

Oxidizing Trends in the Third-transition-series Hexafluorides

By NEIL BARTLETT, S. P. BEATON, and N. K. JHA

(*The Department of Chemistry, The University of British Columbia, Vancouver 8, B.C., Canada*)

THE spontaneous oxidation of molecular oxygen¹ and of atomic xenon,² each of which has a first ionization potential³ of 281 kcal. mole⁻¹, by platinum hexafluoride, has established the remarkable oxidizing power of the hexafluoride. None of the other third-transition-series hexafluorides will oxidize these species. Since it is well established^{1,4} that the platinum hexafluoride-oxygen adduct is the salt $O_2^+[PtF_6]^-$, the lattice energy of which is estimated, employing Kapustinskii's second equation⁵ to be ~ -125 kcal. mole⁻¹, the electron affinity of the PtF_6 molecule is required to be >156 kcal. mole⁻¹, to account for the observed exothermic reaction: $PtF_6(g) + O_2(g) \rightarrow O_2^+[PtF_6]^- (c)$. On the other hand, tungsten hexafluoride does not oxidize nitric oxide.⁶ Since³ $I(NO) = 213$ kcal. mole⁻¹ and the lattice energy for a salt $NO^+[MF_6]^-$ would be ~ -125 kcal. mole⁻¹, then the minimum electron affinity of MF_6 , for salt formation, is required to be ~ -90 kcal. mole⁻¹.

The greater electron affinity of PtF_6 , compared with WF_6 , correlates with the greater nuclear charge of the platinum and with the poor shielding of this charge from the ligands by the, formally

non-bonding, t_{2g} electrons. Since the "non-bonding" t_{2g} valence-electron configurations of the hexafluorides are⁷: WF_6 , 0; ReF_6 , 1; OsF_6 , 2; IrF_6 , 3; PtF_6 , 4; a regular increase in oxidizing power is anticipated from tungsten to platinum. The products of the interactions $ON + MF_6$ and $ONF + MF_6$, a summary of which is presented in the Table, support this prediction.

The $NO + MF_6$ (except $NO + WF_6$)⁶ reactions proceed spontaneously at $\sim 20^\circ$. The reactions were followed tensimetrically. Gaseous products were identified by infrared spectroscopy and the solid products were examined by X-ray powder-photography. Both ReF_6 and OsF_6 formed $NO^+[MF_6]^-$ (cub.) salts and neither salt could be induced to combine with more NO to yield the quadrivalent $(NO)_2MF_6$ compound. In their reactions with nitrosyl fluoride at $\sim 20^\circ$, however, the rhenium and osmium fluorides are clearly differentiated; ReF_6 readily forms a thermally stable 2:1 adduct, which is isomorphous with $(NO)_2WF_6$, whereas the $OsF_6 + ONF$ reaction is complex. The identification of small quantities of nitrogen oxide trifluoride,⁸ in the gaseous product of the reaction, indicate the existence of an

unstable, fluorine-donating, reaction intermediate, since this oxyfluoride is not produced from $\text{ONF} + \text{F}_2$ under the reaction conditions of the experiment. The instability of the 2:1 complex, compared with the analogous rhenium compound, can be attributed to the greater polarizing power of the osmium. As may be seen from the crystal data for the $\text{NO}^+[\text{MF}_6]^-$ salts, the OsF_6^- ion is smaller than ReF_6^- .

probable that fluorine is eliminated molecularly: $2[\text{ONIrF}_7] \rightarrow 2\text{ONIrF}_6 + \text{F}_2$. On the other hand the inefficiency of the $\text{ONF} + \text{PtF}_6$ reaction^{4,8} in yielding ONF_3 indicates that the elimination of fluorine from the reaction intermediate is much more rapid than in the iridium case. Of course the electron affinity of PtF_6 (>156 kcal. mole⁻¹) is sufficiently great for the elimination of the fluorine as atoms. Once the fluorine is molecular

TABLE

Products of $\text{MF}_6 + \text{NO}$ and $\text{MF}_6 + \text{ONF}$ reactions occurring at $\sim 20^\circ$

	$\text{MF}_6 + \text{NO}$	Reaction Products	$\text{MF}_6 + \text{ONF}$
WF_6 Crystal data	no reaction	$1:1 \rightarrow$ (a) NOWF_7 ; $1:2 \rightarrow$ (b) $(\text{NO})_2\text{WF}_8$ (a) cub. a_0 , 5.20 Å; (b) complex	
ReF_6 Crystal data	(c) NOReF_6 (c) cub. a_0 , 10.151 Å		$(\text{NO})_2\text{ReF}_8$ isomorphous with (b)
OsF_6 Crystal data	(d) NOOsF_6 (d) cub. a_0 , 10.126 Å	(d) $\text{NOOsF}_6 +$ (e) $\text{NOOsF}_7 + \text{ONF}_3$ (trace) \rightarrow (e) cub. a_0 , 5.14 Å	
IrF_6 Crystal data	(f) $\text{NOIrF}_6 +$ (g) $(\text{NO})_2\text{IrF}_6$ (g) hex., a 10.01; c , 3.53 Å	(f) $\text{NOIrF}_6 + \text{ONF}_3 \uparrow + \text{F}_2 \uparrow$ (f) cub., a_0 , 10.114 Å	
PtF_6 Crystal data	(h) $\text{NOPtF}_6 + \text{F}_2 \uparrow$ (i) $(\text{NO})_2\text{PtF}_6$ (i) hex., a 10.01; c , 3.53 Å	(h) $\text{NOPtF}_6 + \text{F}_2 \uparrow$ (h) cub., a_0 , 10.112 Å	

Iridium hexafluoride like PtF_6 is a sufficiently powerful oxidizer to liberate fluorine^{4,8} in the mildly exothermic 1:1 reaction at 20° , the sole solid product being the salt $\text{NO}^+[\text{IrF}_6]^-$. These reactions are of special interest as being chemical preparations for fluorine which can be carried out at room temperature, using reactants which can be preserved indefinitely at normal temperatures and pressures. Since the enthalpy of dissociation of $\text{ONF}(\text{g}) \rightarrow \text{ON}(\text{g}) + \text{F}(\text{g})$ has been given⁹ as $+55$ kcal. mole⁻¹, ΔH for the process $\text{ONF}(\text{g}) \rightarrow \text{ON}^+(\text{g}) + \text{F}(\text{g}) + e$ is 268 kcal. mole⁻¹. A minimum electron affinity of MF_6 for an exothermic reaction $\text{ONF} + \text{IrF}_6 \rightarrow \text{ON}^+[\text{IrF}_6]^- + \text{F}$ would therefore be -143 kcal. mole⁻¹, although for the liberation of molecular fluorine this would be reduced to ~ -125 kcal. mole⁻¹. The efficient formation of ONF_3 , when an excess of nitrosyl fluoride is employed,⁸ suggests the interaction of the excess of ONF with a reaction intermediate such as ONIrF_7 . Presumably this intermediate does not dissociate to form atomic fluorine; it is

it is no longer available (under the reaction conditions) for the formation of ONF_3 .

On the basis of these reactions it is evident that $E(\text{MF}_6)$ increases regularly in the sequence $\text{WF}_6 < \text{ReF}_6 < \text{OsF}_6 < \text{IrF}_6 < \text{PtF}_6$, with $E(\text{ReF}_6) > -90$ kcal. mole⁻¹, $E(\text{IrF}_6) > -125$ kcal. mole⁻¹ and $E(\text{PtF}_6) > 156$ kcal. mole⁻¹. The increase in E , with unit change in atomic number of M , appears to be ~ -20 kcal. mole⁻¹, hence $E(\text{AuF}_6)$ could be >176 kcal. mole⁻¹. The change in volume of MF_6^- indicated by the relative formula-unit volumes in the $\text{NO}^+[\text{MF}_6]^-$ (cub.) salts: Ta, 133.4; Re, 130.7; Os, 129.8; Ir, 129.3; Pt, 129.2 Å³, shows that the volume of the PtF_6 group is close to a limiting volume. Presumably the AuF_6^- group would be similar in volume to PtF_6^- , but the fluorine electrons of the former would be more highly polarized than in the latter; spontaneous liberation of fluorine might therefore occur.

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