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High temperature chemistry of the gaseous ruthenium fluorides^{a)}

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Mass spectrometry was used to identify and to thermochemically characterize the gaseous fluorides RuF_4 , RuF_3 , RuF_2 , and RuF generated by fluorination of Ru powder in a platinum effusion cell. Reaction enthalpies and bond dissociation energies were derived from equilibrium measurements involving these species, yielding the following results in kJ mol⁻¹: $D^{\circ}(F_3Ru-F) = 361$; $D^{\circ}(F_2Ru-F) = 339$; $D^{\circ}(FRu-F) = 464$; and $D^{\circ}(Ru-F) = 402$. The results show that the +4 oxidation state dominates the high temperature chemistry of the Ru-F system. Results are compared with the properties of the neighboring Mo-F system.

INTRODUCTION

The high temperature chemistry of many gaseous metal fluoride systems has been worked out in some detail over the last several decades, and much is known about the thermochemistry and chemical bonding. For the most part, the systems studied were relatively stable metal fluorides with average bond energies exceeding 500 kJ mol⁻¹ or more. However, relatively little is known about the less stable fluorides of the platinum group metals. Ruthenium is generally classified as one of the platinum metals, but its ionization potential (7.36 eV) is significantly lower than most members of the group. The fluorides of the Pt group metals are more difficult to study experimentally since the choice of suitable container materials is very limited, but they are nevertheless of considerable interest.

One area of interest involves the possible vapor phase transport of fission product ruthenium in a fluorination step for the reprocessing of nuclear fuels, with potential contamination of the product.¹ Since nothing is known about the high temperature chemistry of the ruthenium fluorides, we have recently studied this system with such an application in mind. Mass spectrometry was used both to identify and to characterize the gaseous ruthenium fluorides, and the results are reported here.

EXPERIMENTAL

Gaseous ruthenium fluoride species were produced in a Pt effusion cell source by reactive vaporization of ruthenium powder in a stream of iodine pentafluoride, IF_5 . The flow of IF_5 , which was admitted through a gas inlet tube in the base of the Pt cell, was controlled precisely with a variable leak valve. The cell contained interior baffling to maximize gas-sample collisions and to promote equilibration. A few checks made by varying the IF_5 flow rate at constant temperature showed that the derived equilibrium data were independent of changes in product species signal levels, indicating attainment of chemical equilibration. Several equilibrium measurements involving the gaseous Ag–AgF couple as a thermochemical reference standard were made by adding elemental silver powder to the ruthenium sample for this purpose.

The Pt effusion cell assembly, surrounded by a tantalum spiral resistance heater and a set of radiation shields, was positioned before the ion source entrance slit in the usual fashion. Cell temperatures were determined by optical pyrometry. Threshold appearance potentials of ions observed in the mass spectrum of the effusion beam were evaluated by the vanishing current method. All of the results reported here were obtained using the magnetic sector mass spectrometer and experimental technique described earlier.^{2,3} The ruthenium powder sample, stated to be > 99.9% purity, was obtained from Spex Industries, while the IF₅ sample was obtained from Matheson Co.

RESULTS

The Ru–F ion species observed for various cell temperatures, their threshold appearance potentials (AP), and the neutral precursors deduced from these results are listed in Table I. The lowest threshold values for the Ru–F ions, ranging from 10 to 12 eV, seem consistent with the expected ionization potentials (IP) of the corresponding neutrals, indicating the presence of RuF₄, RuF₃, RuF₂, and RuF in the molecular effusion beam in the temperature ranges noted. These IPs follow a pattern very similar to those of the neighboring molybdenum fluorides,⁴ although the Ru–F values are 1–2 eV higher than the corresponding Mo–F IP values. In going from Mo (Z = 42) to Ru (Z = 44), the bonding

TABLE I. Threshold appearance potentials and neutral precursors of ions observed in Ru–F studies.

Ion	AP (eV) ^a	<i>T</i> (K)	Neutral precursor
RuF ⁺	12.5	1000	RuF ₄
RuF ⁺	14.0	1000	RuF₄
-	11.2	1400	RuF,
RuF,+	14.0	1100	RuF ₃
-	10.8	1500	RuF ₂
RuF ⁺	13.5	1600	RuF ₂
	9.5	1800	RuF
AgF +	11.0	1300	AgF
Ag ⁺	11.5	1300	AgF
-	7.5	1300	Ag

^aUncertainty ± 0.3 eV.

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apparently is altered considerably, leading to a higher degree of halogen character in the ionizing orbitals. To a first approximation, the ionizing molecular orbital in a metal halide can be considered as a combination of metal and halogen atomic orbitals, with the relative amounts of metal or halogen character determined by the mixing coefficients associated with each orbital. For the ruthenium fluorides, the fluorine orbital coefficients are relatively larger than those of the less noble metals. As will be seen subsequently, the individual bond dissociation energies (BDE) of the Ru-F species are likewise all appreciably lower than those of the corresponding Mo-F species. For the Ag-F reaction partner species, AP (AgF⁺) is close to values of 11.4^{5} and 11.0 eV^{6} reported earlier, while the lowest threshold $AP(Ag^+)$ agrees with the spectroscopic value IP (Ag) = 7.58 eV; a sharp second threshold was observed for Ag^+ at 11.5 eV, due to the strong fragmentation process $AgF + e \rightarrow Ag^+$ + F + 2e. As described below, a correction for this process was applied to third law calculations.

From parent ion intensities measured at 3 eV above threshold to avoid the secondary processes indicated in Table I, the equilibrium constants of the reactions

$$RuF_2(g) + RuF_4(g) = 2RuF_3(g)$$
(1)

and

1

$$1/4Ru(s) + 3/4RuF_4(g) = RuF_3(g)$$
 (2)

were evaluated over sufficiently wide temperature ranges for accurate second law analysis. With silver added to the ruthenium sample, several measurements of the equilibrium

$$RuF_{3}(g) + AgF(g) = RuF_{4}(g) + Ag(g)$$
(3)

were made in the range 1400-1500 K and finally, a single measurement of the reaction

$$RuF(g) + RuF_3(g) = 2RuF_2(g)$$
(4)

at 1767 K was made, again using 3 eV excess ionizing energy. It was not feasible to push the temperature or IF₅ flow rate any higher to enhance the RuF⁺ parent signal, which was the limiting factor in the study of reaction (4). Continued operation at high IF₅ flow rates led to deposition of a conducting film on ion source insulating supports, thereby disabling the source controls. However, the equilibrium constant $K_4 = 570$ at 1767 K was reproducible and is considered to be of acceptable accuracy.

In evaluating absolute equilibrium constants for use in third law calculations, the ion current analogs of reactions (1) and (4) were used directly, without further correction, as described earlier.² For reaction (3), where dissociative ionization of AgF to Ag⁺ predominates significantly over simple parent ionization, a measured fragmentation correction was applied as described earlier.⁶ For reaction (2), an approximate pressure calibration based on the vapor pressure of tin was applied to the ion intensity data, although this was not critical since only the second law enthalpy change was used in the final evaluation. Because there are no experimental or estimated molecular constant data and, therefore no tabulated thermodynamic functions for the Ru–F species, the values used in second and third law calculations were taken from those estimated for the neighboring molybdenum fluorides,⁴ since the ground state electronic structures of Mo ($4d^5$ 5s) and Ru ($4d^7$ 5s) are similar. Although Ru(g) has a slightly higher electronic partition function than Mo(g), the electronic contributions in the molecular species decrease due to splitting of the levels in the field of the fluorine ligands; therefore, differences in electronic contributions to the thermal functions of Mo and Ru molecular fluorides should be minor. In first approximation, it was assumed that the functions of RuF₄, RuF₃, and RuF would be identical to those of the corresponding Mo–F species,⁴ while for RuF₂, a linear configuration was assumed rather than a slightly bent structure. The derived equilibrium constants for reactions (1), (2), and (3) are listed in Table II, while derived second (II) and third (III) law reaction enthalpies are summarized in Table III.

For reactions (1), (2), and (3), the accord between second and third law enthalpies is reasonably good, indicating that third law calculations should be satisfactory for treating a limited number of equilibrium points. We adopt the second law values for reactions (1) and (2), where broad temperature ranges were covered, and the third law values for reactions (3) and (4). In evaluating the thermochemical properties of the Ru–F species, values for the reaction partners Ag(g) and AgF(g) were taken from sources described in Ref. 6. With four independent reaction enthalpies and

TABLE II. Equilibrium constants for the gaseous reactions.

$\overline{RuF_2(g)}$	+ RuF ₄ (g) =	$= 2RuF_3(g)$	K ₁
1/4 Ru(s)	+ 3/4RuF4	$(g) = RuF_3(g)$	K_2
$RuF_3(g)$ -	+ AgF(g) =	$RuF_4(g) + Ag(g)$	K_3
$T(\mathbf{K})$	K_1	$K_2 \times 10^2 (\mathrm{atm}^{1/4})$	$K_3 \times 10^2$
1245	4.30	1.01	
1245	4.30	1.00	
1283	4.95	1.41	
1283	4.40	1.35	
1300	4.85	1.47	
1324	4.90	1.98	
1326	4.55	•••	
1326	4.54		
1326	4.72	•••	
1366	5.32	3.43	
1366	5.08	3.36	
1375		3.16	
1375		2.92	
1416	5.60	4.84	
1422	•••	• • •	1.34
1422	• • •	• • •	1.28
1433	4.91		
1433	4.80	• • •	
1433	4.88		
1452	5.81	5.22	
1472	5.76	7.56	
1472	5.79	7.41	
1503		• • •	1.39
1531	6.18	9.65	
1531	5.95		
1577		9.85	• • •
1624	6.76		•••
1624	6.55		• • •
1624	6.55		
$\log K_1 = 0$	(1.403 ± 0.0)	$(959 \pm 92)/T$	
$\log K_2$ (at	$m^{1/4}$) = (12	.972 + 0.701) - (26094 + 9)	962)/T

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TABLE III.	Thermoc	hemistry	of	Ru–I	⁷ reactions
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	Reaction	Range (K)	ΔH°_{T} (II) ^a	ΔH°_{298} (II) ^a	ΔH°_{298} (III) ^a
(1)	$RuF_2(g) + RuF_4(g) = 2RuF_3(g)$	1245-1624	18.4 ± 1.7	21.8 + 10 ^b	11.7
(2)	$1/4 \operatorname{Ru}(s) + 3/4 \operatorname{Ru}F_4(g) = \operatorname{Ru}F_3(g)$	1245-1576	125.5 + 4.6	$132.2 + 10^{6}$	110.6
(3)	$\operatorname{RuF}_{3}(g) + \operatorname{AgF}(g) = \operatorname{RuF}_{4}(g) + \operatorname{Ag}(g)$	1422-1503	13.0 ± 5.0	5.1	-4.9 ± 12^{b}
(4)	$\operatorname{RuF}(g) + \operatorname{RuF}_3(g) = 2\operatorname{RuF}_2(g)$	1767			$124.6 + 15^{b}$

^a In kJ mol⁻¹.

^bSelected value.

four unknowns, one can now evaluate the thermochemistry of RuF_4 , RuF_3 , RuF_2 , and RuF. Standard enthalpies of formation derived from the reaction enthalpy data are summarized in Table IV, along with individual BDE values evaluated from these results and thermochemical data for Ru(g).⁷

DISCUSSION

Although the gaseous pentafluoride RuF, has been reported,⁸ we did not observe this species in any of the experimental runs. The enthalpy of formation of $RuF_5(g)$ at 298 K is reported⁹ to be -791 kJ mol⁻¹, presumably derived from sublimation and thermodynamic data for the solid. From this enthalpy value and the assumption that the thermodynamic functions of $RuF_5(g)$ can be approximated by those of MoF_5 ,⁴ we estimate that the mol ratio $(RuF_5)/$ (RuF_4) in the vapor at 1000 K would be about 10^{-4} , in accord with our nonobservation of this species. The foregoing enthalpy data also lead to the BDE value D_{298}° $(F_4 Ru-F) = 271 \text{ kJ mol}^{-1}$, much lower than the BDEs in the smaller Ru-F species. In Fig. 1, the Ru-F BDEs are plotted as a function of the number of F ligands, and are compared with analogous values in the Mo-F system. The Ru-F BDEs are uniformly 60 to 160 kJ mol⁻¹ lower than the Mo-F values. This is a clear manifestation of the way in which the continued filling of the 4d shell effects a transformation from the active metals to the left of Ru in the Periodic Table, to the more noble metals on the right. On the other hand, the overall trends in BDE with the number of ligands are similar but not identical in the two systems. There is no a priori reason to expect identical behavior since it is well known that subtle differences in electronic structure can effect changes in the fine structure of bonding patterns. Therefore, the observation that $D(F_2Ru-F) < D(F_3Ru-F)$ does

TABLE IV. Derived	thermochemical	data for	Ru-F	species.
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Gaseous molecule	$\Delta H f_{298}^{\circ}$ (kJ mol ⁻¹)	Bond	D_{298}° (kJ mol ⁻¹)
RuF	328.4 + 18	Ru–F	402
RuF ₂	-55.2 ± 15	FRu-F	464
RuF ₃	-314.2 ± 15	F_2 Ru-F	339
RuF₄	-595.0 ± 15	F ₃ Ru–F	361

not necessarily imply an error in the derived results. Feber's estimated values¹⁰ $D^{\circ}(F_3 Ru-F) = 356$ and $D^{\circ}(F_2 Ru-F) = 360 \text{ kJ mol}^{-1}$ are in reasonable agreement with our experimental values, but the remaining estimates¹⁰ $D^{\circ}(FRu-F) = 410 \text{ and } D^{\circ}(Ru-F) = 439 \text{ kJ mol}^{-1}$ deviate significantly. The measurements reported here extend our knowledge of the less-stable fluorides and provide a more secure basis for further estimates.

The results reported here were used to calculate the relative amounts of gaseous Ru and U species transported by fluorination of the oxides $\text{RuO}_2(s)$ and $\text{UO}_2(s)$ at 600 to 1200 K under equilibrium conditions, in order to see if Ru contamination of reprocessed nuclear fuels¹ can be accounted for on thermodynamic grounds. For this purpose, data for the U–F and U–O–F species were taken from the IAEA compilation,¹¹ while data for the solid oxides were taken from Pankratz.¹² Also included as input species were RuF₅ (g) (with the data noted above), and RuOF₄(g) (using generous stability estimates based on the properties of MoOF₄ and UOF₄). Calculations were made with a computer code for minimizing the Gibbs energy of the system. As expected from the relatively low Ru–F bond strengths, the calculations indicated that transport of gaseous Ru–F



FIG. 1. BDE of molybdenum and ruthenium fluorides as a function of the number of ligands.

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species would be negligible compared to U-F and U-O-F transport in the presence of both $UO_2(s)$ and $RuO_2(s)$. From a thermodynamic viewpoint, transport of gaseous RuF_x or $RuOF_x$ should not be a source of contamination for reprocessed nuclear fuels, provided that the UO₂ content of the sample is not exhausted. Substantial Ru transport will clearly occur, once the oxide fuel is totally depleted. We have identified by mass spectrometry the gaseous oxyfluoride species RuOF₂ and RuOF₃ as products of the fluorination of RuO₂(s) at temperatures up to 1050 K and typical effusion cell pressures up to 10^{-6} atm, but the corresponding ion intensities were lower than those of the RuF_x species observed in the same experiment. It seems unlikely, therefore, that any of the Ru-O-F species can be of such extraordinary stability as to account for enhanced Ru transport on thermodynamic grounds.

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