

TABLE II
 FORCE CONSTANTS OF SeF₆ AND WF₆ (MDYNES/Å)

Species	Force constant	SeF ₆		WF ₆	
		General force field	Urey-Bradley force field ^a	General force field	Urey-Bradley force field ^a
A _{1g}	$F_{11} = f_r + 4f_{rr} + f_{rr}'$	5.64	5.64	6.62	6.59
E _g	$F_{22} = f_r - 2f_{rr} + f_{rr}'$	4.90	4.91	5.02	5.04
F _{1u}	$F_{33} = f_r - f_{rr}'$	4.88 ± 0.10	4.41	4.68 ± 0.08	4.90
	$F_{34} = -2(f_{r\alpha} - f_{r\alpha}'')$	-0.44 ± 0.03	-0.20	-0.03 ± 0.04	-0.42
F _{2g}	$F_{44} = f_{\alpha} + 2f_{\alpha\alpha} - 2f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$	0.64 ± 0.01	0.63	0.28 ± 0.01	0.28
	$F_{55} = f_{\alpha} + f_{\alpha\alpha}''' - 2f_{\alpha\alpha}'$	0.46	0.49	0.29	0.28
F _{2u}	$F_{66} = f_{\alpha} - 2f_{\alpha\alpha} + 2f_{\alpha\alpha}'' - f_{\alpha\alpha}'''$	0.38	0.35	0.26	0.28

^a Data from J. Haraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).

 TABLE III
 ISOTOPIC SPLITTINGS OF THE FUNDAMENTALS OF SeF₆

Species	Abundance, %	ν ₃		ν ₄ calcd shift, cm ⁻¹
		Calcd shift, cm ⁻¹	Obsd shift, cm ⁻¹	
⁸² SeF ₆	8.84	-3.0	-2.5	-1.4
⁸⁰ SeF ₆	49.96	0	0	0
⁷⁸ SeF ₆	23.61	3.2	3.5	1.5
⁷⁷ SeF ₆	7.50	4.8		2.3
			} 6.0	
⁷⁸ SeF ₆	9.12	6.5		3.1
⁷⁴ SeF ₆	0.96	10.0	...	4.6

fields. A comparison is given in Table II between the general force fields which were determined in this work and the modified Urey-Bradley force fields for SeF₆ and WF₆ which were determined by Hiraishi, *et al.*,¹⁵ and more recently by Thakur and Rai.¹⁶ This modified force field, which adds angle and bond interaction constants to the simple Urey-Bradley field, yields

(15) J. Haraishi, I. Nakagawa, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 819 (1964).

(16) S. N. Thakur and D. K. Rai, *J. Mol. Spectry.*, **19**, 341 (1966).

reasonable values for the principal force constants for the molecules studied but differs significantly in the interaction force constants F_{34} . Since the Coriolis ζ constants are quite sensitive to values of F_{34} , the modified Urey-Bradley force field is inconsistent with these coupling parameters.

The trends in the F_{1u} force constants for SF₆, SeF₆, and TeF₆ are the same as for the degenerate species of the group IV tetrafluorides and group V trifluorides. The interaction force constant for all three groups has a large negative value which decreases as the mass of the central or unique atom increases. Since WF₆ is the only group VIa hexafluoride for which an unambiguous value of the interaction force constant has been determined, it would be premature to discuss its possible physical significance.

Acknowledgments.—We wish to express our appreciation to Dr. P. A. G. O'Hare, of the Argonne National Laboratory, who kindly synthesized an extremely pure sample of SeF₆ for this study. S. A. wishes to acknowledge the support of the Air Force Office of Scientific Research, U. S. Department of Defense.

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Reactivity of Transition Metal Fluorides. IV. Oxidation-Reduction Reactions of Vanadium Pentafluoride

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Earlier studies on the comparative reactivities of vanadium, niobium, and tantalum pentafluorides indicated that vanadium pentafluoride was a powerful oxidant. This has been supported by more detailed investigation. Many of the reactions of the pentafluoride with lower fluorides are more complicated than those of corresponding higher fluorides of transition elements, and there is evidence that in these reactions complex formation leads to the production of a fluorovanadium(IV) cation.

Introduction

In the third paper in this series¹ a brief account was given of the reactivity of vanadium pentafluoride. It was shown to be a powerful fluorinating and oxidizing

(1) J. H. Canterford and T. A. O'Donnell, *Inorg. Chem.*, **5**, 1442 (1966).

agent. Also, the marked reactivity of vanadium pentafluoride was found to be consistent with its physical properties and its position in the periodic table. Vanadium pentafluoride was found to undergo a number of oxidation-reduction reactions with suitable reagents.

With certain of these reagents, namely, the trifluorides of phosphorus, arsenic and antimony, there was evidence that the initial oxidation-reduction reaction was followed by a second reaction which involved some type of complex formation. Only the preliminary observations of these reactions were reported.

Further work on these and several other reactions has been completed and we can now report all the results obtained in detail.

Experimental Section

Apparatus.—All but the four reactions outlined below were carried out using the vacuum system and the techniques already described.² The reactions between vanadium pentafluoride and chlorine, bromine, and bismuth trifluoride were carried out in sealed, thick-walled Pyrex tubes. The room-temperature reaction between vanadium pentafluoride and phosphorus trifluoride was carried out in two carefully flamed-out Pyrex bulbs connected by means of a break-seal. Vanadium pentafluoride was distilled into one bulb and phosphorus trifluoride into the other. When the whole system had come to room temperature, the seal was broken with a nickel ball. Violent reaction took place as the phosphorus trifluoride rapidly diffused through the broken seal.

In all of the reactions studied, a large excess of the second reactant was used. This was essential with the reactions carried out in Kel-F apparatus since vanadium pentafluoride has been shown to attack Kel-F.^{1,3}

Reagents.—Arsenic pentafluoride was prepared by the direct fluorination of the powdered element using standard techniques. Commercial cylinder chlorine was dried by means of a sulfuric acid bubbling train. Reagent grade bromine and iodine were purified by vacuum distillation and vacuum sublimation, respectively. Reduction of the appropriate hexafluoride with phosphorus trifluoride was used to prepare molybdenum pentafluoride² and uranium tetrafluoride.⁴ The action of excess anhydrous hydrogen fluoride on vanadium tetrachloride dissolved in trichlorofluoromethane resulted in the formation of vanadium tetrafluoride.⁵ All other reagents were obtained as previously described.¹

Identification of Reaction Products.—Volatile reaction products were identified by means of their infrared and mass spectra, but nonvolatile residues were identified by standard methods of qualitative and quantitative analysis. Fluoride was determined as lead chlorofluoride after separation by Willard-Winter distillation. Reduction with sulfur dioxide followed by oxidation with standard permanganate was used to determine vanadium. Chloride was determined by potentiometric titration against silver nitrate. Hexafluoroarsenate(V), hexafluorophosphate(V), and hydroxopentafluoroantimonate(V) were precipitated as the nitron salts. These salts were identified by means of their melting points, X-ray diffraction patterns, and infrared spectra. The last method of identification was found to be the most useful. Comparison of, for example, the spectra of nitron, potassium hexafluorophosphate(V), and the nitron salts obtained from both potassium hexafluorophosphate(V) and the involatile residue from the vanadium pentafluoride-phosphorus trifluoride reaction (see below) showed clearly that the nitron salts contained the hexafluorophosphate(V) anion. The significance of the presence of this anion in the residue will be discussed later.

Results and Discussion

Table I summarizes the oxidation-reduction reactions of vanadium pentafluoride that have been carried

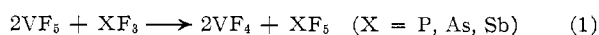
out. Vanadium pentafluoride was distilled onto excess reactant at -196° and the system was allowed to warm to room temperature. To obtain a reaction as complete as possible with the trifluorides of phosphorus, arsenic, and antimony, it was found necessary to cool the reaction tube repeatedly with liquid nitrogen and then rapidly warm it to room temperature. This continuous process will be referred to as thermal cycling. The thermal treatment for each reaction is indicated in the footnote to Table I. Completeness of reaction was checked by following color, pressure, and spectral changes of reactants or products.

TABLE I
OXIDATION-REDUCTION REACTIONS OF
VANADIUM PENTAFLUORIDE

Reactant (excess)	Reaction products	Reactant (excess)	Reaction products
PF ₃	VF ₄ , PF ₅ ^a	SF ₄	No reaction ^e
	VF ₃ +PF ₆ ⁻ , ^b VF ₄ , PF ₅ ^c	CS ₂	VF ₃ , (CF ₃) ₂ S ₂ , (CF ₃) ₂ S ₃ , SF ₄ ^e
	VF ₃ , VF ₄ , PF ₅ ^d		
AsF ₃	VF ₄ , VF ₃ +AsF ₆ ⁻ ^{a,b}	Cl ₂	No reaction ^f
SbF ₃	VF ₄ , VF ₃ +SbF ₆ ⁻ ^{a,b}	Br ₂	No reaction ^f
BiF ₃	No reaction ^e	I ₂	VF ₄ , IF ₅ ^g
S	VF ₄ , SF ₄ ^a	MoF ₅	VF ₄ , MoF ₆ ^g
S ₂ F ₂	VF ₄ , SF ₄ ^e	UF ₄	VF ₄ , UF ₆ ^g

^a The reaction vessel was allowed to warm to room temperature, during which time the reaction had gone to completion. ^b The nature of the VF₃+XF₆⁻ complex is described below. ^c The reaction vessel was subjected to repeated thermal cycling. ^d The reactants were mixed at room temperature. ^e Reported in ref 1. ^f Heated to 125° for 2 days. ^g Reaction proceeds quite rapidly on heating to ca. 60°.

With the trifluorides of phosphorus, arsenic, and antimony the initial reaction appears to be simple oxidation-reduction of the type



When the reaction with phosphorus trifluoride is carried out at room temperature, there is evidence for some formation of vanadium trifluoride. This may be produced by the direct reduction of the pentafluoride or by the thermal decomposition of the vanadium tetrafluoride⁵ initially produced. This latter mechanism is probably the more likely since the amount of trifluoride was considerably less than that of the tetrafluoride and a large amount of heat was produced during the reaction. If direct reduction was favored, then a large amount of vanadium trifluoride would be expected since the phosphorus trifluoride was in great excess.

If the reaction between vanadium pentafluoride and phosphorus trifluoride was subjected to thermal cycling, there was a drop in the total pressure of the system. The hexafluorophosphate(V) anion was identified when the involatile residue remaining after completion of the reaction was hydrolyzed. Weight change measurements indicated that the amount of phosphorus pentafluoride uptake varied considerably; the maximum value obtained was 0.38 mole of phosphorus pentafluoride/mole of vanadium tetrafluoride calculated on

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

(3) L. E. Trevorrow, J. Fischer, and R. K. Steunenber, *J. Am. Chem. Soc.*, **79**, 5168 (1957).

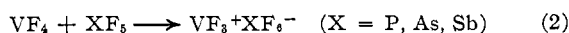
(4) T. A. O'Donnell, D. F. Stewart, and P. W. Wilson, *Inorg. Chem.*, **5**, 1438 (1966).

(5) R. G. Cavell and H. C. Clarke, *J. Chem. Soc.*, 2692 (1962).

the basis of reaction 1. It was also found that prolonged pumping on the samples caused loss of phosphorus pentafluoride. If the reaction tubes were heated to about 50° during pumping, all of the phosphorus pentafluoride was removed and vanadium tetrafluoride remained. Heating caused some decomposition of the vanadium tetrafluoride.

When arsenic and antimony pentafluorides were produced as the initial oxidation products complex formation of the same type occurred. The hexafluoroarsenate(V) and the hydroxopentafluoroantimonate(V) anions⁶ were identified in the hydrolyzed residues. Both products were stable to pumping and heating to about 50°.

The simplest type of complex which involves the formation of the group V hexafluoro anion would be



The stability of such a complex would depend on the Lewis acidity of the group V pentafluoride and the observed stabilities are consistent with the experimentally observed strengths of the group V pentafluorides.⁷

Attempts were made to gain more information about these complexes by preparing them directly from vanadium tetrafluoride and the corresponding group V pentafluoride.

All three complexes were prepared in this way. However, all subsequent experimental work was confined to the complex formed between vanadium tetrafluoride and arsenic pentafluoride. The reason for this choice was that the complex can be easily prepared, since arsenic pentafluoride is quite volatile and is also a powerful Lewis acid.⁷ The most stable complex formed was that with antimony pentafluoride, but, because of the physical properties of antimony pentafluoride, the complex was difficult to prepare in a reasonably pure form. To remove the last traces of uncomplexed antimony pentafluoride it was necessary to heat the reaction vessel to about 150°. This process led to partial decomposition of the complex. Decomposition was probably due to the thermal instability of the vanadium tetrafluoride.⁵

Pressure and weight change measurements indicated that the rate of uptake of the arsenic pentafluoride on thermal cycling decreased as the number of cycles increased. They also showed that the uptake depended very greatly on the absolute amount of vanadium tetrafluoride used. The decrease in the uptake of arsenic pentafluoride per mole of vanadium tetrafluoride as the weight of vanadium tetrafluoride increased is most likely due to the formation of a surface coating of the complex which inhibits further complex formation. For one sample of approximately 80 mg of vanadium tetrafluoride, a maximum of 0.94 mole of arsenic pentafluoride/mole of vanadium tetrafluoride reacted. This is the evidence that is adduced for the 1:1 complex proposed in reaction 2.

The presence of the hexafluoro anions and the lack of phosphate, arsenate, and antimonate in the aqueous solutions of the involatile residues certainly suggests that the complexes are in fact ionic, since the hexafluoro anions cannot be formed directly from the corresponding pentafluoride dissolved in aqueous solutions containing fluoride. Also the hexafluoroarsenate(V) and hexafluorophosphate(V) anions are very stable in water and are only destroyed by distillation with strong mineral acids.^{8,9} The hexafluoroantimonate(V) anion is unstable in aqueous solutions, immediately forming the hydroxopentafluoro species, which, in turn, but much more slowly, forms the dihydroxotetrafluoroantimonate(V) anion.¹⁰ Under the experimental conditions used, only the monohydroxy species was formed. There are insufficient data available to allow one to say whether this species can be formed from aqueous solutions containing antimony(V) and fluoride under conditions similar to those obtained in the present work. The formation of the hydroxopentafluoro species is most likely to be due to the hydrolysis of the hexafluoroantimonate(V) anion.

Further evidence for the ionic character of the complex was obtained from the identification of the hexafluoroarsenate(V) anion when the complex formed between vanadium tetrafluoride and arsenic pentafluoride was dissolved in acetonitrile. A nitron precipitate was obtained and characterized while an infrared spectrum run on the acetonitrile solution contained the single broad peak at 702 cm⁻¹ characteristic of the hexafluoroarsenate(V) anion.¹¹ No unambiguous information could be obtained about the infrared spectrum of the VF₃⁺ cation because the complex reacted with the solvent, and conductivity measurements were meaningless.

There is only one previous account in the literature of the formation of an adduct between a transition metal or actinide fluoride and a group V pentafluoride. This complex was reported as UF₄·SbF₅.¹² However, more recent work¹³ has shown that no complex is formed. The uptake of the antimony pentafluoride has been shown to be due to physical adsorption.

Although there are a large number of stable and well-characterized nonmetallic fluoro cations known, for example, SF₃⁺¹⁴ and BrF₂⁺,¹⁵ only one or two are known for the transition metals. The best established transition metal fluoro cation is probably [Nb₆F₁₂]³⁺ which Schafer, *et al.*,¹⁶ have shown to exist in the compound called diniobium pentafluoride. On the other hand, there are a reasonably large number of

(8) H. M. Dess and R. W. Parry, *J. Am. Chem. Soc.*, **79**, 1589 (1957).

(9) A. G. Sharpe, "Fluorine Chemistry," Vol. II, J. H. Simons, Ed., Academic Press Inc., New York, N. Y., 1954, p 18.

(10) A. Mazeika and H. M. Neumann, *Inorg. Chem.*, **5**, 309 (1966).

(11) D. W. A. Sharp and A. G. Sharpe, *J. Chem. Soc.*, 1855 (1956).

(12) J. J. Katz and E. Rabinowitch, "The Chemistry of Uranium, Part I," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, p 375.

(13) P. W. Wilson, unpublished observations.

(14) F. Seel and O. Detmer, *Z. Anorg. Allgem. Chem.*, **301**, 113 (1959).

(15) A. A. Woolf and H. J. Emelús, *J. Chem. Soc.*, 2865 (1949).

(16) H. Schafer, H. G. Schnering, K. J. Niehues, and H. G. Nieder-Vahrenholz, *J. Less-Common Metals*, **9**, 95 (1965).

(6) L. Kolditz and D. Sarrach, *Z. Anorg. Allgem. Chem.*, **293**, 132 (1957).

(7) A. F. Cliford, H. C. Beachell, and W. M. Jack, *J. Inorg. Nucl. Chem.*, **5**, 57 (1957).

transition metal chloro and bromo cations^{17,18} which are quite stable. In all cases, these cations are polymeric and it would be reasonable to suggest that the fluorovanadium(IV) cation is polymeric, with a structure probably based on the vanadium trifluoride structure. The cation would achieve some degree of stability through polymerization. Even so, the fluorovanadium(IV) cation is not particularly stable, as shown by its formation only with the strongest fluoride ion acceptors.

The reaction between vanadium pentafluoride and carbon disulfide appears to follow a similar path to the reactions of the latter with either molybdenum² or uranium¹⁹ hexafluorides; that is, the reaction probably involves the intermediate formation of the trifluoromethylthio radical.²⁰

Comparison of the relative fluorinating strength of vanadium pentafluoride with other fluorinating agents that have been treated with carbon disulfide^{2,19} is

(17) R. Colton and R. L. Martin, *Nature*, **207**, 141 (1965).

(18) H. Schafer and H. G. Schnering, *Angew. Chem.*, **76**, 833 (1964).

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

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

difficult since in the majority of the reactions experimental conditions, particularly temperature, are not the same.

The reactions of vanadium pentafluoride with sulfur, sulfur monofluoride, iodine, molybdenum pentafluoride, and uranium tetrafluoride are all quite simple, resulting in vanadium tetrafluoride and the corresponding higher fluorides.

It has been previously shown that both molybdenum² and uranium⁴ hexafluorides undergo a number of oxidation-reduction reactions. These reactions readily show that uranium hexafluoride is more easily reduced than molybdenum hexafluoride. The reactions of vanadium pentafluoride with molybdenum pentafluoride and uranium tetrafluoride to form vanadium tetrafluoride and the corresponding hexafluoride thus show that vanadium pentafluoride is a more powerful oxidant than both hexafluorides.

The reactions described above have been found to be most useful in determining relative reactivities and formed part of the basis of the order of reactivities that we previously put forward,¹ that is, $\text{VF}_5 > \text{UF}_6 > \text{MoF}_6 > \text{WF}_6 > \text{NbF}_5 = \text{TaF}_5$, with respect to oxidizing strength.

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Alkali Fluoride Complexes of Tetravalent Protactinium¹

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Complex fluorides containing tetravalent protactinium and the alkali fluorides (Li, Na, K, Rb) were prepared from $\text{MF} + \text{PaF}_4$ starting mixtures and by hydrogen reduction of $\text{MF} + \text{PaF}_5$ compounds at 400–450°. $\text{LiF} \cdot \text{PaF}_4$ is tetragonal: $a = 14.96$, $c = 6.58$ Å. The three rhombohedral compounds, $7\text{MF} \cdot 6\text{PaF}_4$ ($M = \text{Na, K, and Rb}$), are isostructural and have the cell dimensions: $a = 9.16$ Å, $\alpha = 107^\circ 54'$; $a = 9.44$ Å, $\alpha = 107^\circ 09'$; and $a = 9.64$ Å, $\alpha = 107^\circ 0'$, respectively. Monoclinic $4\text{NH}_4\text{F} \cdot \text{PaF}_4$ was formed by direct reaction between NH_4F and PaF_4 at temperatures of 25–90°; cell dimensions are $a = 13.18$, $b = 6.71$, $c = 13.22$ Å; $\beta = 117^\circ 10'$. PaF_4 is monoclinic with cell dimensions: $a = 12.86$, $b = 10.88$, $c = 8.54$ Å; $\beta = 126^\circ 21'$. These protactinium(IV) fluoride compounds are isostructural with their uranium analogs. The absorption spectra of Pa(IV) in $\text{ND}_4\text{F} - \text{D}_2\text{O}$ solution and in various solid fluorides are presented. For $7\text{RbF} \cdot 6\text{PaF}_4$, $3\text{NaF} \cdot \text{PaF}_4$, and PaF_4 , an intense infrared absorption band is observed at ~ 5485 cm^{-1} , giving a value of $\zeta_{\text{eff}} = 1567$ cm^{-1} for Pa(IV) .

Although a number of complex fluorides containing other tetravalent actinides are known,^{2–7} no such com-

(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) L. B. Asprey and R. A. Penneman, *Inorg. Chem.*, **1**, 134 (1962); F. H. Kruse and L. B. Asprey, *ibid.*, **1**, 137 (1962); T. K. Keenan, *Inorg. Nucl. Chem. Letters*, **2**, 155, 212 (1966).

(3) R. Benz, R. M. Douglass, F. H. Kruse, and R. A. Penneman, *Inorg. Chem.*, **2**, 799 (1963); R. A. Penneman, F. H. Kruse, R. S. George, and J. S. Coleman, *ibid.*, **3**, 309 (1964).

(4) G. D. Brunton, H. Inasley, T. N. McVay, and R. E. Thoma, ORNL-3761, Feb 1965; C. J. Barton, *et al.*, ORNL-2548, Nov 1959; R. E. Thoma, *et al.*, *J. Am. Ceram. Soc.*, **41**, 63 (1958); *ibid.*, **41**, 538 (1958); *ibid.*, **46**, 37 (1963); R. E. Thoma, *Inorg. Chem.*, **1**, 220 (1962).

(5) G. D. Brunton, ORNL-3913, Annual Report of Reactor Chemistry Division, Dec 1965, p 10; *Acta Cryst.*, **21**, 814 (1966).

(6) J. H. Burns, R. D. Ellison, and H. A. Levy, ORNL-3913, Annual Report of Reactor Chemistry Division, 1965, p 17.

(7) W. H. Zachariasen, *J. Am. Chem. Soc.*, **70**, 2147 (1948); L. B. Asprey, *ibid.*, **76**, 2019 (1954).

pounds of Pa(IV) have been reported other than in our preliminary communication on $7\text{RbF} \cdot 6\text{PaF}_4$.⁸ (In this paper, formulas of the alkali protactinium fluorides are written $\text{MF} \cdot \text{PaF}_4$ or $\text{MF} \cdot \text{PaF}_5$ solely for ease of displaying the valence of protactinium and have no structural implications.) Our previous work on $4\text{NH}_4\text{F} \cdot \text{UF}_4$ and $4\text{NH}_4\text{F} \cdot \text{AmF}_4$,^{2,3} plus the very extensive work at the Oak Ridge National Laboratory,^{4–6} and earlier work by Zachariasen⁷ on compounds in the alkali fluoride-uranium tetrafluoride systems provided X-ray data for the U(IV) fluoride complexes. We anticipated that the analogous Pa(IV) compounds would be isostructural.

(8) L. B. Asprey, F. H. Kruse, and R. A. Penneman, *ibid.*, **87**, 3518 (1965).