide were laboratory grade reagents distilled before use.

Analysis.—Fluoride was determined by the null-point potentiometric method,⁹ chloride and bromide potentiometrically with silver nitrate. Gravimetric methods based on 8-hydroxyquinoline were used for molybdenum and tungsten, while titanium was determined spectrophotometrically as the complex formed with hydrogen peroxide. Frequently products, particularly volatile ones, were identified from their infrared or ultraviolet spectra or by physical properties such as melting and boiling points.

Results

Oxidation-Reduction Reactions.—Table I summarizes reactions carried out using the procedures outlined above. Usually the more volatile reactant was condensed onto the less volatile one at -196° . The mixture was allowed to warm to room temperature

TABLE I
PRODUCTS OF OXIDATION-REDUCTION REACTIONS

Reactants	Chromium pentafluoride	Molybdenum hexafluoride	Tungsten hexafluoride
PF ₅	CrF ₅ , PF ₅	MoF ₆ , PF ₅ ^a	WF ₆ , PF ₅ ^b
AsF ₅	CrF ₅ , AsF ₅	No reaction ^a	No reaction ^c
SbF ₅	CrF ₅ , SbF ₅ ^d	No reaction ^a	No reaction ^c
BiF ₃	No reaction	No reaction ^a	No reaction ^c
CS ₂	CrF ₅ , CF ₄ , SF ₆ ^e	MoF ₆ , (CF ₃) ₂ S ₂ , S ^f	No reaction ^g
WF ₄	...	MoF ₆ , WF ₆	...

^a Previously reported in ref 3. ^b Reaction did not occur appreciably, except in the presence of liquid HF and after continuous shaking for several days. ^c No reaction at 20° or when heated to 80°. ^d Reaction very slow except in the presence of liquid HF. ^e After slight warming, violent exothermic reaction with flame. ^f Vigorous reaction. ^g Nonreacting system of miscible liquids.

and was maintained there for a sufficiently long time for reaction to appear to reach completion. Continued monitoring, through measurement of pressure, of spectra of reactants or products or of other properties was used to establish completeness of reaction. Usually the final pressure in the apparatus was less than 1 atm. Generally no attempt was made to establish whether the reactions occurred in the gas phase, between liquids, or were heterogeneous.

Halogen-Exchange Reactions.—Chromium pentafluoride was found to react violently with phosphorus trichloride after slight warming. The products were chromium trichloride, phosphorus trifluoride, and phosphorus pentachloride, which resulted from the reaction of chlorine produced initially with excess phosphorus trichloride. The products of halogen-exchange reactions of molybdenum hexafluoride and tungsten hexafluoride are listed in Table II.

TABLE II
PRODUCTS OF HALOGEN-EXCHANGE REACTIONS

Reactants ^a	Molybdenum hexafluoride	Tungsten hexafluoride
PCl ₃	Mo ₂ Cl ₃ F ₆ , ^b MoF ₅ , PF ₅ ^c (MoCl ₅ , PF ₃ , PCl ₅) ^a	No reaction ^d
AsCl ₃	Mo ₂ Cl ₃ F ₆ , AsF ₅ ^c	No reaction
SbCl ₃	Mo ₂ Cl ₃ F ₆ , SbCl ₂ F ₃ ^c	No reaction
TiCl ₄	Mo ₂ Cl ₃ F ₆ , TiF ₄ (MoCl ₅ , TiF ₄ , Cl ₂) ^a	WCl ₆ , TiClF ₃
CCl ₄	Mo ₂ Cl ₃ F ₆ , CCl ₃ F, CCl ₂ F ₂ , CClF ₃ ^e	No reaction ^f
SiCl ₄	Mo ₂ Cl ₃ F ₆ , SiF ₄ ^e	No reaction ^f
BCl ₃	Mo ₂ Cl ₃ F ₆ , BF ₃ , BClF ₂ , BCl ₂ F (MoCl ₅ , BF ₃ , BClF ₂ , BCl ₂ F) ^a	WCl ₃ F ₃ , BF ₃ (WCl ₆ , BF ₃) ^a
PBr ₃	MoBr ₃ , PF ₃ , PF ₅ , Br ₂	WBr ₅ , PF ₃ ^e

^a Products listed in the main body of this table are for reactions involving excess of the hexafluoride in each case. For cases in which the other reactant is in excess, the products are shown in parentheses. ^b Mo₂Cl₃F₆ is the empirical formula of the compound formulated as (Mo^{IV}Cl₃)(Mo^VF₆)₃ later in this paper. ^c Previously reported in ref 3. ^d Reactants remain as two immiscible liquids not reacting up to 150°. ^e Slow reaction. ^f Liquids are miscible, but do not react up to 120°.

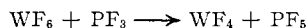
Discussion

Systematics of Reactions.—The reactions of the subgroup VI higher fluorides with trifluorides of group V follow a simple pattern of oxidation of the trifluoride to the corresponding pentafluoride and

(8) A. Edwards, *Proc. Chem. Soc.*, 205 (1963).

(9) T. A. O'Donnell and D. F. Stewart, *Anal. Chem.*, **33**, 337 (1961).

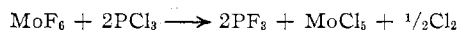
reduction of the higher fluoride to a lower fluoride, *e.g.*



The particular lower fluoride which forms seems to depend on the relative structural stabilities of the lower fluorides. Despite many attempts no pentafluoride of tungsten has been prepared and reduction proceeds to the tetrafluoride. That molybdenum pentafluoride is the preferred product may be due to the fact that its tetrameric structure¹⁰ is particularly stable.

The products of the reaction of molybdenum hexafluoride with carbon disulfide are analogous to those obtained by Fischer and co-workers¹¹ in a similar reaction involving uranium hexafluoride in which they identified $(\text{CF}_3)_2\text{S}_2$ and $(\text{CF}_3)_2\text{S}_3$ as products. Following the work of Haszeldine and Kidd,¹² Fischer suggested that the fluorination of carbon disulfide involves the intermediate formation of trifluoromethylthio radicals $\text{CF}_3\text{S}\cdot$, leading to the formation of compounds such as $(\text{CF}_3)_2\text{S}_2$. It is probable that a similar mechanism is involved in the molybdenum hexafluoride reaction with carbon disulfide. On the other hand, chromium pentafluoride was found to be a far more vigorous fluorinating reagent in its reaction with carbon disulfide, causing rupture of the C-S bonds and complete fluorination of the component atoms.

The initial reaction occurring in all halogen-exchange reactions between chlorides and higher fluorides appeared to be a metathetical one, *e.g.*



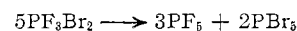
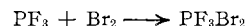
In each case, the highest stable chloride of the particular subgroup VI element was formed, namely, chromium trichloride, molybdenum pentachloride, or tungsten hexachloride.

However, the actual products isolated from reaction mixtures frequently differed from those indicated by the simple metathetical reaction. Secondary reactions occurred in many cases. When excess molybdenum hexafluoride reacted with a chloride, the molybdenum pentachloride produced initially reacted with the excess molybdenum hexafluoride to produce chlorine and a mixed halide of molybdenum of empirical formula $\text{Mo}_2\text{Cl}_3\text{F}_6$. We have previously described the preparation of this compound¹³ by the reaction of molybdenum pentachloride with either molybdenum hexafluoride or anhydrous hydrogen fluoride. Investigations of its conductance and of its magnetic and spectral properties have led us to postulate that this is an ionic compound of mixed oxidation state having the formula $(\text{Mo}^{\text{IV}}_3\text{Cl}_9)(\text{Mo}^{\text{V}}\text{F}_6)_3$.

In the few cases in which reaction occurred between tungsten hexafluoride and a chlorine-containing com-

pound the product was a previously unreported mixed halide, tungsten trichloride trifluoride (WCl_3F_3), which could be sublimed under vacuum with little decomposition. Reaction of tungsten hexafluoride with tungsten hexachloride also produced this mixed halide. Peacock and co-workers¹⁴ have recently isolated tungsten chloride pentafluoride (WCIF_5) after allowing titanium tetrachloride to react with excess tungsten hexafluoride at 5° and distilling the product from a Podbielniak column at -65°. They report that WCIF_5 disproportionates at 25° to tungsten hexafluoride and solid tungsten chloride fluorides. Since our reaction was carried out at room temperature and the volatile products were removed at room temperature, the two observations seem to be consistent with each other.

When phosphorus tribromide reacts with molybdenum hexafluoride and with tungsten hexafluoride, halogen exchange occurs with the formation of the highest stable bromides of molybdenum, MoBr_3 , and tungsten, WBr_5 . In the reaction of molybdenum hexafluoride and phosphorus tribromide, both phosphorus trifluoride and phosphorus pentafluoride were observed in the volatile reaction products. This is consistent with the following series of reactions each of which is known to occur readily¹⁵



In the case of the reaction of phosphorus tribromide with tungsten hexafluoride, the initial metathetical reaction would produce little free bromine and so the subsequent reactions might not be expected to proceed to any great extent. No phosphorus pentafluoride was found in the volatile reaction products in this case.

Relative Reactivities of Higher Fluorides.—There is a marked decrease in chemical reactivity through the series chromium pentafluoride, molybdenum hexafluoride, and tungsten hexafluoride. This generalization holds for both oxidation-reduction and halogen-exchange reactions.

Chromium pentafluoride oxidizes the trifluorides of phosphorus, arsenic, and antimony. However, of these three trifluorides, only phosphorus trifluoride reduces molybdenum and tungsten hexafluorides and the reduction of tungsten hexafluorides occurs extremely slowly, requiring the presence of anhydrous hydrogen fluoride to catalyze the reaction to a reasonable rate.

The reaction between chromium pentafluoride and carbon disulfide involves the rupture of all carbon-sulfur bonds and complete fluorination to carbon tetrafluoride and sulfur hexafluoride, whereas in the molybdenum hexafluoride reaction carbon-sulfur bonds

(10) A. Edwards, R. D. Peacock, and R. W. H. Small, *J. Chem. Soc.*, 4486 (1962).

(11) L. E. Trevorrow, J. Fischer, and W. H. Gunther, *Inorg. Chem.*, **2**, 1281 (1963).

(12) R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3219 (1953).

(13) T. A. O'Donnell and D. F. Stewart, *Nature*, **210**, 838 (1966).

(14) B. Cohen, A. J. Edwards, M. Mercer, and R. D. Peacock, *Chem. Commun.*, 322 (1965).

(15) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, pp 381-382.

are retained in the products. Tungsten hexafluoride does not react with carbon disulfide at all.

Direct evidence that tungsten hexafluoride is more chemically stable than molybdenum hexafluoride was obtained from the reaction between molybdenum hexafluoride and tungsten tetrafluoride to produce tungsten hexafluoride.

Tungsten hexafluoride was found to be relatively inert, showing a marked reluctance to engage in halogen-exchange reactions with covalent chlorides. It reacted only with titanium tetrachloride and boron trichloride, but even then halogen exchange was not always complete; for example, the reaction with titanium tetrachloride produced only a mixed halide of empirical formula $TiClF_3$ and not titanium tetrafluoride. This mixed halide appears identical with that reported by Vorres and Dutton.¹⁶ Tungsten hexafluoride reacted with phosphorus tribromide, but even in this case reaction was quite slow.

Molybdenum hexafluoride reacted very readily with all the chlorine-containing reagents used except carbon and silicon tetrachlorides, where reaction occurred but slowly.

If we consider the violent reaction between chromium pentafluoride and phosphorus trichloride and also the similarity of the reactivity of molybdenum hexafluoride toward a wide range of covalent chlorides including phosphorus trichloride, we would expect ready reaction between chromium pentafluoride and a range of chlorides to produce chromium trichloride (the highest stable chloride of chromium), chlorine, and corresponding fluorides.

Work that we have done with uranium hexafluoride⁷ indicates that it, like molybdenum hexafluoride, is very much more reactive than the corresponding tungsten compound. This generalization is supported by reports of studies of reaction of nitric oxide and nitryl and nitrosyl fluorides with these three hexafluorides.^{17,18} It was found that molybdenum and uranium hexafluorides reacted with nitric oxide to form compounds of the type $NO^+M^VF_6^-$. Tungsten hexafluoride did not react at all with nitric oxide. On the other hand, when nitryl and nitrosyl fluorides were used as reactants all three hexafluorides formed adducts of the type $NOF \cdot M^{VI}F$ and $NO_2F \cdot M^{VI}F$.

(16) K. S. Vorres and F. B. Dutton, *J. Am. Chem. Soc.*, **77**, 2019 (1955).

(17) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 861 (1962).

(18) J. R. Geichman, E. A. Smith, and P. R. Ogle, *ibid.*, **2**, 1012 (1963).

This is particularly significant since no reduction of the hexafluorides was necessary to form these compounds.

Obviously, chromium hexafluoride, which is thermally unstable at room temperature, will be much more chemically reactive than the thermally stable chromium pentafluoride. So we can extrapolate from our observations and say that chromium hexafluoride will be very much more reactive than molybdenum hexafluoride. We have established for the first time a marked difference in the chemical reactivities of molybdenum and tungsten hexafluorides.

The effect of the lanthanide contraction can be used to explain the fact that differences between second and third row transition elements are not as great as between first and second row elements. This effect is greatest in the striking similarity in the chemistry of zirconium and hafnium. Also the pentafluorides of niobium and tantalum have been shown recently to be quite similar in their chemical reactivities.¹⁹ Proceeding to subgroup VI, the differences between molybdenum and tungsten are quite marked.

The available physical evidence indicates that bonding is stronger in tungsten hexafluoride than in molybdenum hexafluoride. Although only a limited amount of thermochemical data is available for the systems we have studied, approximate bond strengths for molybdenum and tungsten hexafluorides can be calculated from known data,^{20,21} and the values for the fluorine to metal bond are 105 and 121 kcal, respectively. Additional evidence for a stronger metal to fluorine bond in tungsten hexafluoride than in the molybdenum compound is provided by the bond-stretching force constants calculated from spectral data,²² the values being 5.13 and 4.73.

It has been suggested² that the volatilities and reactivities of transition metal hexafluorides are related, the least volatile hexafluorides being the most reactive. Our observations on the relative inertness of tungsten hexafluoride support this. The general belief that tungsten hexafluoride is a reactive compound appears to be based largely on one reaction, namely its ready hydrolysis.

(19) J. H. Canterford and T. A. O'Donnell, *ibid.*, **5**, 1442 (1966).

(20) A. Glassner, U. S. Atomic Energy Commission Report ANL-5750.

(21) F. D. Rossini, *et al.*, "Selected Values of Chemical Thermodynamic Properties," U. S. National Bureau of Standards Circular No. 500, Government Printing Office, Washington, D. C., 1952.

(22) H. H. Claassen, *J. Chem. Phys.*, **30**, 968 (1959).