are usually lower than equatorial frequencies,[18] it would seem reasonable to assign the higher frequencies 962, 906 (Raman), and 937 cm^{-1} (infrared) to the equatorial P–F vibrations and 741 (Raman) and 795 cm^{-1} (infrared) to the axial vibrations. The ring vibrations involving axial and equatorial P–N bonds may well follow a similar pattern. The very strong peak at 937 cm^{-1} in $(CH_3NPF_3)_2$ occurs as a doublet, both in the vapor phase at low pressure with maxima at 933 and 937 cm^{-1} (Figure 1) and in CS_2 solution with maxima at 930 and 920 cm^{-1} (Figure 2). The doublet could plausibly arise from Fermi resonance with one of the combination bands which may appear in this region, *e.g.*, $\nu_8 + \nu_{25}$ (627 + 315), or by mixing with another fundamental mode (skeletal or associated with the CH_3 vibrations). The calculation shows that the P–F and even more the P–Cl stretching vibrations are mixed with other skeletal motions.

(5) The low-frequency skeletal modes involving the various angular motions are more difficult to identify with certainty. These fundamentals fall in the same region and it is apparent from the PED parameters obtained that they are strongly coupled. When several groups were involved in a vibration the rather broad description "skeletal" is given in Tables III and IV. The lower frequencies observed in the infrared spectra of the fluorine and chlorine compounds at 75 and 62 cm^{-1}, respectively, were assigned to the ring torsional modes. The PED parameters for these two frequencies showed that they were almost pure torsional bends with contributions of only a few per cent from the other symmetry coordinates. No evidence was found of a band in the far-infrared spectrum of either compound that could be confidently associated with the torsional vibration of the methyl group. This vibration is likely to occur at a very low frequency since for $(CH_3NPF_3)_2$ and $(CH_3NPCl_3)_2$ a sixfold potential function is expected, for which the potential barriers are usually small.[19]

(6) A few weak infrared bands and Raman lines below 1000 cm^{-1} that have not been assigned to fundamental frequencies were satisfactorily interpreted as overtones or combinations of the fundamentals (see Tables I and II). All the bands observed above 1500 cm^{-1}, which must be overtones except for the hydrogen stretching vibrations, have been omitted from the tables.

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[18] E. L. Muetterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, **2**, 613 (1963).

[19] W. G. Fateley and F. A. Miller, *Spectrochim. Acta*, **19**, 611 (1963).

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Hydrazinium(+2) Hexafluorometalates(IV) and -(V) in the 4d and 5d Transition Series[1,2]

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The reactions of hydrazinium(+2) fluoride with some transition metal hexafluorides in hydrogen fluoride were studied at room temperature. Complex fluorides of the type $N_2H_6(MF_6)_2$ and $N_2H_6MF_6$, where M = Mo, Tc, Re, or Os, were obtained depending on which reactant was used in excess. No reaction occurs with tungsten hexafluoride. Infrared absorption frequencies and magnetic susceptibilities of these solid compounds are given. The $N_2H_6MF_6$ (M = Mo, Tc, Re) complexes are of body-centered cubic symmetry with a_0 = 10.55, 10.48, and 10.49 A, respectively. The other compounds are of lower symmetry. The end products of the thermal decompositions of these materials are the metals. For the tetravalent compounds, reduction is quantitative, while for the pentavalent compounds only partial recovery of the metals was observed owing to the volatilization of unknown intermediate products.

Introduction

Hydrazinium(+2) fluoride represents with its reducing properties and ability to form a bivalent cation an interesting substance to treat with hexafluorides. For example, reactions with uranium hexafluoride yield different complexes of lower oxidation number depending on the reaction conditions used.[4,5] The high dielectric constant, wide liquid range, and relative inertness of anhydrous hydrogen fluoride make this solvent a particularly suitable medium for these reactions. The transition metal hexafluorides do not ionize appreci-

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] Part of this paper was presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., Sept 1966.

[3] On leave from the Nuclear Institute "Jozef Stefan," Ljubljana, Yugoslavia.

[4] B. Frlec, B. S. Brčić, and J. Slivnik, *Inorg. Chem.*, **5**, 542 (1966).

[5] B. Frlec and H. H. Hyman, *ibid.*, in press.

ably in this otherwise effective polar solvent.[6] The hydrazinium(+2) ion is the only important cationic species in hydrogen fluoride solutions of hydrazinium(+2) fluoride.

Until now the only known pentavalent metal fluoro complexes were those with alkali metals or ammonia. The bivalent hydrazinium(+2) cation would be expected from a structural standpoint to form different compounds. Moreover, the thermal decompositions of such compounds would be interesting because of the reducing properties of hydrazine.

We have extended the previous work on hydrazinium(+2) fluorouranates(V) to several 4d and 5d transition metal hexafluorides. The reactivity of these fluorides increases toward the more electronegative side of the periodic table and also increases within a given group of elements with increasing atomic number.[7,8] The ability to form lower valent hydrazinium(+2) fluoro complexes might therefore be used as a good criterion for the reactivity of a particular hexafluoride.

In particular, the reactions of hydrazinium(+2) fluoride with the hexafluorides of molybdenum, technetium, tungsten, rhenium, and osmium were investigated. All, except tungsten hexafluoride, react to form both four- and five-valent complexes. Wherever possible, a number of physical properties such as infrared spectra, magnetic susceptibilities, and X-ray diffraction powder data were obtained to characterize these compounds and to establish comparisons with previously known compounds of similar oxidation number.

Experimental Section

Most of the experimental details and techniques used in this work have been described previously.[5] The tungsten and molybdenum hexafluorides (High Purity Material, General Chemicals Division, Allied Chemical Co.) were purified by repeated vacuum sublimations at −78°.[9] Rhenium, technetium, and osmium hexafluorides were prepared by fluorinations of the metals with fluorine and purified as mentioned above.

Reactions were carried out in all-Kel-F systems. In general, mixtures of the hexafluoride and hydrogen fluoride were distilled onto hydrazinium(+2) fluoride cooled with liquid nitrogen. The reaction mixture was warmed up to room temperature with continuous agitation, the evolved gases were measured and pumped off, and finally all volatile constituents were removed. The solids remaining were extremely sensitive to traces of moisture and were therefore handled in a drybox.

Reaction stoichiometries were followed by measuring the amounts of evolved gases and the weights of reactants and products.

Chemical analyses of these materials present a severe problem. No reliable results were obtained, presumably because of formation of complex hydrolysis products of unknown composition to which standard methods of analysis were inapplicable. However, the consistency of the results of gas evolution and weight changes combined with evaluation of their physical properties left no doubt that the compounds of stated composition were obtained.

Infrared spectra were recorded on a Beckman IR-12 spectrophotometer using Nujol mulls on silver chloride windows.

X-Ray diffraction powder patterns were obtained using Cu Kα radiation with a Phillips 114.56-mm diameter camera. Line intensities were estimated visually.

The thermal decompositions were run on a Mettler Recording Vacuum Thermoanalyzer using a macro dta–tga stick with alumina cups. In the isothermal decomposition studies, samples were heated up to a desired temperature at a heating rate of 2°/min and kept at that temperature until a constant weight was recorded. The measured weight losses were corrected for buoyancy effects obtained on an empty container in a calibration run.

Magnetic susceptibilities were measured using the Faraday method with the samples packed into thin-walled screw-capped Kel-F capsules. The apparatus and measuring techniques have been described elsewhere.[10] Diamagnetic corrections were applied using the susceptibility of molybdenum hexafluoride[11] for the 4d and that of tungsten hexafluoride[12] for the 5d series. A correction for the diamagnetism of the hydrazinium(+2) ion of -14×10^{-6} cgsu mole^{-1} was also applied.[13]

From the slope σ of a plot of $1/\chi'_M$ *vs.* T, the Weiss constant θ was calculated if a linear relationship obtained. The effective magnetic moment, μ_{eff}, was then calculated from the expression $\mu_{eff} = 2.828\sqrt{\sigma}$. In cases where the Curie–Weiss law was not obeyed, the magnetic moment was calculated as $\mu_{eff} = 2.828\sqrt{\chi'_M T}$.

Results and Discussion

The conditions and products of the reactions of hydrazinium(+2) fluoride with the investigated hexafluorides in hydrogen fluoride are summarized in Tables I–IV. The compositions of the products were obtained from the material balances and other observations. The calculated quantities obtained were based on equations given later.

Table I

Conditions and Products of the $N_2H_6F_2$–MoF_6 Reaction in Hydrogen Fluoride

Starting mole ratios $N_2H_6F_2$:MF_6:HF and reaction conditions	Material balance: mg of product/mmole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of MF_6	Product compn (color)
1.00:2.06:80 25°, 7 days	304			$N_2H_6(MoF_6)_2$ (yellow)
1.00:1.95:78 25°, 3 days	297	0.307		$N_2H_6(MoF_6)_2$ (yellow)
1.00:0.806:75 25°, 3 days	212	0.299	0.372	$N_2H_6(MoF_6)_2$ (yellow) $N_2H_6F_2 \cdot n$HF (brown) $N_2H_6MoF_6$
1.00:0.662:92 25°, 2 days	178	0.194	0.294	$N_2H_6(MoF_6)_2$ (brown) $N_2H_6MoF_6$ $N_2H_6F_2 \cdot n$HF
Calculated Quantities				
1.00:1.33 *n*	303	0.333	0.250	$N_2H_6(MoF_6)_2$
1.00:0.66:*n*	162	0.333	0.500	$N_2H_6MoF_6$

It should be mentioned that hexafluoride solutions in hydrogen fluoride react with the Kel-F reaction vessels. Extensive discoloration of this transparent material was observed, especially with the more reactive hexafluorides. In Kel-F the reactivity increases as: $WF_6 \ll MoF_6 < ReF_6 < OsF_6 < TcF_6$.

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(7) T. A. O'Donnell and D. F. Stewart, *ibid.*, **5**, 1434 (1966).

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(13) B. Frlec, unpublished data.

TABLE II

CONDITIONS AND PRODUCTS OF THE $N_2H_6F_2$–TcF_6 REACTION IN HYDROGEN FLUORIDE

Starting mole ratios $N_2H_6F_2:MF_6:HF$ and reaction conditions	Material balance: mg of product/mmole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of MF_6	Product compn (color)
1.00:1.28:118 25°, several hours	295	0.34	0.268	$N_2H_6(TcF_6)_2$ (yellowish orange) $N_2H_6TcF_6$
1.00:0.66:116 25°, several hours	171	0.335	0.504	$N_2H_6TcF_6$ (brown)
Calculated Quantities				
1.00:1.33:n	306	0.333	0.250	$N_2H_6(TcF_6)_2$
1.00:0.66:n	165	0.333	0.500	$N_2H_6TcF_6$

TABLE III

CONDITIONS AND PRODUCTS OF THE $N_2H_6Fe_2$–ReF_6 REACTION IN HYDROGEN FLUORIDE

Starting mole ratios $N_2H_6F_2:MF_5:HF$ and reaction conditions	Material balance: mg of product/mmole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of MF_6	Product compn (color)
1.00:2.15:n 25°, 4 days	431	0.336	0.252	$N_2H_6(ReF_6)_2$ (yellow)
1.00:0.78:72 25°	342	0.378	0.483	$N_2H_6(ReF_6)_2$ 29% $N_2H_6ReF_6$ 71% (light brown)
1.00:0.66:75 25°	218	0.29	0.437	$N_2H_6ReF_6$ (gray-brown)
Calculated Quantities				
1.00:1.33:n	423	0.333	0.250	$N_2H_6(ReF_6)_2$
1.00:0.66:n	223	0.333	0.500	$N_2H_6ReF_6$

TABLE IV

CONDITIONS AND PRODUCTS OF THE $N_2H_6F_2$–OsF_6 REACTION IN HYDROGEN FLUORIDE

Starting mole ratios $N_2H_6F_2:MF_6:$ HF and reaction conditions	Material balance: mg of product/mmole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of $N_2H_6F_2$	Material balance: Gas evolution: Mole of N_2/mole of MF_6	Product compn (color)
1.00:2.35:317 25°, several hours	434	0.33		$N_2H_6(OsF_6)_2$ (light violet)
1.00:2.86:392 25°, several hours	434	0.36		$N_2H_6(OsF_6)_2$ (light violet)
1.00:1.33:96 25°, several hours	422	0.334	0.254	$N_2H_6(OsF_6)_2$ (light violet)
1.00:0.66:172 25°, several days	240	0.32	0.48	$N_2H_6OsF_6$ (beige)
1.00:0.44:109 25°, several days	172	0.23	0.53	$N_2H_6OsF_6$ + $N_2H_6F_2 \cdot nHF$ (beige)
Calculated Quantities				
1:1.33:n	428	0.33	0.25	$N_2H_6(OsF_6)_2$
1:0.66:n	225	0.33	0.50	$N_2H_6OsF_6$

Molybdenum Hexafluoride Reaction.—A deep yellow solution was formed immediately after the reaction mixture was warmed up to room temperature. Bright yellow crystalline needles, extremely soluble in hydrogen fluoride, were isolated from this solution. In the presence of excess hydrazinium(+2) fluoride such a solution turned gradually deep brown at room temperature, a brown precipitate deposited, and additional gas evolution was observed. In order to purify it, the second deep brown product was washed repeatedly with fresh hydrogen fluoride.

Both materials isolated are extremely sensitive to moisture. In moist air momentarily a blue-black material is formed. With water, however, a clear reddish brown solution was obtained and vigorous gas evolution was observed. Such hydrolytic behavior is characteristic of molybdenum(V) compounds.[14] The brownish hydrated oxide, $MoO_2 \cdot nH_2O$ is the end product of hydrolysis.

Technetium Hexafluoride Reaction.—Gradual addition of the hexafluoride to hydrogen fluoride established that its solubility at room temperature is approximately 0.89 mole of TcF_4/1000 g of HF. This result is corrected for the amounts of solvent and solute in the vapor phase over the saturated colorless solution. The solubility of technetium hexafluoride is similar to that of the other metal hexafluorides in hydrogen fluoride.[6]

Upon reaction with hydrazinium(+2) fluoride, a straw-colored solution is formed immediately after warming the frozen reaction mixture of both reactants in hydrogen fluoride. The yellowish orange reaction product seems to decompose at room temperature into a brown solid, probably because of the presence of slight excess of the reducing fluoride in the product.

Tungsten Hexafluoride Reaction.—No reaction was observed with hydrazinium(+2) fluoride either in hydrogen fluoride or without solvent. A brownish material was obtained after 2 weeks of contact, indicating possible fluorotungstate formation. However, the product consisted almost entirely of hydrazinium(+2) fluoride.

Rhenium Hexafluoride Reaction.—A deep yellow solution was formed when the reaction mixture was warmed up to room temperature. Very soluble yellow crystalline needles were isolated from such a solution. In the presence of excess hydrazinium(+2) fluoride, a gray-brown precipitate was formed and more nitrogen was evolved slowly at room temperature. If additional rhenium hexafluoride was allowed to react with the brown material, a clear deep yellow solution was again obtained.

The yellow material reacts vigorously with water evolving gas and yielding a black finely divided precipitate. Upon acidification with nitric acid, a yellow solution results. The gray-brown material, on the other hand, reacts with water to form a brown solution which turns lighter when treated with nitric acid. The hexafluororhenate(V) hydrolysis products are probably mixtures of brown hydrated rhenium dioxide, perrhenic acid, a small amount of hexafluororhenate(IV), and hydrofluoric acid.[15]

Osmium Hexafluoride Reaction.—Within a few minutes after the reaction mixture was warmed to room temperature, a pale violet solution was formed accompanied by vigorous gas evolution. The solubility

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(14) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 4212 (1957).

(15) R. D. Peacock, *ibid.*, 467 (1957).

Table V

Infrared Absorption Frequencies of Some Hydrazinium(+2) Hexafluorometalates(V) and -(IV)[a]

$N_2H_6(UF_6)_2$[b]	$N_2H_6(MoF_6)_2$	$N_2H_6(ReF_6)_2$	$N_2H_6(OsF_6)_2$	$N_2H_6MoF_6$	$N_2H_6TcF_6$	$N_2H_6ReF_6$	$N_2H_6OsF_6$	Tentative assignment
			570 w, sho	540 b	545 vs	540 vs	550 vs	ν_3 MF_6^{2-}
526 vs, b	620 vs, b	627 vs, b	640 vs, b	600 b				ν_3 MF_6^-
		950 sho		980 vw	970 w, b			M–O
	1034 m		1035 sho	1025 m			1050 sho	
	1084 s	1072 s, sh	1065 s, sh		1095 sho	1065 sho	1085 s, sh	NH_3^+ rock
1123 vs, sh			1100 sho	1120 s	1122 s	1120 s	1120 sho	
1530 s	1515 s	1527 s	1520 s	1515 s	1510 m	1505 s	1528 m	H–N–H def
1580 s	1565 s	1570 s	1550 s	1535 s	1570 m	1575 w	1550 m	
3100 3150 b, sho	3000 3200 vb, sho	3150 b, sho	3000 3150 vb, sho		3100 b, s		3100 b, sho	NH str

[a] Intensity: vs, very strong; s, strong; m, medium; w, weak. Shape: sh, sharp; sho, shoulder; b, broad. [b] Reference 2.

of the pale violet needle crystals isolated from this solution, identified as $N_2H_6(OsF_6)_2$, exceeds 0.34 mole/1000 g of HF at room temperature. In the presence of excess hydrazinium(+2) fluoride, the reduction proceeds slowly further, more nitrogen is evolved, and a light brown, not very soluble product is formed.

The hydrolysis of the violet material is violent, yielding immediately a black, colloidal solution possessing an odor characteristic of osmium tetroxide. The beige materials, on the other hand, form brown, stable solutions upon hydrolysis. The hydrolytic behavior seems to be complicated, in this case, by the presence of reducing hydrazinium salt. Hexafluoroosmates(V) are expected to dissolve in water without reaction,[16] being apparently on the borderline between powerful oxidizing agents, MF_6^- ions in group VIII, and MF_6^- in groups VI and VII with at least one unoccupied d orbital.

The infrared absorption frequencies observed with the solid products are listed in Table V. The spectrum of hydrazinium(+2) bishexafluorouranate(V) is added for comparison. The observed frequencies in the metal–fluorine bond stretching region agree with those expected for the ν_3 stretching frequency of octahedrally coordinated central metal atoms. As might be expected, the frequencies for a given central metal atom are shifted progressively toward longer wavelengths as lower valence states are attained.

Some of the frequencies agree with previously observed absorptions[17] and some of them (MoF_6^{2-}, TcF_6^{2-}) were observed here for the first time. The ν_3 value of 640 cm^{-1} for the hexafluoroosmate(V) disagrees with the previously reported value of 612 cm^{-1}.[17] However, this new value fits better the observed trends in the 3d transition series.[17] The X-ray diffraction powder patterns of hydrazinium(+2) hexafluoromolybdate(IV), technetate(IV), and rhenate(IV) can each be indexed on the basis of cubic symmetry. However, reference to Table VI shows that many lines of moderate intensity, primarily at small angles, cannot be included in this indexing. The similarities of the patterns, as far as assignment of indices is concerned, leads us to believe that the extra lines, which are not repeated in the various patterns, arise from impurities in the samples. Hence, the indexing given in the table is based on this assumption. If the 111 reflection from the molybdenum complex is eliminated on this basis, all patterns index as body-centered cubic with the dimensions: $N_2H_6MoF_6$, a_0 = 10.55 A; $N_2H_6TcF_6$, a_0 = 10.48 A; $N_2H_6ReF_6$, a_0 = 10.49 A.

Table VI

X-Ray Powder Diffraction Data of Some Hydrazinium(+2) Hexafluorometalates(IV)

$N_2H_6MoF_6$, a = 10.55 A		$N_2H_6TcF_6$, a = 10.48 A		$N_2H_6ReF_6$, a = 10.49 A	
d, A	*I*	*d*, A	*I*	*d*, A	*I*
8.35	5	5.25	7	5.31	5
5.85	5	3.68	7	5.17	9
5.25	8	3.20	3	4.07	4
4.82	2	3.02	4	3.74	5
4.12	2	2.80	2	3.67	9
3.86	3	2.62	2	3.01	6
3.71	9	2.46	3	2.78	1
3.89	5	2.34	4	2.61	5
3.04	4	2.22	4	2.46	4
2.81	3	2.13	6	2.33	7
2.61	3	1.85	5	2.22	4
2.48	3	1.74	6	2.13	9
2.36	4	1.65	5	2.04	4
2.25	4	1.57	5	1.85	7
2.15	6	1.51	4	1.74	6
2.07	4	1.45	5	1.64	6
1.89	3	1.40	5	1.58	6
1.86	4			1.51	5
1.75	5			1.45	6
1.67	4			1.40	7
1.59	4				
1.52	2				
1.46	4				
1.41	5				

The same situation does not hold for the corresponding hexafluorometalates(V) and the hexafluoroosmate(IV). The patterns are reproducible; however, it is evident that these compounds are not isostructural. The patterns[18] are quite complicated and attempts to resolve the symmetry by single-crystal techniques failed, because of the extreme difficulties of manipulating these materials.

The results of the magnetic susceptibility measurements are listed in Table VII. The room-temperature magnetic moments are given, and whenever the Curie–

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[16] R. D. Peacock, *Progr. Inorg. Chem.*, **2**, 222 (1960).

[17] R. D. Peacock and D. W. A. Sharp, *J. Chem. Soc.*, 2762 (1959).

[18] These data are available from the authors upon request.

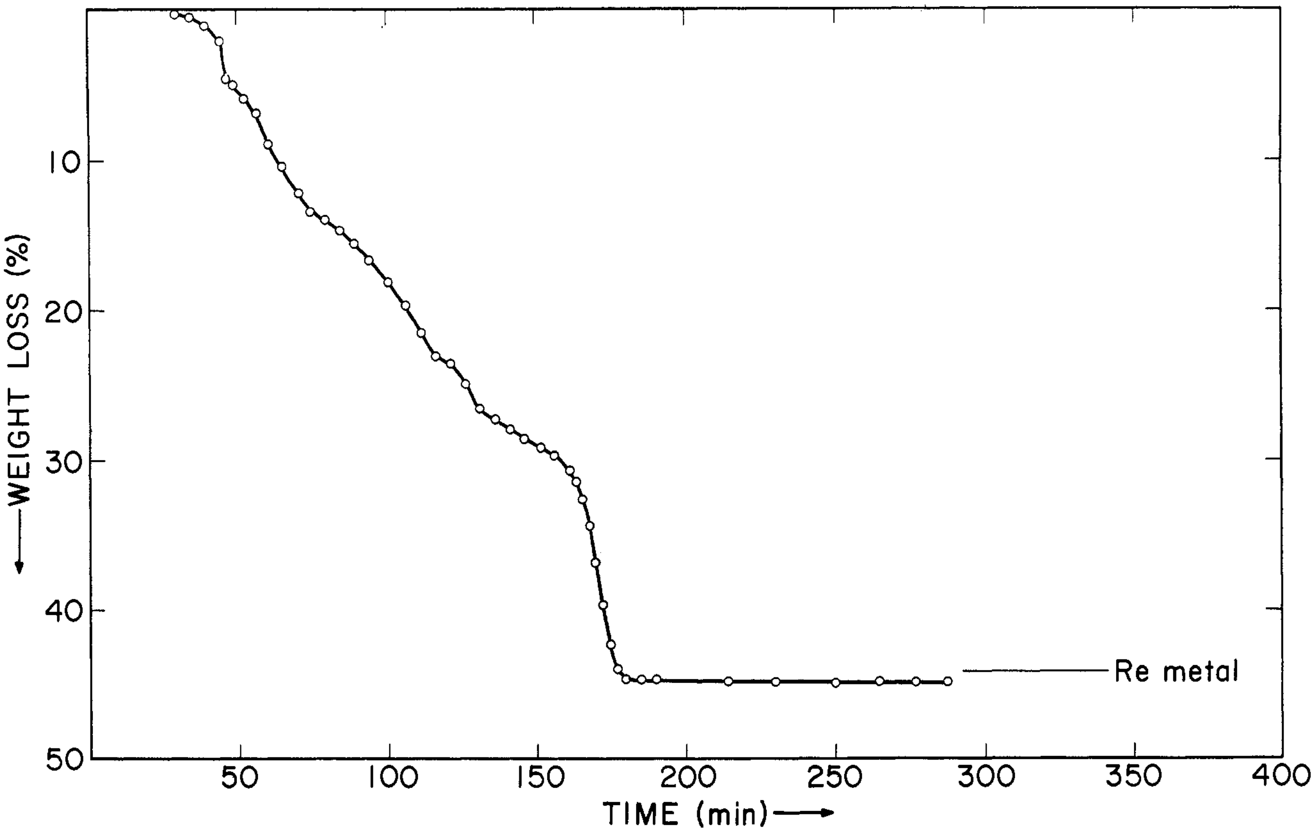

Figure 1.—Thermal decomposition of hydrazinium(+2) hexafluororhenate(IV) in an argon atmosphere, 6 l./hr; heating rate 2°/min.

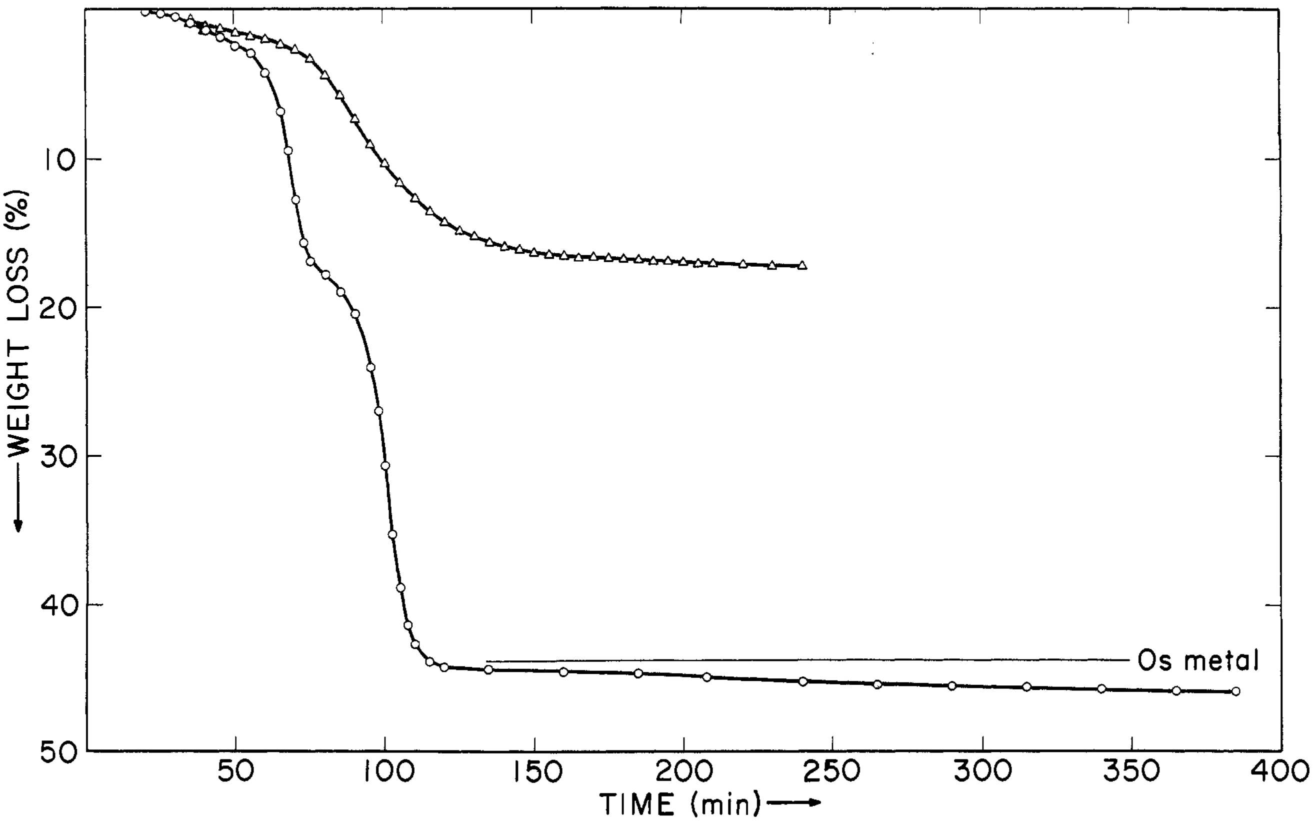

Figure 2.—Thermal decomposition of hydrazinium(+2) hexafluoroosmate(IV) in an argon atmosphere, 6 l./hr; heating rate: ○, dynamic run, 2°/min; △, isothermal run, 150°.

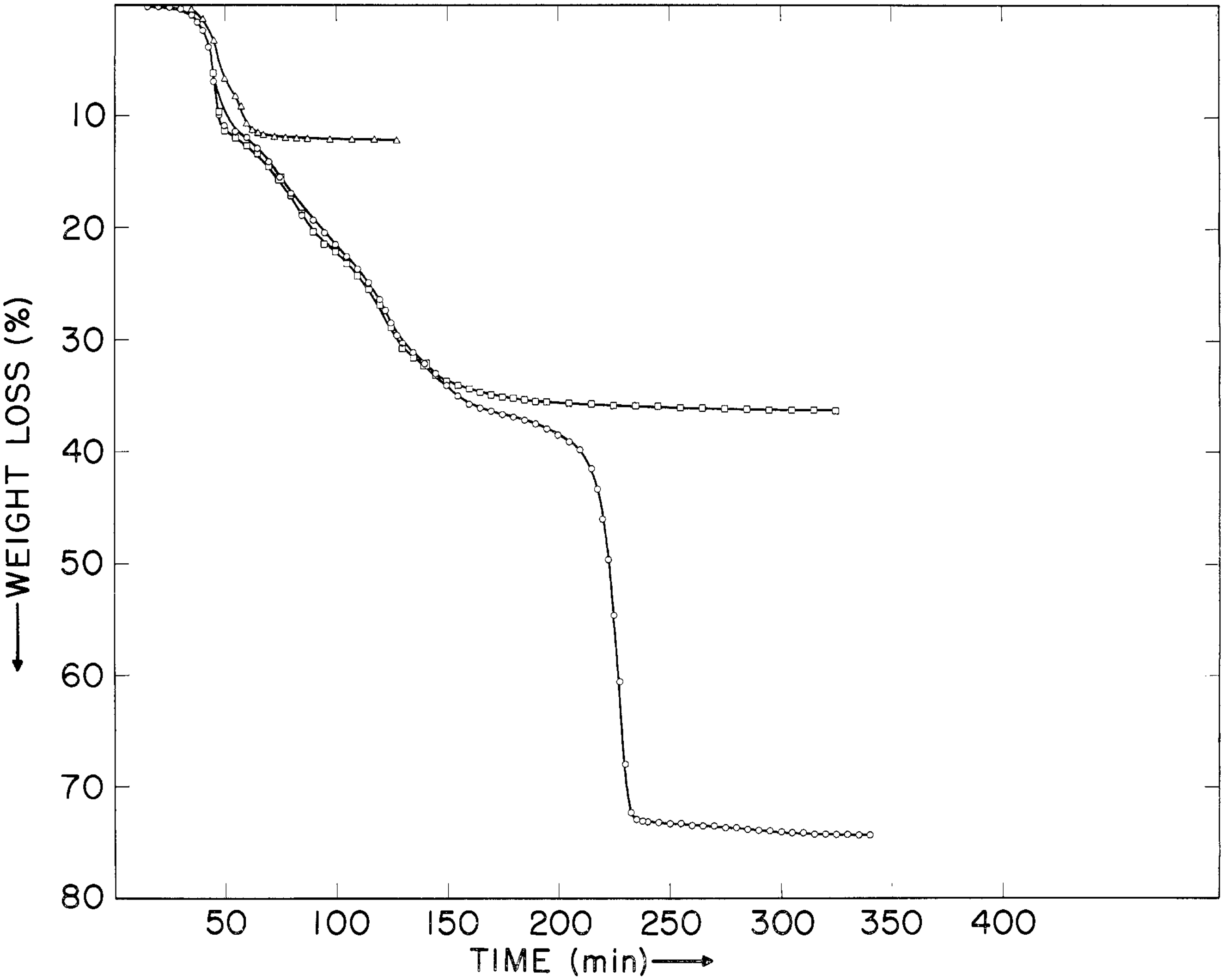

Figure 3.—Thermal decomposition of hydrazinium(+2) bishexafluororhenate(V) in an argon atmosphere, 6 l./hr; heating rate: O, dynamic run, 2°/min; △, isothermal run, 110°; □, isothermal run, 310°.

Table VII

The Magnetic Susceptibilities of Some Hydrazinium(+2) Hexafluorometalates(V) and -(IV)

Temp, °K	$10^3\chi'_M$, cgsu mole^{-1}					
	N_2H_6-$(MoF_6)_2$	N_2H_6-TcF_6	N_2H_6-$(ReF_6)_2$	N_2H_6-ReF_6	N_2H_6-$(OsF_6)_2$	N_2H_6-OsF_6
298		6.041				
295	2.712		1.970	4.556		1.697
296					10.16	
243.3	2.947	7.114	2.145	5.261	11.70	1.876
195	3.187	8.580		6.243		2.101
145	3.686	11.329	2.628	7.810	16.66	2.374
77.4	5.119	21.06	3.205	13.006	25.13	3.724
63.2	6.557	26.20	3.431	15.296	28.74	4.462
4.2	72.716		6.704			35.257

The Room Temperature Magnetic Moments for Some Hydrazinium(+2) Hexafluorometalates(V) and -(IV)

	μ_{eff}^{300}, BM	θ, °K
$N_2H_6(MoF_6)_2$	2.54	
$N_2H_6TcF_6$	3.79	52 (200–300°K)
$N_2H_6(ReF_6)_2$	2.13	
$N_2H_6ReF_6$	3.27	74
$N_2H_8(OsF_6)_2$	4.89	90 (140–300°K)
$N_2H_6OsF_6$	2.29	

[a] χ'_M = molar magnetic susceptibility corrected for the diamagnetism.

Weiss law is obeyed, values of the Weiss constant and the temperature range of validity are listed.

The magnetic susceptibility of the molybdenum(V) complex does not follow the Curie–Weiss law. The observed magnetic moment at room temperature is very large compared with magnetic moments of the alkali hexafluoromolybdates(V), which tend to be not much lower than the spin-only values.[19]

The magnetic moments of the technetium(IV) and rhenium(IV) complexes appear to be normal. They are slightly lower than the spin-only value for three unpaired electrons (3.88 BM), and the Weiss constants indicate that some magnetic interaction takes place. The magnetic moment of the rhenium complex is similar to that of the alkali fluororhenium(IV) complexes[19] and is somewhat lower than that of the corresponding technetium compound, presumably because of the large spin–orbit coupling constant of Re^{4+} (λ ~1000 cm^{-1}) compared to that of Tc^{4+} (λ ~400 cm^{-1}).[20]

The observed magnetic moment for the rhenium(V)

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(19) G. B. Hargreaves and R. D. Peacock, *J. Chem. Soc.*, 3776 (1958).

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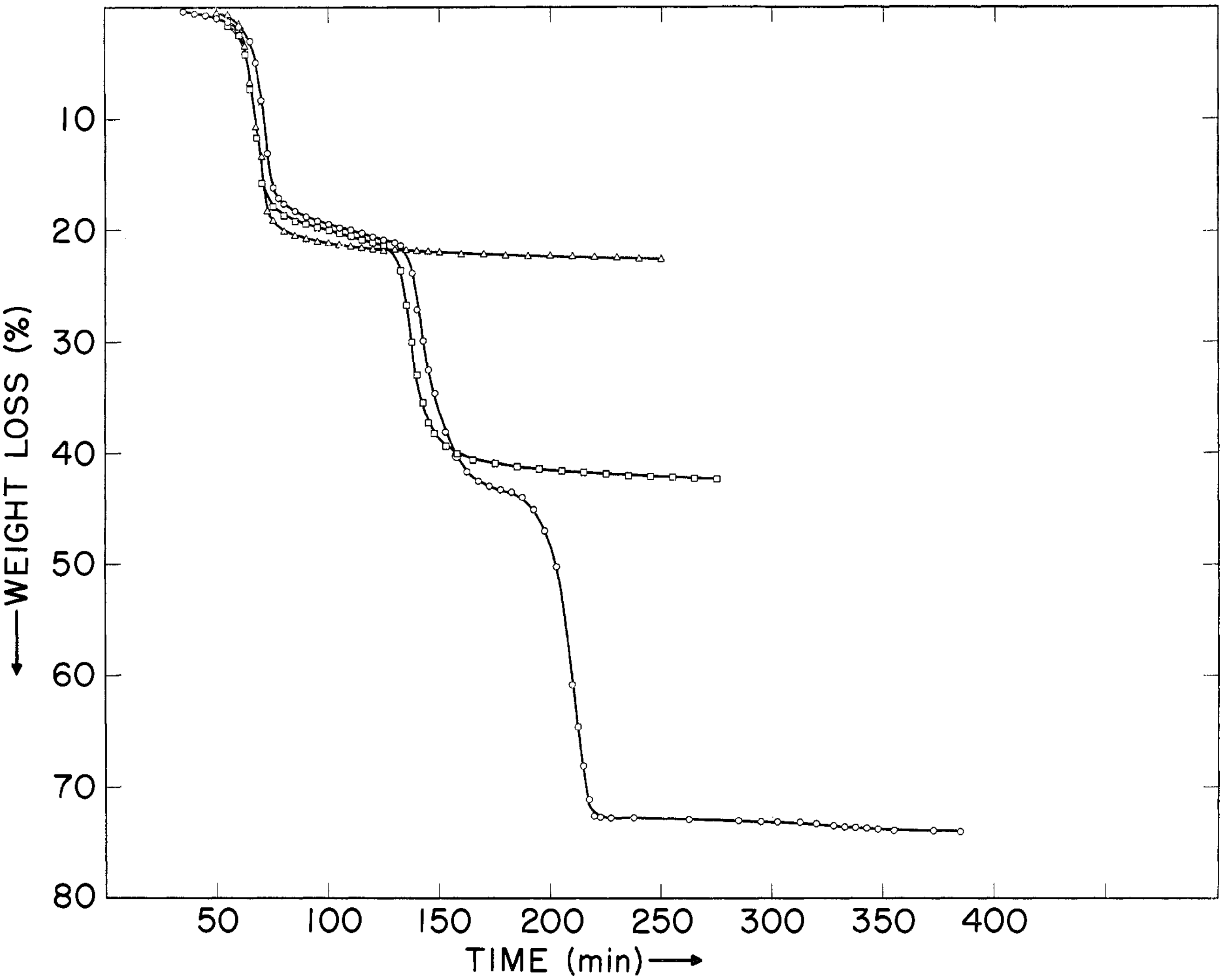

Figure 4.—Thermal decomposition of hydrazinium(+2) bishexafluoroosmate(V) in an argon atmosphere, 6 l./hr; heating rate: ○, dynamic run, 2°/min; △, isothermal run, 155°; □, isothermal run, 315°.

complex is of the order anticipated for the Re^{5+} ion in distorted octahedral stereochemistry.[20] It is considerably larger than those found for the alkali hexafluororhenium(V) complexes (1.53–2.05 BM). In the latter case, however, it was found that the moment is sensitive to the nature of the cation[19] and this may account for the present deviation.

The magnetic moments of the osmium complexes are considerably larger than those obtained previously on corresponding alkali metal complexes. In the case of the alkali metal hexafluoroosmates(IV) the moment appears to depend on the nature of the cation and possibly this accounts for the high moment of the hydrazinium complex, but the magnetic moment of the pentavalent osmium complex is higher than the spin-only value and is at present unexplained. The presence of a more paramagnetic impurity cannot be ruled out.

The thermal decomposition behavior of the newly isolated compounds unfortunately posed more questions than were answered. However, certain remarkable consistencies from one compound to another, the exceptional reproducibility of repeated runs, and agreement between dynamic and isothermal decompositions make it worthwhile to give some of the results. The thermal decomposition curves are given in Figure 1–5.

The hexafluorometalates(IV) of rhenium and osmium are similar in that quantitative reduction to the metal occurs. Both compounds show several poorly resolved steps before final reduction to the metal. In the case of hydrazinium hexafluororhenate(IV), four such steps are discernible while with the osmium(IV) complex only one intermediate step occurs. The nature of the intermediates is unknown, but infrared spectra and X-ray diffraction studies show that they still contain some of the starting materials. The over-all reaction can be represented by

$$N_2H_6MF_6 \longrightarrow M + N_2 + 6HF \ (M = Re, Os) \qquad (1)$$

The bishexafluorometalates(V) of rhenium and osmium also show certain analogies in their thermal decomposition behavior. In both instances X-ray diffraction data show the end products to be the metals. In the case of the rhenium complex, several well-defined as well as some poorly resolved steps occur. None of the intermediates could be identified. However, infrared spectra showed that the first intermediate contained both rhenium(V) and rhenium(IV) as well

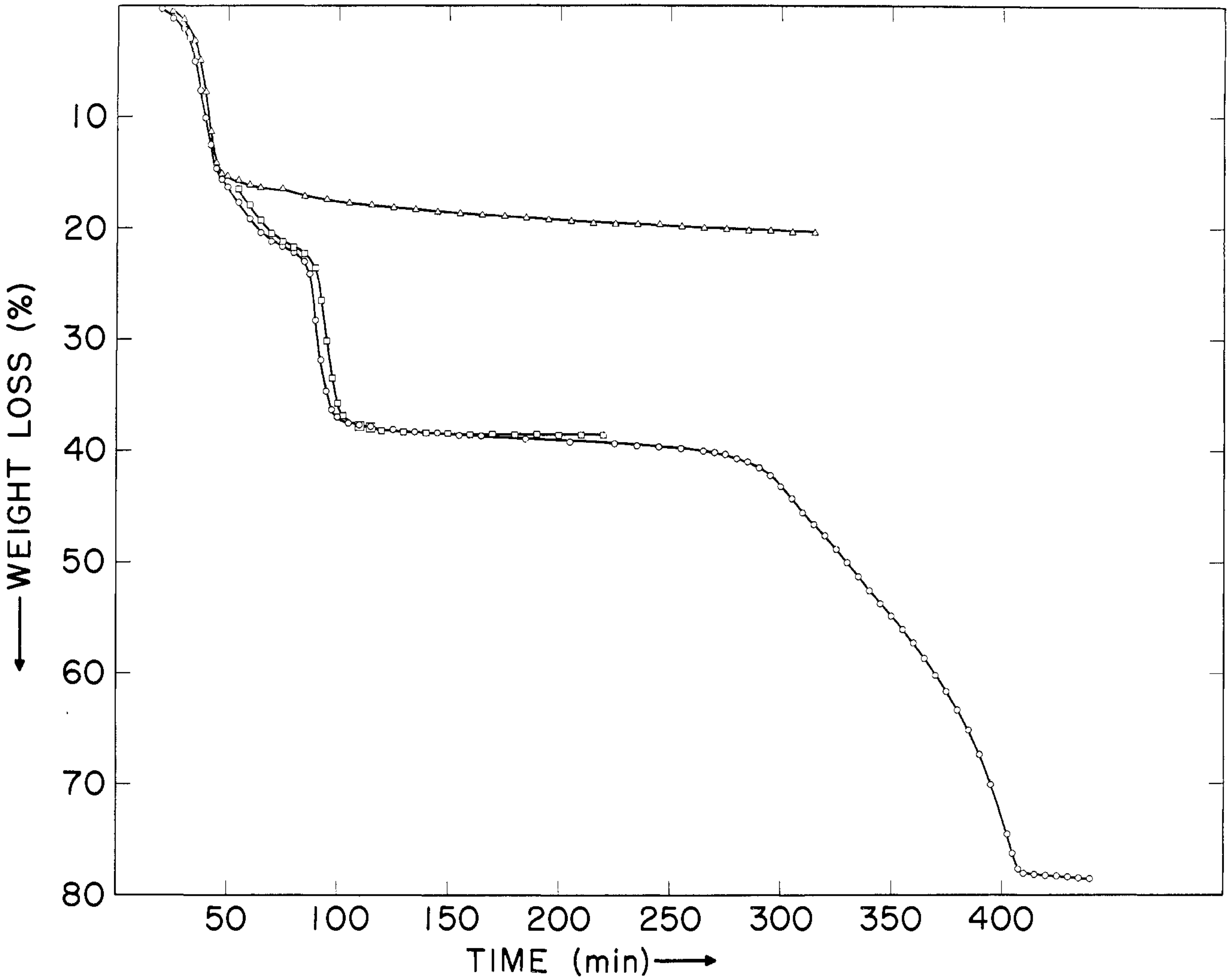

Figure 5.—Thermal decomposition of hydrazinium(+2) bishexafluoromolybdate(V) in an argon atmosphere, 6 l./hr; heating rate: O, dynamic run, 2°/min; Δ, isothermal run, 110°; □, isothermal run, 215°.

as $N_2H_6^{2+}$ ions. Moreover, volatilization, possibly of rhenium pentafluoride, took place during the first step. Later steps still showed the occurrence of volatilization and further products still contained rhenium(V) and rhenium(IV) but no $N_2H_6^{2+}$ ion. However, rhenium metal was present after the first step.

In the thermal decomposition of hydrazinium(+2) bishexafluoroosmate(V), four well-defined steps occur. According to infrared spectra, the product of the first step contains osmium(V), osmium(IV), and $N_2H_6^{2+}$ ions. Volatilization takes place during the second step starting at 250° and ending at 390°. The second intermediate still contains osmium(V), osmium(IV), and $N_2H_6^{2+}$ ions, as well as osmium metal and a new phase which may be a nitridofluoride similar to the known compounds of rhenium and technetium (ReNF, TcNF).[21] The decomposition appears to be nearly complete after a third step ending at 470°.

The decompositions of pentavalent complexes of rhenium and osmium have several common features. In both cases a distinct weight loss of about 1% occurs near 600°. The small weight change suggests that this may be decomposition of a nitride or nitridofluoride to the metal. In both cases, intermediate steps involve volatilization of what are most likely binary metal fluorides. The over-all final percentage weight losses are identical and can be described by

$$8N_2H_6(MF_6)_2 \longrightarrow 7M + 9MF_x\uparrow + \text{other unknown products} \quad (2)$$

where M = Re or Os.

Although the thermal decomposition of the pentavalent molybdenum complex resembles that of the other bishexafluorometalates(V), it differs in that there is no evidence for a nitridofluoride. The overall stoichiometry shows that exactly half of the molybdenum is present as the metal at the end

$$N_2H_6(MoF_6)_2 \longrightarrow Mo + MoF_x\uparrow + \text{other unknown products} \quad (3)$$

The first intermediate appears to contain both molybdenum(V) and molybdenum(IV). The second intermediate, which is stable up to 500°, has only one strong infrared absorption at 535 cm^{-1} and hence may be a binary molybdenum fluoride. Volatilization occurs during the second step.

Although it would have been interesting to observe

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[21] D. W. LaValle, R. M. Steele, and W. T. Smith, Jr., *J. Inorg. Nucl. Chem.*, **28**, 260 (1966).

where the technetium complexes fit into the scheme, these data were not obtained to avoid radioactive contamination of the apparatus.

The foregoing results show that the thermal decompositions are extremely complex. Although internal oxidation–reduction occurs, interpretations are complicated by the volatilization of intermediate products.

Conclusion

The reaction of transition metal hexafluorides with hydrazinium(+2) fluoride in anhydrous hydrogen fluoride can be represented by

$$3N_2H_6F_2 + 4MF_6 \longrightarrow 2N_2H_6(MF_6)_2 + N_2 + 6HF \quad (4)$$

This reaction is fast and is complete within a few minutes at room temperature. The hydrazinium(+2) bishexafluorometalates(V) formed are very soluble in hydrogen fluoride. In the presence of excess hydrazinium(+2) fluoride, the reduction proceeds further

$$3N_2H_6F_2 + 2N_2H_6(MF_6)_2 \longrightarrow 4N_2H_6MF_6 + N_2 + 6HF \quad (5)$$

The second reaction is, however, much slower. It is complete only after several days at room temperature. Hydrazinium(+2) hexafluorometalates(IV) are much less soluble in hydrogen fluoride than the corresponding pentavalent complexes. It is interesting that it is possible to oxidize the freshly formed tetravalent complex to the pentavalent one if the former is treated with an excess of metal hexafluoride in hydrogen fluoride.

The formation of hydrazinium(+2) bishexafluorometalates(V) requires an excess of hexafluoride over that required stoichiometrically by eq 4. If the reaction is carried out with exact stoichiometric amounts, invariably mixtures of the pentavalent and tetravalent complexes result.

The over-all reaction in the presence of excess reducing agent may be written

$$3N_2H_6F_2 + 2MF_6 \longrightarrow 2N_2H_6MF_6 + N_2 + 6HF \quad (6)$$

No evidence was obtained for the formation of hydrazinium(+2) heptafluorometalates(V) in this work, although a compound of that type was isolated with uranium hexafluoride.[4]

Although the crystallographic and infrared data observed are consistent with the expected compound hydrazinium(+2) hexafluoromolybdate(IV) for the final complex isolated in the molybdenum system, we were unable to isolate a pure product, even after repeated washing with hydrogen fluoride. No reliable magnetic data were possible.

In general, the results of this study confirm the trend in reactivities of the transition metal hexafluorides. In particular, the relative inertness of tungsten hexafluorides compared to other hexafluorides was amply demonstrated.

The properties of the hexafluorometalates isolated in this study appear to set this class of compounds apart from the previously known analogous alkali metal complexes. Presumably, the responsibility lies with the unique nature of the hydrazinium(+2) cation.

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The Hexafluoroiodine(VII) Cation, IF_6^+

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The 1:1 adduct between AsF_5 and IF_7 has been investigated. The X-ray powder diffraction pattern of the white, crystalline solid can be indexed in the face-centered cubic system with a = 9.49 A. Density measurements indicate four molecules per unit cell. A pressure–temperature curve gives a heat of reaction, 43.9 kcal mole^{-1}, for the dissociation process: complex (s) = IF_7(g) + AsF_5(g). Infrared and Raman measurements show that $IF_7 \cdot AsF_5$ has the ionic structure, $IF_6^+AsF_6^-$, in the solid state. The IF_6^+ cation has an octahedral configuration (point group O_h). The force constants of IF_6^+ are calculated and compared with those of isoelectronic SbF_6^- and TeF_6. These calculations indicate that the bonding in IF_6^+ is best described by a mainly covalent sp^3d^2 hybridization model.

Introduction

Halogen mono-, tri-, penta-, and heptafluorides exist and their structures are relatively well established. Owing to their amphoteric nature these fluorides can form (by combining with strong Lewis acids and bases) cations and anions containing one F^- ion less or more than the parent molecule. However, the structure of and the bonding in these ions have not been investigated. This group of compounds offers a unique chance to study the influence of the number of free-electron pairs, of coordination number, and of a positive or negative charge at the central atom on the structure and bonding. Therefore, a systematic investigation of these halogen fluoride ions has been initiated.