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CHEMICAL REACTIONS OF MOLYBDENUM HEXAFLUORIDE

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Abstract—Previous accounts of the chemical properties of molybdenum hexafluoride are restricted to comments on the ease of hydrolysis of the compound and to a few very simple observations on its reactions with a short series of unrelated substances. This paper describes a systematic study of the chemical reactions of the hexafluoride with the lower fluorides of some elements of Groups V and VI and with Group V trichlorides.

Some new techniques for studying the reactions of volatile fluorides and for fractionation of the products within the reaction system are described.

THE preparation of molybdenum hexafluoride was first reported by RUFF and EISNER,⁽¹⁾ who used platinum apparatus for the reaction. With the limited experimental procedures then available, they were not able to provide any worthwhile account of the chemical reactivity of the hexafluoride, apart from a comment on the ease of hydrolysis and some very simple observations on its apparent reaction with a few unrelated compounds. Some physical properties of the hexafluoride were studied by RUFF and ASCHER⁽²⁾ and very recently CADY and HARGREAVES⁽³⁾ have measured vapour pressures and related properties. Spectroscopic studies, such as those of GAUNT⁽⁴⁾ have been carried out for structure determination. BRADY and co-workers⁽⁵⁾ have provided thermodynamic data for this and other volatile fluorides.

Recent Russian work⁽⁶⁾ provides the most detailed account of the hydrolysis of molybdenum hexafluoride and the formation of oxyfluorides. The ready hydrolysis of the volatile fluorides of the metallic elements accounts for the slow progress in the study of the reactions of these compounds because of the difficulty of handling them in glass apparatus. Etching reactions lead to complete hydrolysis of the compounds. Techniques employing glass vacuum systems based on packless all-metal valves, and in which the glass was carefully dried by evacuation and flaming, were developed specifically for the handling and characterization of molybdenum hexafluoride.⁽⁷⁾

Most of the published work on the higher fluorides of the metallic elements, such as that on the hexafluorides of osmium,⁽⁸⁾ platinum⁽⁹⁾ and the transuranic elements,⁽¹⁰⁾ has been concerned primarily with identification and with physical properties.

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b. O. E. MYERS and A. P. BRADY, *J. Phys. Chem.* **64**, 591 (1960).
(6) N. S. NIKOLAEV and A. A. OPALOVSKII, *Russian J. Inorg. Chem.* (Eng. trans.), **5**, 532 (1959).
(7) T. A. O'DONNELL, *J. Chem. Soc.* 4681 (1956).
(8) B. WEINSTOCK and J. G. MALM, *J. Amer. Chem. Soc.* **80**, 4466 (1958).
(9) B. WEINSTOCK, H. H. CLAASSEN and J. G. MALM, *J. Amer. Chem. Soc.* **79**, 5832 (1957).
(10) B. WEINSTOCK and J. G. MALM, *J. Inorg. Nucl. Chem.* **11**, 104 (1959).

FISCHER and RUDZITIS[11] have shown that bismuth pentafluoride is a very vigorous fluorinating agent converting sulphur and iodine to fluorides rapidly at room temperature. However, there is little published work on the chemical reactions of the higher fluorides to form a basis for discussion of the reactions of molybdenum hexafluoride. This difficulty is illustrated by recent observations[12] that tungsten hexafluoride, which might be expected to be almost identical with the molybdenum compound, differs markedly in its chemical reactivity.

Early observations of the reactions of molybdenum hexafluoride with carbon disulphide and phosphorus pentachloride indicated vigorous reactivity, although it was subsequently shown that iodine dissolved readily without change in molybdenum hexafluoride and that sulphur was also unaffected. It was then decided to study the ability of molybdenum hexafluoride to oxidize the lower fluorides of some non-metals to higher fluorides and surprisingly small reactivity was observed. The present investigation was then completed by a study of the reactions between the hexafluoride and trichlorides of some Group V elements. In these cases reactions occurred which could be related to those of the corresponding trifluorides and to the known chemistry of the halides of the Group V elements concerned.

EXPERIMENTAL

Preparation of reagents

Molybdenum hexafluoride was prepared by direct fluorination of the metal in a copper reactor and collected in a glass trap containing sodium fluoride and cooled to −78° C. It was then purified by distillation in a glass system. Hydrolysis was prevented by using the rigorous precautions previously reported.[7] The sample was stored in a carefully dried glass-trap fitted with a metal valve.

Phosphorus trifluoride was prepared by a method which was essentially that of CHATT and WILLIAMS,[13] phosphorus trichloride being added to an excess of antimony trifluoride. The product was fractionated to remove phosphorus trichloride. Reaction of a stoicheiometric mixture of arsenious oxide and calcium fluoride with excess concentrated sulphuric acid produced arsenious trifluoride. Commercial laboratory reagent grade antimony trifluoride was sublimed at 180° C and 10^{-5} mm pressure. Bismuth trifluoride was prepared by condensing anhydrous hydrogen fluoride on to bismuth hydroxide in a polyethylene container, which was then sealed for 15 hr. Water and excess hydrogen fluoride were removed subsequently by evaporation.

Sulphur tetrafluoride was obtained commercially in a cylinder and purified by shaking with mercury and by fractionation. Direct fluorination of selenium at 0° C using a 1:1 mixture of fluorine and nitrogen[14] resulted in the formation of selenium tetrafluoride.

Phosphorus trichloride was a laboratory reagent grade chemical, purified by re-distillation. The reaction of arsenious oxide and hydrochloric acid was used to prepare arsenic trichloride, which was then distilled.

Antimony trichloride was prepared by direct chlorination of antimony, maintaining an excess of the metal, followed by sublimation.

Apparatus and experimental

The reactions of molybdenum hexafluoride were studied in a glass vacuum system fitted with Hoke valves (No. 432), which were incorporated in the system through copper–glass seals brazed directly to the valves or joined with unions. The glass was carefully dried by evacuation and flaming before the reagents were admitted.

[11] J. FISCHER and E. RUDZITIS, *J. Amer. Chem. Soc.* **81**, 6375 (1959).

[12] C. PALLAGHY. Unpublished observations.

[13] J. CHATT and A. A. WILLIAMS, *J. Chem. Soc.* 3061 (1951).

[14] E. E. AYNSLEY, R. D. PEACOCK and P. L. ROBINSON, *J. Chem. Soc.* 1231 (1952).

For each reaction, a special reaction system was designed to handle the particular reagents and the expected products. A typical system fitted with Hoke valves at *V* is shown in Fig. 1. A bulb of volume appropriate to the quantities of reagents used was connected to a conventional vacuum system at *K* and to it were attached various side-tubes, each connected through a capillary, so that these side-tubes could be removed subsequently by heating the capillary. If both reagents were volatile, the less volatile was first distilled from its source trap. For example, some molybdenum hexafluoride might be distilled from the trap *D* to the side-arm *F* and subsequently exposed to a volatile reactant such as phosphorus trifluoride, contained in a trap *B* of appropriate size and fitted with a break-seal *C*. In the case of a reaction involving an involatile compound, e.g. bismuth trifluoride, the main part of the system was evacuated and flamed and then filled with carefully dried air. The involatile reactant was introduced into *G* from a tube fitted at *J* through a ground joint. The system was then sealed at *H*, evacuated and flamed and some molybdenum hexafluoride distilled from *D* to *G*.

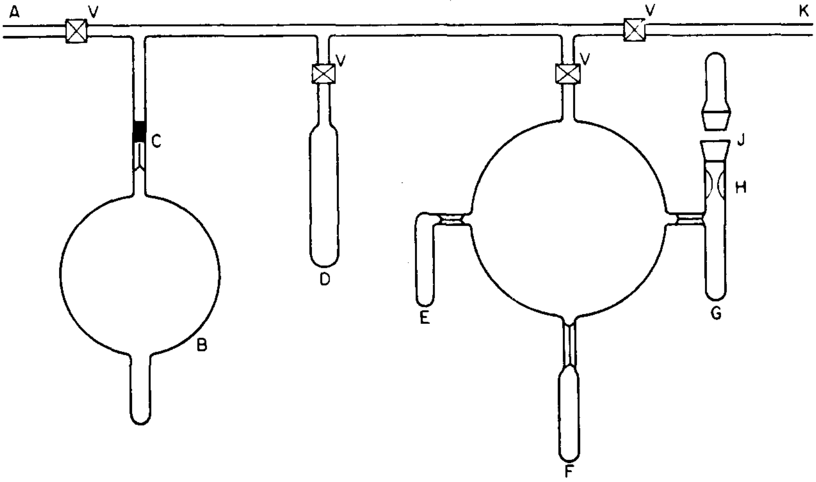

FIG. 1.—System for study of reactions of molybdenum hexafluoride.

When a particular reaction was complete, the main bulk of the involatile products of reaction would be in one side-tube, e.g. *G*. Partial fractionation of the products was then achieved by maintaining *G* at room temperature and cooling *E* or *F* to —183° C. Tube *G*, containing the involatile products of reaction, was then drawn off by sealing the capillary and its contents analysed. By use of suitable coolants, the products of intermediate volatility could be fractionated between the remaining tubes *E* and *F* and isolated in these tubes. The very volatile products remained in the bulb and could be removed at *A* for examination by infra-red spectroscopy or some other procedure.

Analytical methods

Involatile products of reactions were identified usually by chemical analysis. Fluoride was determined by the null-point potentiometric method.(15) Molybdenum was determined gravimetrically with 8-hydroxyquinoline and volumetrically by the method of RAO and SURYANARAYANA.(16) Hydrogen peroxide was used to ensure that molybdenum was present initially as Mo(VI), which was then reduced to Mo(V) with hydrazine sulphate and Mo(V) was titrated against ceric sulphate. Potentiometric titration against silver nitrate was used for chloride because molybdate interferes with Mohr and Volhard methods.

Volatile products were identified by infra-red and ultra-violet spectroscopy and by their physical properties, such as melting and boiling points.

(15) T. A. O'DONNELL and D. F. STEWART, *Analyt. Chem.* **33**, 337 (1961).

(16) G. G. RAO and M. SURYANARAYANA, *Z. Analyt. Chem.* **168**, 177 (1959).

REACTIONS OF MOLYBDENUM HEXAFLUORIDE

Phorphorus trifluoride

The trifluoride was added gradually to a known amount of molybdenum hexafluoride in a vacuum system fitted with Hoke valves. Controlled addition of phosphorus trifluoride was achieved by admitting it to a bulb of known volume, measuring the pressure and condensing this aliquot of the reactant in the side-arm containing the hexafluoride. The reaction was studied under conditions ranging from excess molybdenum hexafluoride to excess phosphorus trifluoride. The only products of reaction were molybdenum pentafluoride and phosphorus pentafluoride which was identified by its infra-red spectrum. With excess molybdenum hexafluoride, molybdenum pentafluoride was present in yellow solution in the hexafluoride, while with excess phosphorus trifluoride the yellow solid, molybdenum pentafluoride, was isolated and identified by chemical analysis and by its melting point, previously reported by PEACOCK.(17)

Arsenious trifluoride

There was no reduction of molybdenum hexafluoride even when the two fluorides were heated to 150°C in a sealed thick-walled glass tube. The two compounds remained as colourless, immiscible liquids.

Antimony trifluoride

The solid trifluoride and liquid hexafluoride did not react at temperatures up to 150°C.

Bismuth trifluoride

No reaction on heating to 80°C.

Sulphur tetrafluoride

There was no evidence of reaction at room temperature.

Selenium tetrafluoride

The two fluorides remained as immiscible colourless liquids on heating in a sealed tube to 150°C. At 200°C, there was extensive glass attack but no colouration indicative of formation of lower molybdenum fluorides.

Phosphorus trichloride

In this case, the reaction appeared to proceed in two steps, the nature of the second step depending on which of the two reactants was in excess. The first step was a metathetical reaction producing phosphorus trifluoride and a mixture of lower molybdenum chlorides and chlorine. Frequently, it appeared that the first molybdenum chloride produced was the black pentachloride, which in a few hours changed to the brown or red tetrachloride or trichloride.

When molybdenum hexafluoride was in excess, the second step in the reaction was reduction of the hexafluoride to molybdenum pentafluoride by the phosphorus trifluoride produced in the first step. Under these conditions, infra-red spectroscopy showed that the volatile products of reaction contained phosphorus pentafluoride, but no phosphorus trifluoride, and chlorine was identified by its ultra-violet spectrum.

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(17) R. D. PEACOCK, *Proc. Chem. Soc.* 59 (1957).

However, when there was excess phosphorus trichloride, only phosphorus trifluoride was found in the volatile products. There was no formation of phosphorus pentafluoride and the chlorine reacted with excess trichloride to form phosphorus pentachloride. Analysis indicated that the involatile reaction products contained phosphorus pentachloride and molybdenum pentachloride. The colour of this residue also indicated the presence of the pentachloride rather than lower chlorides.

Arsenic trichloride

Analysis of the involatile products of reaction indicated the formation of molybdenum trichloride. The volatile products were arsenic trifluoride and chlorine. There was no evidence in the infra-red spectrum of the presence of arsenic pentafluoride.

Antimony trichloride

There was no formation of antimony pentafluoride. The reaction appeared to give lower molybdenum chlorides and chlorine, which then reacted with antimony (III) to produce mixed chlorofluorides of antimony(V). The formation of one such compound was indicated when a white sublimate was isolated with a melting point close to that of SbF_2Cl_3.

DISCUSSION OF REACTIONS

Oxidation of lower fluorides

Molybdenum hexafluoride was shown to be relatively inert as an oxidant. Of the lower fluorides studied, only phosphorus trifluoride was oxidized and there was no evidence of the formation in that reaction of a molybdenum fluoride lower than MoF_5. The reaction $2MoF_6+PF_3 \rightarrow 2MoF_5+PF_5$ provides a more satisfactory method for preparing molybdenum pentafluoride than that previously reported by PEACOCK.(17) The observation that the hexafluoride does not oxidize bismuth trifluoride is in general agreement with the reaction reported by FISCHER and RUDZITIS(11) in which bismuth pentafluoride readily oxidized UF_4 to UF_6.

Nature of molybdenum chlorides formed

The compound $MoCl_6$ is unstable and has never been isolated. In many of these reactions, there was evidence of the initial formation of $MoCl_5$ which usually dissociated within a few hours to lower chlorides, for which the chloride to molybdenum ratio varied for different reactions. The ratio, which appeared to depend on experimental conditions such as the volume of the reaction system and the relative proportions and nature of reagents, ranged from five in the reaction with excess phosphorus trichloride to about three in reactions in which molybdenum hexafluoride was in great excess.

Under the experimental conditions it might be expected that the pentachloride should be formed. However, the formation of lower chlorides can be explained in the light of the recent work of PEARSON and GARNER(18), who have shown that chlorine is released when $MoCl_5$ is dissolved in carbon tetrachloride at room temperature, to produce lower molybdenum chlorides of indefinite stoicheiometry. In the introduction to this present paper it was stated that $MoFCl_5$ is an excellent solvent for iodine,

(18) I. M. PEARSON and C. S. GARNER, *J. Phys. Chem.* **65**, 690 (1961).

resembling CCl_4 in this respect. Also WF_6 and CCl_4 have been shown to mix mutually without reaction.(12) It seems very reasonable then to suggest that MoF_6 acts as an inert solvent for the $MoCl_5$ formed initially and that the pentachloride then dissociates to lower chlorides.

Scheme of reactions with trichlorides

The general reaction with trichlorides was in the first instance a metathetical one:

$$4\ XCl_3+2\ MoF_6 \rightarrow 4\ XF_3+2\ MoCl_5+Cl_2.$$

Subsequent reaction depended on the nature and proportion of the reactants.

Only in the case of the PCl_3 reaction was the trifluoride, formed initially, oxidized to the pentafluoride and then only when MoF_6 was in excess. Also, in excess MoF_6, $MoCl_5$ dissociated to $MoCl_4$ or $MoCl_3$ and chlorine. These reaction steps can be represented as:

$$4\ PCl_3+2\ MoF_6 \rightarrow 4\ PF_3+2\ MoCl_5+Cl_2$$
$$2\ MoCl_5 \rightarrow 2\ MoCl_4\ (\textit{or}\ MoCl_3)+Cl_2$$
$$2\ MoF_6+PF_3 \rightarrow PF_5+2\ MoF_5.$$

The overall reaction could be written:

$$2\ PCl_3+5\ MoF_6 \rightarrow 4\ MoF_5+MoCl_4+2\ PF_5+Cl_2.$$

When PCl_3 was in excess a simpler reaction occurred. No PF_5 was formed and the chlorine formed initially reacted with excess PCl_3 to form PCl_5. In the absence of excess MoF_6, the $MoCl_5$ did not dissociate.

$$4\ PCl_3+2\ MoF_6 \rightarrow 4\ PF_3+2\ MoCl_5+Cl_2$$
$$PCl_3+Cl_2 \rightarrow PCl_5$$

Overall reaction: $5\ PCl_3+2\ MoF_6 \rightarrow 4\ PF_3+2\ MoCl_5+PCl_5$.

As expected from the earlier work on reactions between MoF_6 and the trifluorides, there was no oxidation of the trifluorides first formed in the reaction of MoF_6 with $AsCl_3$ and with $SbCl_3$. In the $AsCl_3$ reaction, chlorine did not react with excess $AsCl_3$, due to the instability of $AsCl_5$, and AsF_3 and Cl_2 were observed as separate volatile products. DESS *et al.*(19) state that reaction occurs between AsF_3 and Cl_2 only in the presence of small amounts of water. KOLDITZ(20) in earlier work, while not commenting on the possible role of water, suggested that $[AsCl_4]^+[AsF_6]^-$ is formed at 0°C in the presence of a large excess of chlorine. It seems reasonable that, at room temperature and reduced pressures and with water rigorously excluded, there should be no interaction between AsF_3 and Cl_2. The overall reaction in the presence of excess MoF_6 can be summarized as:

$$2\ AsCl_3+MoF_6 \rightarrow 2\ AsF_3+MoCl_4\ (\textit{or}\ MoCl_3)+Cl_2.$$

A reaction similar to the above could be written for $SbCl_3$ with the addition of a representative equation:

$$SbF_3+Cl_2 \rightarrow SbF_3Cl_2.$$

The identity of the mixed halides of Sb (V) will depend on the relative proportions of reagents. For example, SbF_3 and chlorine formed in the initial reaction could react with $SbCl_3$ to form SbF_2Cl_3, indicated experimentally as one of the products.

$$SbCl_3+2\ SbF_3+3\ Cl_2 \rightarrow 3\ SbF_2Cl_3.$$

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(19) H. M. DESS, R. W. PARRY and G. L. VIDALE, *J. Amer. Chem. Soc.* **78**, 5730 (1956).

(20) L. KOLDITZ, *Z. Anorg. Chem.* **280**, 313 (1955).