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Author

Bartlett, N.

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N. Bartlett, S. Yeh, K. Kourtakis, and T. Mallouk

December 1983

DISCLAIMER

THE FLUOROBASICITIES OF ReF_7 AND IF_7 AS MEASURED BY THE ENTHALPY CHANGE $\Delta H°(EF_{7(g)} \rightarrow EF_6^+{}_{(g)} + F^-{}_{(g)})$.

NEIL BARTLETT, SAM YEH, KOSTANTINOS KOURTAKIS, AND TOM MALLOUK

Department of Chemistry, University of California, and the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, Berkeley, California

94720 (U.S.A.)

This paper is dedicated to the memory of the late Professor Jože Slivnik. He was a chemist of dynamic energy, creative imagination, daring, and resourcefulness.

SUMMARY

Iridium hexafluoride oxidizes ReF_6 (via an ReF_6^+ salt) and at room temperatures IrF_6, ReF_6, ReF_7 and $(IrF_5)_4$ are each present in the equilibrium mixture. From these and related findings: $\Delta H°(ReF_6 \rightarrow ReF_6^+ + e^-) = 1092 \pm 27$ kj mole^{-1}(261 $\pm$ 6 kcal mole^{-1}), and thermodynamic data are selected to yield $\Delta H°(ReF_{7(g)} \rightarrow ReF_{6(g)}^+ + F_{(g)}^-) = 911 \pm 33$ kj mole^{-1}(218 $\pm$ 8 kcal mole^{-1}). From observations on the stability of $IF_6^+BF_4^-$ and the lattice enthalpy evaluation for the salt, $\Delta H°(IF_{7(g)} \rightarrow$

$IF_{6(g)}^+ + F_{(g)}^-) = 870 \pm 24$ kj mole^{-1}(208 $\pm$ 6 kcal mole^{-1}). These findings are in harmony with the observation that IF$_7$ quantitatively displaces ReF$_7$ according to the equation:

$$IF_{7(g)} + ReF_6^+AuF_6^-_{(c)} \rightarrow IF_6^+AuF_6^-_{(c)} + ReF_{7(g)}.$$

INTRODUCTION

In their highest oxidation states, compounds of the transition elements often exhibit a close physical relationship to those of group relatives of main-group elements [1]. Thus OsO$_4$ and XeO$_4$ are tetrahedral [2,3] (Os-O = 1.74; Xe-O = 1.74 Å), WF$_6$ and TeF$_6$ are octahedral [4,5] (W-F = 1.833; Te-F = 1.833 Å), IOF$_5$ and ReOF$_5$ are each pseudo-octahedral (C$_{4v}$) [6] monomeric species and both IF$_7$ and ReF$_7$ are monomeric fluxional molecules [6], in which the F ligands undergo rapid intra molecular exchange.

The finding [6] of ready intramolecular exchange of F ligands in ReF$_7$ and IF$_7$ led Beaton [7] to attempt the synthesis of ReF$_6^+$AsF$_6^-$ by analogy with IF$_6^+$AsF$_6^-$. The latter, first prepared by Seel and Detmer [8] had demonstrated the fluorobasicity of IF$_7$. The intramolecular exchange in IF$_7$ had been related by Bartlett and Beaton to transient ion pair (IF$_6^+$F$^-$) formation. Beaton was unable to detect ReF$_6^+$AsF$_6^-$ precipitation from cooled solution of ReF$_7$ in WF$_6$ saturated with AsF$_5$. ReF$_6^+$ salts were first prepared and described by Jacob and Fahnle [9].

In this study an attempt has been made to measure the fluorobasicity of ReF$_7$ as expressed in the enthalpy change:

$$\Delta H^\circ(ReF_{7(g)} \rightarrow ReF_{6(g)}^+ + F_{(g)}^-) \qquad (1)$$
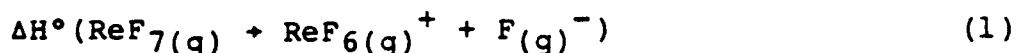
and to compare it with the related enthalpy change for IF_7:

$$\Delta H^\circ (IF_{7(g)} \rightarrow IF_{6(g)}^+ + F_{(g)}^-) \tag{2}$$
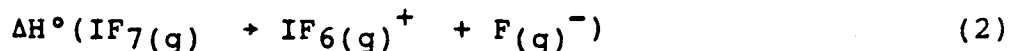
These basicities are compared with those of other fluorobases and are found to be remarkably similar to those of the general class of hypervalent fluorides.

DISCUSSION

In the first demonstration of the fluoride ion donor capabilities of ReF_7, Jacob and Fahnle [9] provided convincing evidence for the salt $ReF_6^+SbF_6^-$. Spectroscopic evidence was also obtained by Jacob [10] for the salt $ReF_6^+PtF_6^-$, from the interaction of the parent hexafluorides at low temperatures. Studies related to the present ones have shown [11] that, at room temperatures, there are fast quantitative reactions, which, depending upon stoichiometry, proceed as follows:

$$1:1 \quad ReF_{6(g)} + PtF_{6(g)} \rightarrow ReF_{7(g)} + 1/4(PtF_5)_{4(c)}$$

and $\quad 2:1 \quad 2ReF_{6(g)} + PtF_{6(g)} \rightarrow 2ReF_{7(g)} + 1/n(PtF_4)_{n(c)}$
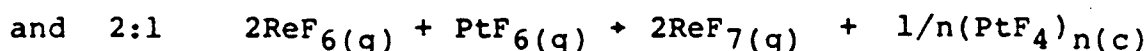
It is probable that these reactions proceed via $ReF_6^+PtF_6^-$ and possibly even $(ReF_6^+)_2PtF_6^{2-}$, with F^- capture by the cation leading to the observed products. The observations, in the present study of ReF_6 interaction with IrF_6, are in harmony with an initial reaction step:

$$ReF_6 + IrF_6 \rightarrow ReF_6^+IrF_6^-{}_{(c)} \tag{3}$$
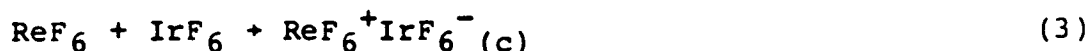
since at ~200 K the ReF_6^+ species is clearly observed via its characteristic intense ν_1 vibration at 796 cm^{-1}. The

experimental evidence shows that the salt is unstable with respect to the dissociation:

$$ReF_6{}^+IrF_6{}^-{}_{(c)} \rightarrow ReF_7 + \tfrac{1}{4}(IrF_5)_4 \tag{4}$$
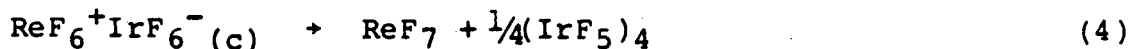
It is probable that the interaction of ReF_7 with $(IrF_5)_4$:

$$ReF_7 + 1/4(IrF_5)_4 \rightleftharpoons ReF_6 + IrF_6 \tag{5}$$
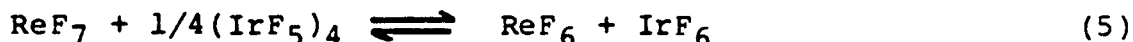
proceeds via $ReF_6{}^+IrF_6{}^-$, with subsequent electron transfer. From the equilibrium expressed in equation (5), since $\Delta G°(5) \approx 0$

$$\Delta G_f°(ReF_7) - \Delta G°{}_f(ReF_6) \approx \Delta G_f°(IrF_6) - \Delta G_f°(\tfrac{1}{4}(IrF_5)_4) \tag{6}$$

Peacock and his coworkers [12,13], from calorimetric work have determined $\Delta H_f°(ReF_{7(g)}) = -1429 \pm 13$ kj mole^{-1} and $\Delta H_f°(ReF_{6(g)}) = -1350 \pm 10$ kj mole^{-1}. From the standard entropies [14] (in joules mole^{-1}K^{-1}) given in parentheses,

$$ReF_{6(g)} + \tfrac{1}{2}F_{2(g)} \rightarrow ReF_{7(g)} \tag{7}$$
$$\;(343) \qquad (102) \qquad (368)$$
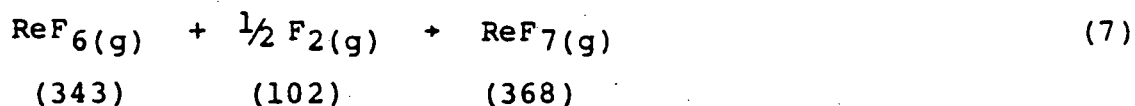
$\Delta S° = -77$ j mole^{-1} K^{-1}. Hence, $-T\Delta S° = 23$ kj mole^{-1} and the left hand side of equation (6) equals -56 ± 16 kj mole^{-1}. This is consistent with the efficient formation of ReF_7 at 600 K since at that temperature $T\Delta S°$ (~ -46 kj mole^{-1}) is still well below the $\Delta H°$ for equation (7), of -79 kj mole^{-1}.

The equilibrium involving ReF_6, IrF_6, ReF_7 and $(IrF_5)_4$ occurs in the condensed phase at ordinary temperatures. Because ReF_6 and IrF_6 are each in equilibrium with appreciable pressures of the vapors [15,16] at room temperature, $\Delta G°$ for equation (3) can be taken as approximately equal to $\Delta G°$ for equation (8):

$$ReF_{6(g)} + IrF_{6(g)} \rightarrow ReF_6^+IrF_6^-{(c)} \qquad (8)$$
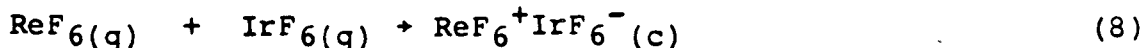
The formation of $ReF_6^+IrF_6^-$ as an intermediate in (5) means that $\Delta G°(8) \approx 0$. An estimate of the entropy change for equation (8) has been made. It has been found that the standard entropies $S_{298}°$ of closely packed solids are in approximately linear relationship with their formula unit volumes. The empirical relationship is

$$S°(j\ mole^{-1}K^{-1}) = 1.84\ V(Å^3) \qquad (9)$$

Thus for the salt $ReF_6^+IrF_6^-$, which is assumed to have the same volume as $IF_6^+AsF_6^-$ (see Table 1), $S° = 393\ j\ mole^{-1}K^{-1}$. This is judged to be reliable to within $\pm 39\ j\ mole^{-1}K^{-1}$. Since [14] $S°(ReF_{6(g)}) = 343$ and $S°(IrF_{6(g)}) = 358\ j\ mole^{-1}K^{-1}$, $\Delta S°(8)$ = $308 \pm 39\ j\ mole^{-1}\ K^{-1}$. Thus, at room temperatures, $T\Delta S° \approx -92 \pm 12\ kj\ mole^{-1}$. Therefore for $\Delta G(8)° \approx 0$, $\Delta H°(8)$ must be $\approx -92 \pm 12\ kj\ mole^{-1}$. The lattice enthalpy for $ReF_6^+IrF_6^-$ (see Table 1 and EXPERIMENTAL) is $527 \pm 16\ kj\ mole^{-1}$. Thus, since other evidence [17] indicates that $\Delta H°\ (IrF_{6(g)} + e^- \rightarrow IrF_{6(g)}^-) = -657 \pm 18\ kj\ mole^{-1}$ the required value of $\Delta H°(ReF_{6(g)} \rightarrow ReF_{6(g)}^+ + e^-)$ becomes $(527 \pm 16) + (657 \pm 18) - (92 \pm 12)\ kj\ mole^{-1} = 1092 \pm 27\ kj\ mole^{-1}$.

A wide range of values exists for physical measurements of the ionization potential of ReF_6. McDiarmid gives [18] 7.99 eV, Ellis finds [19] 10.7 eV, Brundle and Jones are quoted [20] as finding 11.15 eV and Bloor and Sherrod [20] estimate 11.88 eV. A photoionization study by Vovna et al. [21] yielded 11.1 $\pm$ 0.1 eV and this value is quoted in a recent NBS tabulation [22]. This last value (1071 $\pm$ 10 kj mole^{-1}) is

TABLE 1

Lattice enthalpy of $IF_6{}^+AsF_6{}^-$

Space group Pa3; unit cell: a_o = 9.4935(5)Å; z = 4; V = 855.62(8) Å^3

Atomic positions: 4I in 4b; 4 as in 4a; 6F in 24(d) x = 0.0980 y = 0.1377 z = -0.0489
and 6F in 24d x = 0.6001; y = 0.6431; z = 0.4411.

	a	b	c	d	e	f	
	U_{elec}	U_{dd}	U_{dq}	U_r	U_z	U_L (OK)	ΔH_L^o (298K)
kjoules mole^{-1}	515.2	188.8	22.7	201.9	0.8	523.8	528.8
(kcal)	(123.15)	(45.13)	(5.42)	(48.26)	(0.2)	(125.2)	(126.4)

(the basic radius $\bar{r}_F$ = 1.100 Å for the $IF_6{}^+AsF_6{}^-$ structure)

(a) $U_{elec} = \dfrac{18\pi R^2}{V} \underset{hkl}{\Sigma} |F(hkl)|^2 \dfrac{(\sin\alpha - \alpha\cos\alpha)^2}{\alpha 8} - \dfrac{3}{5R} \underset{j}{\Sigma} q_j{}^2$

where $F(hkl) = \underset{j}{\Sigma} q_j \exp(2\pi i \underline{h} \cdot \underline{r}_j)$, $\alpha = 2\pi R / d_{hkl}$, q_j is the charge on atom j (obtained

using the electronegativity equalization procedure of Jolly and Perry [35]), $\underline{h} \cdot \underline{r} = hx_j + ky_j + lz_j$, and (x_j, y_j, z_j) are the fractional coordinates of atom j. R is one-half

the shortest interatomic distance in the crystal, d_{hkl} is the distance between hkl

lattice planes and V is the volume of the unit cell. In all calculations enough terms

TABLE 1 (footnotes continued)

are included in the infinite sum over all hkl reciprocal vectors so that the series termination error introduced is less than 0.8 kcal mole^{-1}. The sum over j includes the atoms in one unit cell.

(b) $$U_{dd} = -3/2 \quad \Sigma_{i \neq j} \quad \frac{\alpha_i \alpha_j \epsilon_i \epsilon_j}{(\epsilon_i + \epsilon_j)} \; r_{ij}^{-6}$$

where α and ϵ are respectively the polarizability and characteristic energy of the ion.

(c) U_{dq} is given by a summation in r_{ij}^{-8}; it is however generally 10-15°% of U_{dd}. In this case it is taken as 0.12 U_{dd}.

(d)   The Born and Mayer equation [36] was used:

$$U_r = b \, \Sigma_{i \neq j} \, (1 + q_i/n_i + q_j/n_j) \exp\{(\bar{r}_i + \bar{r}_j - r_{ij})/\rho\}$$

n is the number of electrons in the outer shell of the ion, q is the charge on the ion, $\bar{r}$ is its "basic radius" and $\underline{r}_{ij}$ is the distance between $\underline{i}$ and $\underline{j}$. The constants $\underline{b}$ and ρ have the values 10^{-12} erg molecule^{-1} and 0.333 Å respectively. The central atom in both the cation and anion were assumed to make no contribution to U_r. Variation of ρ between 0.333 and 0.360 Å produced a variation of less than

TABLE 1 (footnotes continued)

8 kj mole^{-1} in the $IF_6^+AsF_6^-$ lattice enthalpy. Likewise a variation of U_{dd} + U_{dq} by 20% ($\sim$ 10 kcal mole^{-1}) produced a change in the calculated lattice enthalpy of less than 12 kj mole^{-1}, because of compensating changes induced in U_r.

(e)   For relatively large, massive ions such as these in $EF_6^+MF_6^-$ crystals the zero point energy is small: $U_z \approx 0.8$ kj mole^{-1}.

(f) $U_L = U_{elec} + U_{dd} + U_{dq} - U_r - U_z$

indistinguishable from the Brundle and Jones value, and is within the compass of our estimate.

From the heats of formation of ReF_7 and ReF_6 given by Peacock and his coworkers[12,13] and [14] $\Delta H_f^{\circ}(F^-) = -260 \pm 10$ kj mole^{-1},

$$\Delta H^{\circ}(ReF_{7(g)} \rightarrow ReF_{6(g)}^+ + F_{(g)}^-) = -\Delta H_f^{\circ}(ReF_{7(g)}) +$$

$$\Delta H_f(ReF_{6(g)}) + I(ReF_6) + \Delta H_f(F_{(g)}^-) = 911 \pm 33 \text{ kj mole}^{-1}.$$

Beaton's failure to prepare $ReF_6^+AsF_6^-$ by precipitation from WF_6 solution has been confirmed by the present studies and SO_2ClF solutions of ReF_7 have not yielded precipitates with AsF_5, even at ~213 K. This stands in marked contrast with the high thermal stability [8] of $IF_6^+AsF_6^-$. Unfortunately the fluoride-ion affinity of AsF_5 is not yet well defined. To assess $\Delta H^{\circ}(IF_{7(g)} \rightarrow IF_{6(g)}^+ + F_{(g)}^-)$ the fluoroacid BF_3 has been used. A recent re-evaluation [23] has confirmed the $\Delta H^{\circ}(BF_{3(g)} + F_{(g)}^- \rightarrow BF_{4(g)}^-)$ given by Bills and Cotton [24] and rejected that of Altshuller [25]. We therefore take $\Delta H^{\circ}(BF_{3(g)} + F_{(g)}^- \rightarrow BF_{4(g)}^-) = -385 \pm 13$ kj mole^{-1}.

The salt $IF_6^+BF_4^-$ was first reported by Seel and Detmer [8] but an evaluation of its thermodynamic stability has so far been lacking. The present studies show that

$$\Delta G_{213}^{\circ}(IF_{7(g)} + BF_{3(g)} \rightarrow IF_6^+BF_4^-{}_{(c)}) \approx 0$$

At 213K the estimated value of $-T\Delta S^{\circ}$ is 67 ± 12 kj mole^{-1}. Thus

$$\Delta H^{\circ}(IF_{7(g)} + BF_{3(g)} \rightarrow IF_6^+BF_4^-{}_{(c)}) \approx -67 \pm 12 \text{ kj mole}^{-1}$$

From the lattice enthalpy (see EXPERIMENTAL),

$$\Delta H^\circ(IF_6^+{}_{(g)} + BF_4^-{}_{(g)} \to IF_6^+ BF_4^-{}_{(c)}) = -552 \pm 17 \text{ kj mole}^{-1},$$

hence $\Delta H^\circ(IF_7 \to IF_6^+{}_{(g)} + F^-{}_{(g)}) = 870 \pm 24 \text{ kj mole}^{-1}.$

The interaction of IF_7 with $ReF_6^+ AuF_6^-$ to quantitatively displace ReF_7, like the high stability of $IF_6^+ AsF_6^-$ and the instability of $ReF_6^+ AsF_6^-$, indicated the superior basicity of IF_7 relative to ReF_7. Since, in the reaction:

$$IF_{7(g)} + ReF_6^+ MF_6^-{}_{(c)} \to IF_6^+ MF_6^-{}_{(c)} + ReF_{7(g)}$$
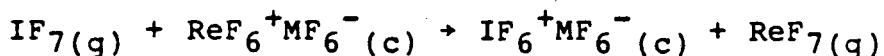
the lattice enthalpies of the reactant and product salts are nearly the same, as are the entropies of reactants and products, the free energy change is approximately given by the difference

$$\Delta H^\circ(IF_{7(g)} \to IF_{6(g)}^+ + F_{(g)}^-) - \Delta H^\circ(ReF_{7(g)} \to ReF_6^+ + F_{(g)}^-).$$

The small exothermicity of this difference in the fluorobasicities is sufficient to account for the quantitative displacement of IF_7 by ReF_7.

The surprise in these findings, however, is the closeness of the values for $\Delta H^\circ(EF_{7(g)} \to EF_{6(g)}^+ + F_{(g)}^-)$. As may be seen from Table 2, the values are similar to those previously noted for the separation of F^- from the xenon fluorides and SF_4.

The almost constant value of the F^- separation enthalpy for the hypervalent fluorides can be simply accounted for [26]. The enthalpy change can be represented as deriving from the sum of three processes:

(a) the conversion of the resonance hybrid of the two

TABLE 2

Enthalpies of fluoride ion separation from IF_7, ReF_7 and other fluorides.

Process	ΔH° kjoules mole^{-1} (kcal mole^{-1})	Reference
$ReF_{7(g)} \rightarrow ReF^+_{6(g)} + F^-_{(g)}$	911 ± 33 (218 ± 8)	present work
$IF_{7(g)} \rightarrow IF^+_{6(g)} + F^-_{(g)}$	870 ± 24 (208 ± 6)	present work
$XeF_{6(g)} \rightarrow XeF^+_{5(g)} + F^-_{(g)}$	874 (209)	(a)
$XeF_{4(g)} \rightarrow XeF^+_{3(g)} + F^-_{(g)}$	925 (221)	(a)
$XeF_{2(g)} \rightarrow XeF^+_{(g)} + F^-_{(g)}$	906 (216)	(a)
$SF_{4(g)} \rightarrow SF^+_{3(g)} + F^-_{(g)}$	883 ± 33 (211 ± 8)	(b)
$ONF_{(g)} \rightarrow ON^+_{(g)} + F^-_{(g)}$	786 ± 4 (188 ± 1)	(c)(d)

Table 2 references

(a) J. Berkowitz, W.A. Chupka, P.M. Guyon, J.H. Holloway, and R. Spohr, J. Phys. Chem., 75 (1971) 1461.

(b) T.E. Mallouk, G.L. Rosenthal, G. Müller, R. Brusasco and N. Bartlett, Inorg. Chem., submitted for pubication.

(c) JANAF Thermochemical Table, Dow Chemical Co., Mich. 1971.

(d) H.S. Johnston, and H.J. Bertin, J. Am. Chem. Soc., 81 (1959) 6402 and J. Mol. Spectroscopy, 3 (1959) 683.

dominant canonical forms of a three-center-four-electron bond $\{(F-E)^+F^-$ and $F^-(E-F)^+\}$ to one form: an $(F-E)^+F^-$ ion pair,

(b) the contraction of $(E-F)^+$ and the enhancement of the energy of that bond $\{(E-F)^+long \rightarrow (E-F)^+ short\}$, and

(c) the work necessary to separate $(E-F)^+$ and F^- to infinity.

The first step is a measure of the more favorable energy associated with the delocalization of an electron over two F ligands rather than its association with one F ligand. For the noble-gas difluorides this resonance energy has been empirically evaluated [24] as contributing approximately 210 kj mole^{-1} to their stability. Such a resonance stabilization should hold approximately for all of the hypervalent fluorides. The second process exothermically contributes to the F^- separation process by less than 10 kj mole^{-1}. The third process requires the greatest energy. For a separation of ions of 2.0 Å the work amounts to 694 kj mole^{-1}. With smaller inter-ion separations the work would, of course, be greater. Thus the sum of the first and third steps is expected to amount to ~900 kj mole^{-1}-- a value close to the observed enthalpies of F^- separation for the hypervalent fluorides and IF_7. Of course in a case where the resonance stabilization does not occur the ion-pair separation work will be the only important term. This probably accounts for the high basicity of ONF, a molecule which appears to be close to an ion pair ON^+F^-[27].

Thus it seems that ReF_7 behaves as a hypervalent molecule. Perhaps in this high oxidation-state compound the 5d orbitals have been greatly contracted by the high ligand field such that they are behaving more like inner shell orbitals. If

so the bonding of the seven ligands, like the case of IF_7, would be primarily dependent upon the Re 6s and 6p orbitals and the 2p orbitals of the F ligands.

EXPERIMENTAL

Apparatus and techniques

Because of the hydrolytic instability of most of the materials used in this study preparations were carried out under strictly anhydrous conditions. Metal vacuum systems as previously described [26] and a vacuum atmospheres DRILAB were employed.

Raman spectra were obtained from samples contained in quartz capillaries or tubes, or Teflon FEP tubes of $\frac{1}{4}$ in. diameter. For lower temperatures (to ~100 K) samples were held in a stream of cold nitrogen (jacketed by warm nitrogen to prevent ice formation). Spectra were recorded from a J-Y Ramanor HG25 Spectrometer with a double holographic grating monochromator, using either a krypton (647.1 nm) or an argon ion (514.5 or 488.0 nm) laser.

X-ray powder photographs were obtained using a General Electric Precision camera (Straumanis loading) with Ni filtered CuKα radiation. Finely powdered samples (loaded in the DRILAB) were sealed into 0.3 - 0.5 mm thin-walled quartz capillaries (Charles Supper Co., Natick, Mass.).

Infrared spectra were obtained using a Perkin Elmer 597 Grating Spectrophotometer. For gases a Monel cell (8 cm path) fitted with AgCl windows cut from 1 mm sheet (Harshaw Chemical Co., Solon, Ohio) was used.

Reagents

Rhenium hexafluoride was prepared by heating rhenium metal (Johnson, Mathey & Mallory) to 250° in gaseous fluorine in a Monel metal bomb, Re being in slight molar excess of that required by the ReF_6 formula. If ReF_7 was present it was removed by heat with Re metal. The infrared spectrum provided a convenient check for purity [15]. $ReF_{6(c)}$ possesses Raman bands at ν_1, 753 and ν_5, 235 cm^{-1}.

Rhenium heptafluoride was prepared in a similar fashion but with a large F_2 excess. When $ReOF_5$ was formed (from oxide impurity) it was removed from the ReF_7 by condensing the mixture onto SbF_5, with which the $ReOF_5$ complexes preferentially [11]. The ReF_7 was removed from the mixture with SbF_5 by vacuum sublimation at room temperatures to traps cooled at -196°. Its purity was checked by infrared spectroscopy [28]. The most intense Raman band is at 733 - 736 cm^{-1} in condensed phases.

Iridium hexafluoride was made by burning Ir metal (Englehardt) in excess F_2, as in the ReF_7 preparation. Excess F_2 was removed under vacuum with the product at -196°, then the IrF_6 was vacuum sublimed to a Monel can provided with a Swagelock KS4 valve for storage. Infrared spectrocopy [29] was employed to monitor its purity.

Iridium pentafluoride, Ir_4F_{20}, was made similarly, using approximately the required Ir:F_2 molar stoichiometry, the lid of the reactor being water cooled. The yellow-green crystalline solid was checked for purity by X-ray powder photography [30] and by Raman spectra. The strongest Raman

bands are at 719 and 648 cm^{-1}.

Tungsten hexafluoride and boron trifluoride (Matheson Gas Products) were used following trap to trap distillation. Infrared spectroscopy was utilized to monitor purity.

Iodine heptafluoride was made from well dried KI (300° in vacuo) by fluorinating with excess F_2 in a Monel bomb at 200°. It was necessary to de-oxygenate the bomb and an initial preparation of IF_7, which was invariably contaminated with IOF_5, served to do this. Infrared spectroscopy provided a convenient monitor for purity, the $\nu(I=O)$ at 926 cm^{-1} being a sensitive indicator of IOF_5 contamination [31].

Reactions

Interaction of ReF_6 with IrF_6 Co-condensation of ReF_6 and IrF_6 in a quartz tube at -196° yielded a deep purple solid which, on warming to room temperature, yielded a mixture (by Raman spectroscopy) of ReF_6, ReF_7, IrF_6 and $(IrF_5)_4$. A similar interaction occurred in WF_6 solution. As the deep purple color (associated with the initial ReF_6-IrF_6 interaction) faded, a bright yellow crystalline solid precipitated. Raman spectroscopy and X-ray powder photography proved the latter to be $(IrF_5)_4$. Raman spectroscopy of the brown supernatant solution showed, however, that ReF_7, ReF_6 and IrF_6 were present in it. Cooling this solution to ~200 K re-established the purple color (ReF_6/IrF_6 interaction). The Raman spectra of the mixture at room temperature gave evidence of a new species characterized by a sharp intense band at 793 cm^{-1} (ν_1 ReF_6^+) when blue light (4880 Å) of the argon ion-laser was used to irradiate the interface between the precipitate and the

solution. This band was not observed for the solution itself.

Interaction of ReF_7 and $(IrF_5)_4$. ReF_7 and $(IrF_5)_4$ (with Ir and Re in equimolar quantities) were dissolved in WF_6 at room temperatures. A brown color slowly developed and the presence of ReF_6 and IrF_6, as well as the starting materials, was quickly established using Raman spectroscopy. The intensities of the ReF_6 and IrF_6 bands (typified by ν_1 at 756 and 702 cm^{-1} respectively) each grew steadily at the expense of the ReF_7 (represented by ν_1 at 736 cm^{-1}). The solubility of $(IrF_5)_4$ was low in the WF_6. The mixture attained equilibrium in approximately one week.

Interaction of IF_7 with $ReF_6^+AuF_6^-$. The salt $ReF_6^+AuF_6^-$ was prepared [11] by interaction of ReF_7 with an HF solution of $Kr_2F_3^+AuF_6^-$, the HF being removed at −78° under vacuum. To ensure complete interaction the dry solid remaining was warmed to ~60°. Completion of the interaction was signaled by cessation of gas evolution. The product, an orange solid, was kept at −78° until needed. The Raman spectrum of $ReF_6^+AuF_6^-$ was characterized by the following bands: ReF_6^+: ν_1, 796; ν_5, 356; AuF_6^-: ν_1, 601; ν_5, 223, 213 cm^{-1}. The solid was allowed to interact with gaseous IF_7 at room temperatures for three days. The volatiles were rich in ReF_7 and the yellow solid product was shown by Raman spectroscopy and X-ray powder photography [32] to be $IF_6^+AuF_6^-$.

Interaction of IF_7 with BF_3. Condensation, at 213 K, of BF_3: IF_7 mixtures (in ~ 4:1 molar ratio) generated a solid in which IF_6^+ bands (ν_2, 735; ν_1, 711; and ν_5, 343 cm^{-1}) were observed along with those of IF_7 (ν_1, 682, ν_2 643 cm^{-1}). The $IF6^+$ species was not observed at higher temperatures. With

lower pressures of BF_3 the IF_6^+ bands were diminished in intensity.

Lattice enthalpy evaluations for $EF_6^+MF_6^-$ salts

The electrostatic part of the lattice enthalpy was calculated for the $IF_6^+AsF_6^-$ case by the method of Bertaut [33] as modified by Templeton [34]. Details of procedures used for $SF_3^+BF_4^-$, $(SF_3^+)_2GeF_6^{2-}$, $NO^+UF_6^-$, and $ClO_2^+BF_4^-$ have been given elsewhere [23]. The parameters and results for the $IF_6^+AsF_6^-$ calculation are given in Table 1. In related work [23] the lattice enthalpies of simple and complex fluorides have been shown to obey a roughly linear relationship with the reciprocal of the cube root of the formula unit volume. The latter approximates to the average primitive unit cell edge. Such a relationship is to be expected since the lattice energy for salts A^+B^- is dominated by the Coulombic term (the repulsion energy and the dispersion energy terms being largely mutually canceling over a wide range of $r_A + r_B$ values. The linear empirical relationship is:

$$\Delta H_L^\circ (\text{kjoules mole}^{-1}) = 2323 \ V^{-1/3}(Å^{-1}) + 110$$

The formula unit volume for all $EF_6^+MF_6^-$ salts must be close to that for $IF_6^+AsF_6^-$. Because of the high London energy term in such salts their lattice enthalpies are ~29 kj mole^{-1} higher than given by the best straight line value.

Lattice enthalpy of $IF_6^+BF_4^-$

Because structure of the $IF_6^+BF_4^-$ salt is unknown, the lattice enthalpy was estimated from the empiricial lattice

enthalpy formula unit volume relationship (for which a formula unit volume of 172 A^3 was assumed) and a London energy enhancement of 25 kj mole^{-1} was assumed to yield ΔH_L° ($IF_6^+BF_4^-$) = 552 ± 17 kj mole^{-1} (132 ± 4 kcal mole^{-1}).

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$$\Delta G°(Cl_{2(g)} + IrF_{6(g)} \rightarrow Cl_2^+IrF_6^-{}_{(c)}) \approx 0.$$
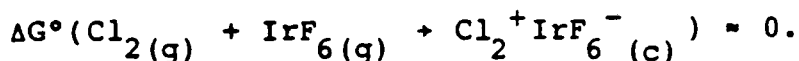
Since the formula unit volume of Cl_2 in the solid phase is 57.7 $Å^3$ (R.G. Wykoff, Crystal Structures Vol. 1, Interscience Publishers New York, London, 1969) and that of IrF_6 is 105.4 $Å^3$ (S. Siegel and D.A. Northrop, Inorg. Chem., 5 (1966) 2187) the formula unit volume of the salt $Cl_2^+IrF_6^-$ should be close to that volume sum, which is 163 $Å^3$. From the lattice enthalpy-cube root of volume relationship (see EXPERIMENTAL), $\Delta H_L°(Cl_2IrF_6^-) = 535$ kj mole^{-1}. From tabulated data (ref. 14) $S°(Cl_{2(g)}) = 223$, $S°(IrF_{6(g)}) = 358$ and $S°(Cl_2^+IrF_{6(c)}^-)$, estimated from the $S°$-formula unit volume relationship (equation 9) to be 300 j mole^{-1}K^{-1},

$$\Delta S°(Cl_{2(g)} + IrF_{6(g)} \rightarrow Cl_2^+IrF_{6(c)}^-) = -281 \pm 30 \text{ j mole}^{-1}K^{-1}.$$

Therefore since $T\Delta S°$ for this process at room temperatures must be -84 ± 9 kj mole^{-1}, this provides a measure of $\Delta H°$ for that reaction. From these estimates and $\Delta H°(Cl_{2(g)} \rightarrow Cl_{2(g)}^+ + e^-) = 1108$ kj mole^{-1} (ref. 37):

$$\Delta H°(IrF_{6(g)} + e^- \rightarrow IrF_{6(g)}^-) = 657 \pm 18 \text{ kj mole}^{-1}.$$

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