Synthesis, Mass Spectrometric Identification, and Crystallography of Osmium Oxide Tetrafluoride

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Summary Osmium oxide tetrafluoride $OsOF_4$ has been prepared in good yield by the reduction of $OsOF_5$ on a hot tungsten filament and has been characterized by chemical analysis, molecular beam mass spectroscopy, and X-ray crystallography.

Few oxide fluorides of the platinum metals are known.[1,2a] Although a golden-yellow solid which forms in small yield during preparations of OsF_6 has been assigned[2b,3] the stoicheiometry $OsOF_4$, osmium oxide tetrafluoride has not been unequivocally identified. We have prepared $OsOF_4$ in good yield by the reduction of $OsOF_5$ on a hot tungsten filament.[4,5] Static heating of the three elements also gave $OsOF_4$, but with heavy contamination by OsF_5 and an involatile residue.

$OsOF_5$, prepared by oxyfluorination of osmium metal,[6] was reduced using a technique similar to that used by Schröder and Grewe[7,8] for WF_5. $OsOF_5$ was condensed into a Pyrex reactor[4] in which was suspended a coil of tungsten wire which could be heated resistively *via* copper rods brazed to Kovar to Pyrex seals. The reactor was immersed either in an ice bath or in a water bath between 10° and 18°, and the wire was heated to a dull red glow for 30—60 min. A grey-green deposit was removed from the reactor walls by scraping in a dry, oxygen-free atmosphere.

Fused samples, analysed with a fluoride ion electrode, gave F = 26·4 ± 0·6% (required for $OsOF_4$ = 26·9%). Other samples which were dissolved in aqueous sodium hydroxide–sodium hypochlorite solutions and subsequently analysed for osmium by X-ray fluorescence gave Os = 66·5 ± 1·5% (required for $OsOF_4$, 67·4%). X-Ray powder photographs of $OsOF_4$ gave complex patterns indicative of low symmetry. The material did not melt sharply.

Relative abundance of ions from $OsOF_4$ *at* 90°, 70 *eV electron energy*

Ion	Mass[a]	Intensity[b] relative to $OsOF_3^+$ = 100
$OsOF_4^+$	284	22
OsF_4^+	268	6·6
$OsOF_3^+$	265	100
OsF_3^+	249	5·9
$OsOF_2^+$	246	42
OsF_2^+	230	15
$OsOF^+$	227	8·6
OsF^+	211	16
OsO^+	208	5·6
Os^+	192	21

[a] Intensities are compared for ^{192}Os mass peaks. Oxyfluoride peaks also contain contributions from ^{189}Os fluoride ions, for which corrections have been made. [b] Intensities have been adjusted for changes in quadrupole transmission with mass.[10]

Crystals of $OsOF_4$, grown from the vapour at *ca.* 100°, were shown by the X-ray precession method to be orthorhombic: a = 5·56(1) Å, b = 9·56(1) Å, c = 12·83(2) Å, V = 682 Å^3, D_m = 5·50 g cm^{-3}, Z = 8. The only systematic absences noted among the reflections are $h00$ for h odd, and $00l$ for l odd, leading to the most probable space group $D_2^3 \equiv P2_122_1$. The nonstandard orientation is chosen to indicate the close similarity of the cell constants with those found by Mitchell and Holloway[9] for OsF_5, despite the substantially different symmetry, $P2_1/c$. Since 17 Å^3 per oxygen or fluorine atom are available for both species, the presumption is strong that $OsOF_4$ also consists of tetramers, but with structure and/or packing different from that in OsF_5.

The relative abundances of ions from $OsOF_4$ are given in the Table. To obtain this data, a molecular-beam mass spectrometer was used,[10] with a 0·010 orifice on the effusion source. As expected, the most abundant ion is that in which F^- is lost from the parent molecule, $OsOF_3^+$. This mass spectrum is consistent with those of other transition metal fluorides and oxide fluorides and is that to be expected for $OsOF_4$.

A careful mass spectrometric search for $OsOF_4$ oligomers showed none to be present; sensitivity for dimeric ions was >1 in 10^4.

The mass spectrum in conjunction with chemical and physical evidence unequivocally identifies this grey-green compound as $OsOF_4$. The material dissolves in water to give a black precipitate and a solution which is colourless or slightly grey-blue.

We thank C. L. Luke and E. Bloom, jun. for the chemical analyses.

(*Received, 28th June* 1972; *Com.* 1132.)

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