REACTIVITY OF TRANSITION METAL FLUORIDES—XI OXIDATION-REDUCTION REACTIONS OF RUTHENIUM HEXAFLUORIDE[†]

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Abstract—Oxidation-reduction reactions of ruthenium hexafluoride with a selected series of reductants have been studied. The results of this investigation have been correlated with those of previous studies of the higher fluorides of the transition metals. An alternative procedure for the preparation of the thermally unstable hexafluorides of the transition metals (and actinides) is described, which requires only simple apparatus. New synthetic methods are reported for RuF₅ and derived hexafluororuthenate(V) salts and for RuF₄ and the preparation of [Ru(PF₃)F₄]_n, a trifluorophosphine complex of Ru(IV), is described.

INTRODUCTION

From a study of the chemical reactivities of the higher fluorides of the *d*-transition metals, particularly those of subgroups V and VI and the hexafluorides of the third row, in conjunction with the available thermodynamic evidence, it has been established that the oxidant strength of a particular fluoride increases with increasing atomic number across any row of the Periodic Classification, but decreases with increasing atomic number within any group[1,2]. Furthermore, it has also been shown that significant chemical differences develop and increase progressively for successive pairs of second and third row elements moving from zirconium and hafnium across the transition metals series[1].

For the higher fluorides of the third row transition metals the studies of Bartlett *et al.* [2-4], and others [5-8], on the reactions of the hexafluorides with nitric oxide, nitrosyl fluoride and oxygen, together with previous studies in this series on the hexafluorides and on TaF₅[9-12], have provided much chemical information regarding the relative oxidizing abilities of these fluorides. However, for the higher fluorides of the second row transition metals, apart from studies on NbF₅ and MoF₆[11, 12], the available chemical data is not so extensive. Very few reactions have been reported for TcF₆, and less is known about the thermally unstable and hence highly reactive hexafluorides of ruthenium and rhodium, both of which oxidize xenon[4, 13, 14].

As part of a continuing survey of the relative reactivities of the higher fluorides of the d- and f-transition elements we have therefore studied some oxidationreduction reactions of RuF_6 with a selected series of reductants, similar to those used in previous investigations of this series. This study therefore enables a comparison of the oxidizing ability of RuF_6 to be made with the oxidizing abilities of other higher fluroides of the transition metals, particularly with other second row transition metal fluorides and with OsF_6 , its third row congener.

A secondary feature of the work reported here is that, it was undertaken prior to and in preparation for a related study of the chemical reactivity of $PuF_6[15]$. A safety requirement for the later work was that PuF_6 reactions were to be studied using about 50 mg of the hexafluoride, whereas most of the earlier work in this series had been conducted on about the 0.5-1g scale. Therefore it was decided to study the reactions of RuF_6 , expected to be fairly similar to PuF_6 , on the smaller scale in preparation for the later work. Special apparatus and procedures were developed which could, when necessary, be used in glove-boxes, because of the radioactive nature of plutonium and its compounds. In particular, a preparative method for RuF_6 and PuF_6 , very much simpler than those previously reported, was designed and used and is described later in this paper.

EXPERIMENTAL

Apparatus and materials. All work was carried out in monel, stainless steel and Kel-F apparatus, essentially similar to that described by Canterford and O'Donnell [16]. Reactions were conducted in small Kel-F reaction tubes, which were machined from 5/8 in. diameter Kel-F rod and had a capacity of about 3 cm³. Each tube had a flared open end, which was fitted with a stainless steel taper plug and Whitey valve (SS-1KS4), or, if a high pressure was anticipated as a result of reaction, the plug could be replaced by an expansion bulb (ca. 25 cm³). Reactions were carried out in this type of apparatus in order to check on its feasibility and reliability for a similar investigation to be carried out on PuF₆[15], as indicated earlier.

Preparation of ruthenium hexafluoride. Although the thermally unstable hexafluorides (RuF₆, RhF₆, PtF₆, and PuF₆) decompose quite rapidly above 200°C, this does not prevent their preparation at high temperatures, at which they are formed by reaction of the respective metal and fluorine, provided that they are quickly cooled to temperatures at which dissociation into a lower fluoride and fluorine occurs very slowly [17, 18]. To achieve this, quite sophisticated experimental arrangements have been developed, such as induction heating by coils cooled with liquid nitrogen [19, 20]. In this work, however, RuF_6 (and also PuF_6 [15]) was prepared in good yields using the same principle of immediate cooling upon formation, but with simple apparatus. A typical system is shown in Fig. 1, and consisted of a reaction vessel, furnace and cooling collar.

The reaction vessel was a 300 cm³ Sample Cylinder (Whitey 304-HDF-4-300) with a Cajon pipe plug welded into the bottom outlet of the cylinder. The metal-to-metal connection between the outlet of the cylinder and valve (Whitey SS-14DKM4-S4) was made by coating the pipe thread of the valve with soft solder and tightening until a vacuum seal was effected. This type of seal may be broken and remade many times. The bottom section of the reactor could be inserted into the metal block of the furnace. This block had been machined so as to fit the contours of the cylinder and plug, thereby allowing good heat transfer during preparation of the cylinder Plug to house a thermocouple, which passed through the centre of the metal furnace block from below. This allowed the temperature to be constantly monitored during

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Fig. 1. Apparatus for the preparation of ruthenium hexafluoride.

use. The cooling collar consisted of a brass dish, which contained an acetone-solidCO₂ cold bath during preparation of the hexafluoride. A liquid-tight seal was effected between the cylinder and collar by means of a wedge-shaped Teflon gasket at the base of the collar. Using this apparatus, RuF₆ was prepared by heating *ca.* 1 g of the metal (Koch-Light, 99.99%) at 350–400°C with a slight deficiency of fluorine for one hour. On formation, the hexafluoride condensed in the upper regions of the reactor in the vicinity of the cooling collar. Excess fluorine was removed after cooling, and the hexafluoride was used directly from the reactor. Any incompletely fluorinated ruthenium remained as involatile fluorides in the reactor.

Other reagents. Anhydrous hydrogen fluoride (Matheson 99.8% min) was distilled on a column similar to that described by Shamir and Netzer [21], and ClF₃ (Matheson, 98% min) was doubly distilled in a vacuum system before use.

All other reagents were prepared and/or purified as described previously[11], or were of reagent grade purity.

Reaction procedures. All volatile reagents were transferred by vacuum distillation, while solid reagents were handled inside an argon-filled glove box. Reactions were carried out by condensing excess reductant, if volatile, onto a sample of the hexafluoride at -196° C. For solid reductants, the hexafluoride was condensed directly onto excess reagent, or in AHF, at -196° C. In either case the reactants were then allowed to warm slowly to room temperature. The procedure for studying an extremely exothermic reaction of a hexafluoride under controlled conditions in cold anhydrous hydrogen fluoride has been described previously[9]. The adduct, ClF₃:RuF₅, was prepared by reacting a small amount of urtuenium metal with ClF₃ at room temperature (*caution*; *extremely violent reaction*). The pale yellow product was subsequently isolated by removal of the volatile species (m.p. 163–164°C, dec.). Some relevant analytical results are given in Table 1.

Identification and characterization of products. Upon completion of a reaction the volatile products were removed and, after fractionation if necessary, were identified by their IR spectra. Solid products were transferred to the dry-box for subsequent handling and were identified by chemical analysis and other procedures. Solid samples were decomposed in an alkaline oxidative flux of NaOH-Na₂CO₃-NaNO₃ and the solid melt extracted with water. Alternatively, samples were hydrolysed in 2 M KOH. In either case, ruthenium was then oxidized to a mixture of ruthenate and perruthenate using $K_2S_2O_8$ and determined by the ruthenate-perruthenate isosbestic point at 415 nm[22]. Fluoride, phosphorus and arsenic were determined as described previously[9]. So as to avoid interference in the determination of phosphorus, RuO₄ was removed by a preliminary distillation with 60% perchloric acid.

IR and electronic diffuse reflectance spectra, X-ray powder photographs and magnetic measurements were obtained as described previously [9], while Raman spectra were recorded on a Spex Industries Ramalog 5, with the Raman scattered light being collected at 90° to the incident light. Excitation was provided by the green 5145 Å line of a Spectra Physics 164 Ar⁺ laser and the compounds were contained in sealed Pyrex capillary tubes.

RESULTS AND DISCUSSION

Systematics of oxidation-reduction reactions of RuF_6 , and the products of reaction

A summary of results of the reactions of RuF_6 that were studied in this investigation is given in Table 2. Like the oxidation-reduction reactions of the higher fluorides of other transition metals with the lower fluorides of the non-metals, the reactions of RuF_6 followed a simple pattern, with oxidation of the particular lower fluoride to its respective higher fluoride and reduction of the hexafluoride to oxidation state (V) or (IV). Also, as in previous studies, the solid products of reaction that were isolated were not the pentafluoride or tetrafluoride, but adducts or complexes. These products were formed in secondary reactions which depended upon the Lewis acid-base or π -acceptor characteristics of the reaction products and excess reactants.

Previously, the reactions of OsF₆ and IrF₆ with PF₃ have been found to be extremely exothermic, resulting in thermal decomposition or high-temperature reduction of the products of reaction to give residues containing the respective free metals [9]. Stoichiometric compounds were subsequently isolated by conducting the reactions in liquid anhydrous hydrogen fluoride (AHF) at low temperatures, where the solvent could act as a "thermal sink". In view of the similar behaviour expected for RuF₆, based on its thermal instability, the reaction between RuF₆ and PF₃ was also studied in AHF under the same conditions. In AHF, this reaction produced PF5 and rust-brown tetrafluoro(trifluorophosphine)Ru(IV), $Ru(PF_3)F_4$. Although monomeric penta-coordinated complexes of ruthenium are known [23], spectroscopic results show that the compound is polymeric, so that it is best formulated as [Ru(PF₃)F₄]_n. Under the same conditions OsF₆ and PF₃ gave monomeric trans-Os(PF_3)₂ F_4 as the solid product.

The compound $[Ru(PF_3)F_4]_n$ is insoluble in AHF, unlike $Os(PF_3)_2F_4$ which is quite soluble in this solvent. This also supports the postulate that the ruthenium compound is

Table 1	. Anal	ytical	results

Ru %		I	F %		P, As or Cl %	
Theor.	Found	Theor.	Found	Theor.	Found	
38.1	37.4	50,2	49.0	11. 7	12.2	
29.1	30.0	49.3	48.4	21.6	20.4	
35.0	34.4	52.7	51.8	12.3	-	
	Rt <u>Theor.</u> 38.1 29.1 35.0	Ru % Theor. Found 38.1 37.4 29.1 30.0 35.0 34.4	Ru % Theor. Theor. 38.1 37.4 50.2 29.1 30.0 49.3 35.0 34.4 52.7	Ru % F % Theor. Found Theor. Found 38.1 37.4 50.2 49.0 29.1 30.0 49.3 48.4 35.0 34.4 52.7 51.8	Ru % F % P, As of theor. Theor. Found Theor. Found Theor. 38.1 37.4 50.2 49.0 11.7 29.1 30.0 49.3 48.4 21.6 35.0 34.4 52.7 51.8 12.3	

Reactivity of transition metal fluorides-XI

Reagent	Products
PF ₃ /AHF	$[\operatorname{Ru}(\operatorname{PF}_3)\operatorname{F}_4]_n$, PF_5
AsF ₃	$RuF_4 \cdot AsF_5$
SbF ₃	RuF ₅ , SbF ₅ ^(b)
BiF ₃	RuF ₅ , BiF ₅ ^(b)
CIF ₃	$ClF_3 \cdot RuF_5, ClF_5 \cdot RuF_5$
CS ₂ (a)	CF ₄ , SF ₄
H ₂ /AHF	$\operatorname{RuF}_5 \rightarrow \operatorname{RuF}_4^{(c)}$
Ru/AHF	RuF ₅
Ru/KF/AHF	K RuF ₆

Table 2. Oxidation-reduction reactions of ruthenium hexafluoride

(a) Only volatile products are listed.

(b) Only the pentafluorides are reported here as no attempt was made to determine if adducts had formed between the products of reaction and excess reactants and/or between the products themselves.

(c) On standing RuF_5 is slowly reduced to RuF_4 by hydrogen, in

AHF.

polymeric. It decomposes in water with the evolution of PF_3 and the formation of a brown solution, from which a precipitate of the hydrated dioxide forms. The related $Os(PF_3)_2 F_4$ also decomposes in water with the evolution of PF_3 , but gives a stable yellow solution. This difference in behaviour parallels the difference in hydrolytic stability of the respective hexafluorometallate (IV) anions[24, 25]. The IR data for $[Ru(PF_3)F_4]_n$ are listed in Table 3,

together with data for PF₃ and an assignment of the bands. The P-F stretching and F-P-F bending modes are easily identified by comparison with the free ligand and with Os(PF₃)₂F₄. As in Os(PF₃)₂F₄, as found in other halogenotrifluorophosphine metal compounds [27], the P+ F stretches in [Ru(PF₃)F₄]_n are found at relatively higher frequencies than in free PF₃, which is explained by assuming that the P-F bond has some double bond

[Ru(PF3)F4]n (solid, Nujol mull)	PF3 ^(a) (gas)	Approximate description of mode ^(b)
1155 w, br (c)		
978 sh)
960 s, br	893 .2 s	
899 s	858.4 s	\rangle ν (P - F)
848 s		
781 w)
617 m, sh		$\nu(\mathrm{Ru} + \mathrm{F})_{\mathrm{terminal}}$
563 s		$\mathbf{v}(\mathrm{Ru} - \mathrm{F})_{\mathrm{bridging}}$
512 s	486.5 m	h(F - P - F)
408 m	345.6 w	<pre></pre>

Table 3. IR data (cm^{-1}) for $[Ru(PF_3)F_4]_n$ and PF_3

a) Reference 26.

(b) ν refers to a stretching mode and δ refers to a bending mode.

(c) s = strong, m = medium, w = weak, br = broad, sh = shoulder.

character and that this is affected by the oxidation state of the metal [27].

In the transition metal-fluorine stretching region two bands are observed. One band occurs at 617 cm⁻¹, and this is attributed to a transition metal-terminal fluorine vibration. These are observed in the range 760- 600 cm^{-1} [26, 28]. The other band occurs at 563 cm $^{-1}$, appearing in the range usually associated with transition metal-bridging fluorine vibrations, 570-510 cm⁻¹[26, 28], and is quite close to the Ru-F stretch at 556 cm⁻¹ found RuF₃, which has a totally fluorine-bridged in structure [29]. The appearance of the bridging fluorine vibration indicates that the compound is polymeric and probably involves octahedral coordination of the metal atoms. This appears in agreement with the electronic diffuse reflectance data for $[Ru(PF_3)F_4]_n$, which correlate fairly well with the data for K₂RuF₆ and Cs₂RuF₆[30, 31], as listed in Table 4. The appearance of the lower energy band in the case of $[Ru(PF_3)F_4]_n$ presumably arises because the ligand field does not have strict octahedral symmetry. Magnetic susceptibility measurements on $[Ru(PF_3)F_4]_n$ gave a μ_{eff} of 1.81 B.M. (per Ru atom) at 293°K, which is considerably lower than the range of 2.8-3.0 B.M. at room temperature expected for $4d^4$ Ru(IV) in an octahedral or near-octahedral environment [32]. The low magnetic moment for $[Ru(PF_3)F_4]_n$ probably arises from strong magnetic exchange in the solid state as was also observed in the case of $Os(PF_3)_2F_4$.

In passing, it is also noted that polymeric $[Ru(PF_3)F_4]_n$ and $Os(PF_3)_2F_4$ are both four electrons short of the stable noble gas configurations of xenon (54 electrons) and radon (86 electrons), respectively, and thus do not obey the "effective atomic number" rule. This demonstrates the breakdown of the rule for this type of compound where the metal is in a high oxidation state.

Ruthenium hexafluoride was found to oxidise AsF₃ to AsF₅, being reduced in turn to Ru(IV). The dark brown adduct, RuF₄·AsF₅, was isolated in this reaction, even in the presence of excess AsF₃. This adduct is analogous to the previously reported compounds IrF₄·AsF₅[9] and VF₄·MF₅, where M = P, As and Sb[33]. All of these adducts were prepared in a similar manner, that is, reaction of either IrF₆ or VF₅ with the appropriate lower fluoride, or in the case of VF₄ adducts, by direct interaction of VF₄ with the appropriate pentafluoride. Previous studies have also suggested that these species have polymeric cations and are best formulated as, for example, (IrF₃)_nⁿ⁺(AsF₆⁻)_n in the case of IrF₄·AsF₅.

IR spectra of solid RuF₄·AsF₅ showed bands at 726(s), 540 (m, br) and 393 (w) cm⁻¹. The bands at 726 and 393 cm⁻¹ may be assigned as ν_3 and ν_4 for the AsF₆⁻ anion (729 and 395 cm⁻¹ in IrF₄·AsF₅), while the band at 540 cm⁻¹ (550 cm⁻¹ in IrF₄·AsF₅) appears in the range expected for a fluorine-bridged system and may be assigned, formally, to an RuF₃⁺ cation. It is also quite close to the ruthenium-bridging fluorine stretch of 556 cm⁻¹ in RuF₃. No ruthenium-terminal fluorine stretches appear in the IR spectrum so that, like all of the above adducts, RuF₄·AsF₅ is best formulated as $(RuF_3)_n^{n+}(AsF_6)_n$, where the structure of the cation is probably based on that of RuF₃, which has a fluorine-bridged structure with octahedral coordination of the ruthenium atoms.

The adduct was amorphous to X-rays, but magnetic susceptibility measurements gave a value for μ_{eff} of 3.10 B.M. at 295°K, based on the formula RuF₄·AsF₅. As in the case of IrF₄·AsF₅ this value is not readily interpretable because of the lack of information about the structure, but is not inconsistent with octahedrally coordinated Ru(IV) as suggested above.

The reactions of RuF_6 with SbF_3 and BiF_3 both occurred at about room temperature to give RuF_5 and either SbF_5 or BiF_5 . The existence of the free pentafluorides was not established in either case but, rather, on completion of a reaction, the products were first converted to their respective salts by reaction with excess potassium fluoride in AHF (e.g. RuF_5 gives $KRuF_6$). The presence of the pentafluorides was subsequently inferred by identification of the derived salts by Raman and IR spectroscopy [26, 32, 34, 35]. No attempt was made to establish the nature of the initial reaction mixtures in view of their probable complexity, that is, whether there was any adduct formation between the products of reaction and excess trifluoride and/or between the products themselves.

Ruthenium hexafluoride oxidized CIF₃ to CIF₅, being reduced to Ru(V). The solid product of this reaction proved to be a mixture of $ClF_3 \cdot RuF_5$ and $ClF_5 \cdot RuF_5$. This was shown by chemical analysis and by the appearance of bands in the IR and Raman spectra of the product that could be attributed to the ClF_2^+ , ClF_4^+ and RuF_6^- ions [35–38]. For comparative purposes, a pure sample of CIF3. RuF5 was prepared and the IR and Raman data for this compound are reported in Table 5, together with an assignment of the bands. To a first approximation the spectra may be assigned on the basis of isolated $ClF_2^+(C_{2\nu})$ and $RuF_6^-(O_h)$ ions but, in view of the splitting of $\nu_1(A_1)$ for the ClF₂⁺ ion (a factor group splitting) and the violation of the mutual exclusion rule and splitting of some of the bands for the RuF₆⁻ anion, a more extensive treatment is warranted. However, without definite knowledge of the structure of this adduct, no work

Table 4. Electronic diffuse reflectance spectra (cm⁻¹) for [Ru(PF₃)F₄]_n, K₂RuF₆ and Cs₂RuF₆

$[Ru(PF_3)F_4]_n$	$K_2 RuF_6^{(a)}$	$Cs_2RuF_6^{(b)}$	Assignment (c)
19,200 sh	-	-	•
25, 400	26,800 sh	27,000	${}^{3}T_{1g}(t_{2g}^{4}) \rightarrow {}^{3}T_{1g}, {}^{3}E_{g}, {}^{3}T_{2g}(t_{2g}^{3}e_{g}^{1})$
32, 500	31,000	31,000	${}^{3}T_{1g} \rightarrow {}^{3}A_{1g}, {}^{3}A_{2g}, {}^{3}E_{g}(t_{2g} {}^{3}e_{g}^{1})$

(a) Reference 30. (b) Reference 31.

(c) For a discussion of assignment, see reference 30.

Infrared	Raman	(b)
(solid) ^(a)	(solid)	Assignment
1228 w, br	-	-
808 m, sh	807 (14) ^(c)	$\nu_3 (B_1) \operatorname{ClF}_2^+$
707 .	791 (47)	(A) CID ⁺
(8/ S	787 (44)	v_1 (A ₁) CIF ₂
	718 (4)	Ru ₂ F ₁₁ ?
690 m, sh	684 (100)	$v_1 (A_{1g}) \operatorname{RuF}_6$
635 s	631 (34)	$\nu_3(T_{lu}) \operatorname{RuF}_6$
	554 (27)	
555 w, br	535 (11)	ν_2 (Eg) RuF ₆
	520 (8)	
	384 (4)	ν_2 (A ₁) ClF ₂ ⁺
	277 (31)	
	272 (38)	5 ¹² g/ ^{Kur} 6

Table 5. IR and Raman data (cm⁻¹) for C1F₃·RuF₅

(a) Spectrum run on solid as ${\rm ClF}_3^{}{}^{}{\rm RuF}_5^{}$ reacts explosively

with Nujol.

(c) Relative intensities in parentheses.

was attempted along these lines. X-Ray powder photographs of ClF₃·RuF₅ were complicated and could not be indexed on the basis of any simple cell, indicating low symmetry, while magnetic susceptibility measurements gave a μ_{eff} of 3.64 B.M. at 296°K, typical of octahedrally coordinated 4d³ Ru(V) at room temperature [32].

In previous investigations in this series, reactions of the higher fluorides with SF_4 and SeF_4 have also been used as a guide to reactivity. However, as both lower fluorides are more easily oxidizable than SbF_3 in reactions of this type[9], they were not investigated in this study of RuF_6 .

Previous studies have shown that metal and non-metal fluorides react with CS_2 to give different products depending on the oxidizing strength of the particular fluoride. With weak fluorinating agents, such as MoF₆ and IF₅, one C-S link is broken and it has been postulated that the reaction involves the intermediate formation of trifluoromethylthio radicals, CF₃S, which lead to the formation of compounds such as (CF₃)₂S₂ through radical recombination reactions [38]. However, with strong fluorinating agents, all C-S bonds are ruptured and complete fluorination occurs to give CF₄ and SF₄, or even SF₆. Ruthenium hexafluoride reacted with CS₂ to produce only CF₄ and SF₄, characteristic of a strong fluorinating agent.

It has been shown that the reactions of ReF_6 , OsF_6 and IrF_6 with hydrogen or the respective metal in AHF provide improved synthetic pathways for the formation of the respective pentafluorides and, in the case of OsF_6 and IrF_6 , the corresponding hexafluorometallate(V) salts when the latter reactions are carried out in the presence of potassium fluoride [9]. Similar reactions were investigated for RuF_6 in this study. In the presence of AHF, RuF_6 was reduced quite readily by hydrogen to RuF_5 . However, when RuF_5 was left in the presence of excess hydrogen, in AHF, for a few hours, further reduction occurred to give RuF_4 . Also, excess of RuF_6 reacted with ruthenium metal in AHF to give RuF_5 and, in the presence of potassium fluoride, with a mole ratio for metal: KF of 1:6 gave KRuF₆. These reactions provide new and convenient synthetic routes for the preparation of the above compounds and also demonstrate the Lewis acid behaviour of RuF_5 . The preparation of KRuF₆ in this way was also used to advantage in the identification of RuF_5 as a product in the reactions of RuF_6 with SbF₃ and BiF₃, as described above.

Comparative reactivity of ruthenium hexafluoride

Prior to the present study of RuF_6 , very few reactions had been reported for this hexafluoride; RuF_6 had been shown to react with xenon[13] and to oxidize water in HF to give an oxonium salt, $H_3O^+RuF_6^-$, and oxygen[39], while reaction with boric oxide in an inert solvent gave RuF_5 , BF_3 and oxygen as identifiable products of reaction[40]. From the summary of reactions given in Table 2, together with the above three reactions, it is evident that RuF_6 is an extremely powerful oxidant.

Considering the relative oxidizing abilities of the higher fluorides of the second row transition metals, then previous studies in this series have shown that MoF_6 is a stronger oxidant than NbF_5 [11, 12]. Little is known about

⁽b) References 35 and 36.

the chemistry of TcF_6 , but the available evidence shows that it is more easily reduced, that is it is a stronger oxidant, than MoF₆. For example, reduction of MoF₆ by potassium iodide in IF₅ gives KMoF₆[41], which contains Mo(V), while under the same conditions TcF_6 is reduced to Tc(IV), probably forming KTcF₅[42]. Now, based on the reactions with NO and NOF, TcF₆ has been shown to be a weaker oxidant than the third row transition metal hexafluorides OsF₆ and IrF₆[2], both of which are weaker oxidants than RuF₆. Ruthenium hexafluoride reacts with SbF3, BiF3 and xenon, while IrF₆ oxidizes only SbF₃ and OsF₆ shows no reaction with any of these three reagents [9]. It is therefore apparent that RuF_6 is a stronger oxidant than TcF_6 . Very few reactions have been reported for RhF₆, and not one that can distinguish it from RuF_6 in oxidizing ability. However, rhodium hexafluoride has been reported to be even more thermally unstable than RuF₆ and hence might be expected to be a somewhat stronger oxidant than the latter hexafluoride [18]. For palladium, no hexafluoride has as yet been prepared, and the highest thermally stable fluoride is PdF4. From these considerations it may be concluded that the order of oxidant strength of the hexafluorides of the second row transition metals is $RhF_6 > RuF_6 > TcF_6 > MoF_6$, while, within the framework of reactions with the same series of reductants, MoF₆ has been shown to be a stronger oxidant than NbF₅, the highest fluoride of niobium. Such a trend has been discussed previously [1, 2], based primarily on thermodynamic considerations in conjunction with the available chemical data, which was not extensive. The current study on RuF₆ has therefore provided considerable chemical support for the above trend. For the higher fluorides of the third row transition metals, an identical trend in oxidizing abilities has been well-established on the basis of extensive chemical studies [2, 3, 9].

For the second and third row transition metals, it is interesting to compare the differences in chemical reactivity of the higher fluorides across the group, especially in light of the present study of RuF₆. As a consequence of the lanthanide contraction, the chemical behaviour within pairs of second and third row elements is very similar, at least for members of subgroups IV and V, but increasing chemical differences occur on passing across the transition metals group. This has been shown from previous studies in this series. For example, there are slight kinetic differences in the reactions of ZrF_4 and HfF₄ with boron trichloride [43], while slightly greater kinetic differences occur in the halogen-exchange reactions of NbF₅ and TaF₅[12]. In both cases the second row fluoride is the most reactive. It should be noted that in the latter study not one reaction showed a difference between NbF₅ and TaF₅ in terms of oxidizing ability. However, MoF₆ has been shown to be a slightly stronger oxidant than $WF_6[11, 44]$, while the available chemical evidence shows that TcF_6 is more easily reduced, that is, it is a stronger oxidant, than ReF₆[42, 45, 46]. The lack of a technetium heptafluoride is also good evidence that the higher fluorides of technetium are more reactive than those of rhenium. It is apparent that differences in reactivity are increasing across the transition metals group. The results of this study are in accord with this observation, as RuF_6 has been found to be a markedly stronger oxidant than OsF_6 , in that it oxidized PF_3 , AsF_3 , SbF₃ and BiF₃, while OsF₆ has been reported to react with only PF₃ and AsF₃[9]. For the remaining higher fluorides data for comparison is not as extensive, but RhF_6 has been shown to be a stronger oxidant than IrF_6

as it oxidizes xenon and IrF_6 does not [4, 13, 14], while palladium and platinum no longer form the same higher fluorides, giving PdF_4 and PtF_6 , respectively. All of these observations support the generalization that significant differences progressively develop between successive pairs of second and third row elements across the transition metals group.

The available physical evidence for all of the observed trends in chemical reactivity of the higher fluorides of the transition metals has been discussed by Bartlett[2, 18], Galkin and Tumanov[47] and by O'Donnell[1, 48]. Correlations have been made with average thermochemical bond energies and thermodynamic stability constants, and with other physical data such as bond stretching force constants and, in the case of the hexafluorides, the frequency of the $\nu_1(A_{1g})$ stretching mode. The pattern of reactivities of the higher fluorides, as established by studies of the type shown here, has always been found to be consistent with trends in the physical properties of the compounds.

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