

CONTRIBUTION FROM THE DEPARTMENT OF INORGANIC CHEMISTRY,
UNIVERSITY OF MELBOURNE, VICTORIA, AUSTRALIA**Reactivity of Transition Metal Fluorides. II. Uranium Hexafluoride**

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Reactions have been studied between uranium hexafluoride and a series of lower fluorides of other elements. The study has also included reaction with a wide range of covalent chlorides. The reactivity of uranium hexafluoride is compared with that of the higher fluorides of d-transition elements, chromium, molybdenum, and tungsten, and considered in the light of uranium as an f-transition element.

Considering the technological importance of uranium hexafluoride it is surprising that its chemistry has received so little attention. In this context Katz and Seaborg have commented:¹ "By comparison with the research carried out on its physical properties, much remains to be done on the chemical properties and reactions of uranium hexafluoride."

There are reports of reactions of uranium hexafluoride with substances such as carbon disulfide,² hydrogen sulfide,² carbon tetrachloride,³ nitric oxide,⁴ nitryl and nitrosyl fluorides,⁵ hydrogen halides,⁶ and ammonia.⁷ There is a brief wartime report of reactions with phosphorus trichloride, silicon tetrachloride, and thionyl chloride.⁸ However, there is no simple relationship between these compounds, and it is impossible to use them to systematize the reactivity of uranium hexafluoride.

In earlier studies we have carried out a systematic series of reactions of the higher fluorides of the subgroup VI elements molybdenum,^{9,10} tungsten,¹⁰ and chromium.¹⁰ These reactions were designed to show the ability of the higher transition metal fluorides to oxidize lower fluorides of group V elements or to enter into halogen-exchange reactions with covalent chlorides such as those of groups IV and V. Historically uranium has been considered an element of subgroup VI, but in recent years it has seemed more reasonable to consider it a member of the actinide series. Therefore, it seemed of interest to subject uranium hexafluoride to a series of reactions similar to those used with the higher fluorides of chromium, molybdenum, and tungsten to seek further information on whether uranium acts as a d-type or f-type transition element; that is, what similarities and differences exist between

the chemistry of uranium hexafluoride and that of the higher fluorides of the subgroup VI elements.

Experimental Section

Apparatus.—Most reactions were carried out in a metal vacuum system fitted with Kel-F traps. This has been described previously.¹⁰ The reactions of uranium hexafluoride with boron trichloride, aluminum trichloride, titanium tetrachloride, and antimony trichloride were carried out in glass apparatus so that the products could be separated by fractional sublimation. The reaction of uranium hexachloride and phosphorus trichloride was also carried out in glass.

In addition, the possible reaction of uranium hexafluoride with uranium hexachloride has been studied using nuclear magnetic resonance spectroscopy.

Reagents.—Uranium hexafluoride was prepared by fluorinating the oxide U_3O_8 at 400° in a system similar to that used to prepare molybdenum hexafluoride.⁹ Molybdenum pentafluoride and tungsten tetrafluoride were prepared by reduction of the respective hexafluorides with phosphorus trifluoride.¹⁰ The preparation of all other reagents except boron tribromide, which was prepared directly from the elements, has been previously described.¹⁰

Analysis.—The volatile products were identified by their infrared spectra and the involatile products by chemical analysis. Methods for the determination of fluoride, chloride, bromide, tungsten, molybdenum, and titanium have been described previously.¹⁰ Phosphate was determined potentiometrically with silver nitrate¹¹ after removing uranium with a cation-exchange resin. Aluminum was determined gravimetrically as the 8-hydroxyquinoline complex, and uranium was determined spectrophotometrically as the hydrogen peroxide complex.

Results

With three exceptions, all reactions were carried out by condensing the more volatile onto the less volatile reactant at -196° and allowing the mixture to warm to room temperature and to equilibrate. In the case of reaction with carbon tetrachloride, silicon tetrachloride, and uranium hexachloride, the reaction mixture was then heated to 100° .

Reactions of Uranium Hexafluoride.—Where reaction occurred, the uranium halide formed depended on the ratio of reactants (Tables I and II).

Reactions of Uranium Hexachloride.—It was felt that uranium hexachloride might be an initial product in many of the reactions of Table II. In order to throw light on the reaction schemes involved in the over-all reactions listed there, the following reactions of uranium hexachloride were investigated.

(a) UCl_6 and UF_6 .—Uranium hexafluoride dis-

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(1) J. J. Katz and G. T. Seaborg, "The Chemistry of the Actinide Elements," Methuen and Co. Ltd., London, 1957, p 181.

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

(3) J. S. Nairn, D. A. Collins, and J. C. Taylor, *Proc. U. N. Intern. Conf. Peaceful Uses At. Energy, 2nd, Geneva*, **4**, 191 (1958).

(4) J. R. Geichman, E. A. Smith, S. S. Trond, and P. R. Ogle, *Inorg. Chem.*, **1**, 661 (1962).

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

(6) A. D. Tevebaugh and F. Vaslow, U. S. Patent 2,638,406 (May 12, 1953).

(7) O. Ruff and A. Weizelmann, *Ber.*, **42**, 495 (1909).

(8) V. P. Calkins, U. S. Atomic Energy Commission Report CD-0.350.4 (1945).

(9) T. A. O'Donnell and D. F. Stewart, *J. Inorg. Nucl. Chem.*, **24**, 309 (1962).

(10) T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, **5**, 1434 (1966).

TABLE I
REACTIONS OF UF₆ WITH LOWER FLUORIDES

Reactants	Products (excess reactant)	Products (excess UF ₆)
PF ₃	UF ₄ , PF ₅ ^c	UF ₆ , ^b PF ₅
AsF ₃ ^a	UF ₄	
SbF ₃	No reaction	No reaction
MoF ₆	UF ₄ , MoF ₆	UF ₆ , ^b MoF ₆
WF ₄	UF ₄ , WF ₆	UF ₆ , ^b WF ₆

^a Only slight reaction. ^b Or other intermediate fluorides such as U₂F₈, U₄F₁₇. ^c T. A. O'Donnell, Australian Patent Application 21128/62.

TABLE II
REACTIONS OF UF₆ WITH COVALENT CHLORIDES AND BROMIDES

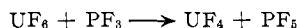
Reactants	Products (excess reactant)	Products (excess UF ₆)
PCl ₃	UCl ₄ (PCl ₃) ₂ , UF ₄ , PF ₃ , PF ₅	UCl ₄ , UF ₄ , PF ₃ , PF ₅
AsCl ₃	UF ₄ , AsF ₃ , Cl ₂	UF ₄ , AsF ₃ , Cl ₂
SbCl ₃	UF ₄ , SbF ₃ , Cl ₂	UF ₄ , SbF ₃ , Cl ₂
TiCl ₄	UCl ₄ , UF ₄ , TiF ₄ , Cl ₂	UF ₄ , TiF ₄ , Cl ₂
CCl ₄	UF ₄ , CCl _{4-y} F _y , Cl ₂	UF ₄ , CCl _{4-y} F _y , Cl ₂
SiCl ₄	UF ₄ , SiF ₄ , Cl ₂	UF ₄ , SiF ₄ , Cl ₂
AlCl ₃	UCl ₄ , AlF ₃	UF ₄ , AlF ₃ , Cl ₂
BCl ₃	UCl ₄ , BF ₃	UF ₄ , BF ₃ , Cl ₂
BBr ₃	UF ₄ , BF ₃ , Br ₂	UF ₄ , BF ₃ , Br ₂
PBr ₅	UF ₄ , PF ₃ , Br ₂	UF ₄ , PF ₃ , Br ₂

solved in trichlorofluoromethane was observed to have a single peak in its nmr spectrum at 720 ppm downfield with respect to trichlorofluoromethane. When uranium hexachloride was added to the solution the peak remained unaltered. After standing for some time uranium tetrafluoride precipitated from solution. Solid uranium hexafluoride was mixed with solid uranium hexachloride and was allowed to react at room temperature and at 100°. In both cases only uranium tetrafluoride was produced.

(b) **UCl₄ and PCl₃.**—Reaction was found to occur readily between uranium hexachloride and phosphorus trichloride to produce a complex chloride of uranium (IV) which analyzed to the formula UCl₄(PCl₃)_x, where *x* varied between 0 and 1.4. The reason why *x* was less than the expected value of 2 is discussed below.

Discussion

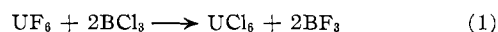
Systematics of Reactions.—The oxidation reactions of uranium hexafluoride studied could be represented by the over-all equation



However, the actual composition of the uranium fluoride formed depended on the ratio of reactants and was apparently a mixture of uranium tetrafluoride and uranium pentafluoride or intermediate fluorides. This could be due to a stepwise reduction of the uranium hexafluoride or to the reaction of uranium tetrafluoride formed initially with excess uranium hexafluoride to form intermediate fluorides. Fischer and co-workers² obtained a similar mixture of uranium tetrafluoride and uranium pentafluoride from the reaction of carbon disulfide with uranium hexafluoride, and it is known that uranium hexafluoride will react

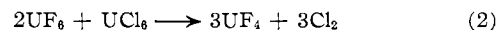
with uranium tetrafluoride to produce intermediate fluorides.¹²

The reaction of uranium hexafluoride with excess boron trichloride, aluminium chloride, and titanium tetrachloride has been found to be a simple metathetical one such as

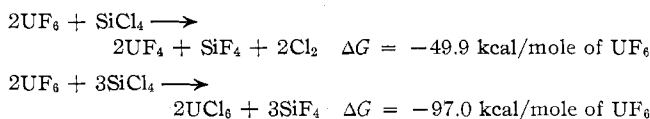


However, the reaction of uranium hexafluoride with phosphorus trichloride is more complex. When the reactants are mixed in stoichiometric amounts, reaction proceeds to produce uranium hexachloride and phosphorus trifluoride in a simple halogen-exchange reaction. However, when phosphorus trichloride is in excess, the final product of reaction is UCl₄(PCl₃)_x, where *x* varies between 0 and 1.4 according to the conditions of preparation. The complex is not very stable and is easily decomposed to uranium tetrachloride by slight heating or by pumping. Allison and Mann¹³ have isolated complexes of the type UCl₄(PR₃)₂, where R is an alkyl radical. Here it is assumed that the product of reaction of uranium hexafluoride with excess phosphorus trichloride is UCl₄(PCl₃)₂ initially. It has been shown that uranium tetrachloride is produced when uranium hexachloride and phosphorus trichloride react. Thus uranium hexafluoride and phosphorus trichloride react to produce uranium hexachloride and this uranium hexachloride can react with excess phosphorus trichloride to produce uranium tetrachloride. The uranium tetrachloride may then form a complex with the phosphorus trichloride. Small amounts of uranium tetrafluoride are always produced during reaction. Since phosphorus pentafluoride has been identified as a reaction product the uranium tetrafluoride must result from the reduction of uranium hexafluoride by phosphorus trifluoride produced in the initial halide-exchange reaction.

As indicated above the reaction of uranium hexafluoride with uranium hexachloride produces uranium tetrafluoride. This can be written



for which $\Delta G_{25^\circ} = -29$ kcal/mole of UF₆.¹⁴ This result is particularly significant as it appears to account for the production of uranium tetrafluoride in the reaction of excess uranium hexafluoride with chlorides such as carbon tetrachloride, silicon tetrachloride, antimony trichloride, or arsenic trichloride where uranium hexachloride may be produced initially. At 25° the two possible reactions of uranium hexafluoride and silicon tetrachloride are



The products isolated from the reaction are silicon

(12) P. A. Agron, A. Grenall, A. Kemin, and S. Weller, U. S. Atomic Energy Commission Report TID-5290, Book 2 (1958), p 652.

(13) J. A. C. Allison and F. G. Mann, *J. Chem. Soc.*, 2915 (1949).

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

tetrafluoride and uranium tetrafluoride. This suggests that the initial reaction is a halide-exchange reaction which produces uranium hexachloride and this immediately reacts with the uranium hexafluoride to produce uranium tetrafluoride.

The final product obtained from reaction of uranium hexafluoride with a chloride depends on the comparative rates of reactions 1 and 2. When the halide-exchange reaction is fast only uranium hexachloride is produced; however, if the halide-exchange reaction is slow uranium hexafluoride is always effectively present in excess and all the uranium halide is ultimately converted to uranium tetrafluoride after passing through an intermediate stage of uranium hexachloride. If the rates of (1) and (2) are comparable, then both uranium hexachloride and uranium tetrafluoride can be isolated as is the case when titanium tetrachloride is the reactant.

Uranium bromides are not produced when uranium hexafluoride is allowed to react with boron tribromide or phosphorus pentabromide. This is consistent with the thermodynamic instability of the uranium bromides. In this case the uranium hexafluoride is reduced directly to uranium tetrafluoride.

Comparative Reactivity of Uranium Hexafluoride.—Comparison of the reactions of uranium hexafluoride listed in Table I with those of the higher fluorides of chromium, molybdenum, and tungsten previously reported¹⁰ shows that uranium hexafluoride is a stronger oxidant than both molybdenum and tungsten hexafluorides but weaker than chromium pentafluoride.

Thus tungsten hexafluoride is reduced only with great difficulty by phosphorus trifluoride whereas molybdenum hexafluoride reacts much more readily with phosphorus trifluoride, although there is some evidence of an equilibrium in the reaction. Neither molybdenum nor tungsten hexafluoride is reduced by arsenic trifluoride. However, uranium hexafluoride reacts readily with phosphorus trifluoride and is reduced to some extent by arsenic trifluoride.

Unequivocal evidence that uranium hexafluoride is a stronger oxidant than molybdenum and tungsten hexafluorides is provided by the fact that uranium hexafluoride readily oxidizes tungsten tetrafluoride and molybdenum pentafluoride to the corresponding hexafluorides.

However, uranium hexafluoride is considerably less reactive than chromium pentafluoride, which oxidizes arsenic trifluoride readily and can oxidize antimony trifluoride also. The reactivities of these higher fluorides are therefore in the order chromium pentafluoride, uranium hexafluoride, molybdenum hexafluoride, and tungsten hexafluoride.

A similar pattern emerges if the halogen-exchange reactions for uranium hexafluoride from Table II are compared with the corresponding ones for the chromium, molybdenum, and tungsten fluorides.¹⁰ Again, uranium hexafluoride is considerably less reactive than chromium pentafluoride but much more reactive than tungsten hexafluoride. However, a

simple comparison with molybdenum hexafluoride is obscured somewhat because of the different reaction pattern for uranium hexafluoride, *i.e.*, in many uranium hexafluoride reactions uranium tetrafluoride is a product whereas in the molybdenum reactions lower chlorides are formed.

Although the implications were not considered, a published study⁴ supports our systematization of the reactivities of the hexafluorides. Nitrous oxide was found to react readily in the temperature range 25–60° with molybdenum and uranium hexafluorides to produce compounds of the type $\text{NO}^+\text{M}^{\text{VI}}\text{F}_6^-$. However there was no reaction with tungsten hexafluoride. That this reflects the ease of reduction of $\text{M}^{\text{VI}} \rightarrow \text{M}^{\text{V}}$ was shown by the subsequent observations⁵ that all three hexafluorides form simple adducts of the type $\text{NOF}\cdot\text{M}^{\text{VI}}\text{F}_6$ and $\text{NO}_2\text{F}\cdot\text{M}^{\text{VI}}\text{F}_6$ with nitrosyl and nitryl fluorides. Nitrosyl chloride differs from nitrosyl fluoride in its reaction with the three hexafluorides but again the reaction pattern fits our systematics perfectly.

Trevorrow, Fischer, and Gunther² investigated the reaction of uranium hexafluoride with carbon disulfide and found the principal products of reaction at 25° to be uranium tetrafluoride, sulfur tetrafluoride, bistrifluoromethyl disulfide, and bistrifluoromethyl trisulfide. At higher temperatures reaction is more vigorous and sulfur hexafluoride and tetrafluoromethane are also produced. Fischer and co-workers comment that the room temperature reaction of uranium hexafluoride and carbon disulfide results, in the main, in the cleavage of only one carbon to sulfur bond but that the more reactive plutonium hexafluoride reacts to produce cleavage of both carbon to sulfur bonds to give tetrafluoromethane.

In another study¹⁰ we have observed that chromium pentafluoride fluorinates carbon disulfide right through to carbon tetrafluoride and sulfur hexafluoride, molybdenum hexafluoride produces bistrifluoromethyl sulfides but no sulfur tetrafluoride, and tungsten hexafluoride does not react with carbon disulfide at all. Again the following order of reactivity is established, $\text{CrF}_5 > \text{UF}_6 > \text{MoF}_6 > \text{WF}_6$.

The chemical evidence collected here for greater reactivity of the metal to fluorine bonds in uranium hexafluoride by comparison with those in molybdenum and tungsten hexafluorides is supported by physical evidence from spectral data. Claassen¹⁵ has calculated the bond-stretching force constants as 3.78, 4.73, and 5.13 for uranium, molybdenum, and tungsten hexafluorides, respectively. There is also a significant decrease in bond length along this series.

If uranium is considered in its historical position as a member of the subgroup with chromium, molybdenum, and tungsten, that is, implicitly, as a d-transition element, its reactivity is anomalous. We have established a marked decrease in reactivity of higher fluorides with increase in atomic number of the transition element in passing from chromium to molybdenum

to tungsten. However, uranium hexafluoride is somewhat more reactive than the molybdenum compound and markedly more so than tungsten hexafluoride. This would appear to be consistent with the more recent classification of uranium as an f-transition element, an actinide.

Katz and Seaborg¹⁶ and more recently Cunningham¹⁷ have surveyed the physical evidence for uranium as an f-transition element. Cunningham quotes a ground-state configuration for the neutral gaseous uranium atom of $5f^36d7s^2$ based on the atomic beam resonance method. He cites bulk magnetic susceptibility measurements in aqueous solution in assigning a configuration of $5f^3$ to the U^{3+} ion.

An interesting case can be made from chemical evidence for uranium as an actinide element by considering fluorides. The only stable fluorides of actinium and thorium are AcF_3 and ThF_4 . PaF_5 is by far the most stable fluoride of protactinium, although PaF_4 can be made relatively easily. Uranium has the stable UF_6 but intermediate fluorides UF_5 , U_2F_9 , and U_4F_{17} occur between it and the very stable UF_4 . UF_3 , while not stable in aqueous medium, has reasonable thermal and chemical stability. If neptunium were a d-transition element a heptafluoride NpF_7 , following rhenium heptafluoride, would be expected to be quite stable. In fact the stability of the hexafluorides decreases markedly through the elements uranium, neptunium, and plutonium. The thermal instability of plutonium hexafluoride is such as to have allowed a study of the kinetics of thermal decomposition in the temperature range 140–173°.¹⁸ In addition, Weinstock and Malm¹⁹ have shown that although UF_6 is produced by the action of BrF_3 , PuF_6 readily oxidizes BrF_3 to BrF_5 , itself being reduced to PuF_4 . NpF_6 acts similarly but less readily. A striking demonstration of the relative stabilities of uranium and plutonium hexafluorides is that plutonium hexafluoride oxidizes uranium tetrafluoride, being itself reduced to plutonium tetrafluoride.¹⁹

Stability of higher fluorides decreases continuously along the series. No americium hexafluoride has been

produced and, as in the lanthanides, an oxidation state of 3 is established as the stable one from curium onward.

We see in this series typical d-transition element fluorides in actinium, thorium, and perhaps protactinium. However, at uranium and certainly as we proceed through curium we see the development of f-transition element character. It has been suggested¹⁶ that from element 89 through to element 91 or 92 binding energies are lower for 6d than for 5f electrons, but that at about that point a crossover occurs and 5f electrons have the lower binding energies.

It would seem that 5f electrons in uranium, with comparatively low binding energies, are available for bonding. Several authors^{20,21} have considered that f orbitals participate in metal-oxygen bonding in the uranyl ion, UO_2^{2+} . It has been shown that hybrid orbitals employing f orbitals would show a favorable degree of overlap,²² and Coulson and Lester²³ have shown that f-orbital involvement in bonding in uranium(VI) compounds would be energetically favorable. Thus the bonds in uranium hexafluoride could well use the hybrid d^2sf^3 . While it is likely that this structure makes some contribution to the bonding, the situation is obviously very complex and it may well be, as Coulson and Lester state, that: "in heavy atoms where there are many electrons in the same valency shell, or at comparable distances from the nucleus, the simple language which has been devised to account for bonding between light atoms is no longer applicable. There is—so it would appear—no uniquely compelling description, but rather there are several alternative descriptions which could be employed."

Whatever the final situation on the bonding in uranium hexafluoride, it seems from our work and from work such as that outlined above that the bonding is different from that in the hexafluorides of the typical d elements, molybdenum and tungsten, where it is always assumed that d^2sp^3 hybridization occurs.

Acknowledgment.—We wish to acknowledge gratefully that part of this work was carried out with support from a research contract from the Australian Atomic Energy Commission.

(16) Reference 1, pp 463–470.

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