Difluoride Dioxides of Molybdenum(VI) and Tungsten(VI)

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Summary ^{19}F N.m.r. and i.r. spectroscopy, mass spectrometry, and chemical analysis show that MoO_2F_2 is the main product of reaction of MoO_2Cl_2 with anhydrous HF at elevated temperature and pressure or XeF_2 at low temperature, evidence for MoO_2ClF also being obtained in the MoO_2Cl_2–XeF_2 reactions; controlled hydrolysis of WOF_4 gives WO_2F_2, and reaction of the difluoride dioxides with XeF_2 gives $XeF_2{\cdot}MoOF_4$ and $XeF_2{\cdot}WOF_4$.

Although there is spectroscopic evidence for MoO_2F_2 the compound has not been prepared in bulk or properly characterized. In 1907 the analysis of a solid resulting from the reaction of MoO_2Cl_2 with anhydrous HF suggested that the product was MoO_2F_2.[1] More recently it has been claimed as the product of hydrolysis of MoF_6 in HF at −5 °C[2] and the reaction of MoO_3 with IF_5.[3] Evidence for the preparation of bulk WO_2F_2 is even more sparse, there being only one paper which claims synthesis by the hydrolysis of WF_6 in anhydrous HF.[2] We now describe the preparation, isolation, and characterization of MoO_2F_2, together with some of its chemistry, and present good evidence for WO_2F_2.

Stoicheiometric quantities of MoO_2Cl_2 and anhydrous HF were heated at 280—300 °C in a nickel reactor [equation (1)].

$$MoO_2Cl_2 + 2HF \longrightarrow MoO_2F_2 + 2HCl \qquad (1)$$

After 3—4 h volatile material was removed at 0 °C and a pale lilac solid was obtained. A similar product and the expected volume of xenon and chlorine was obtained when stoicheiometric quantities of MoO_2Cl_2 and XeF_2 were warmed to 0 °C in anhydrous HF (equation (2)].

$$MoO_2Cl_2 + XeF_2 \longrightarrow MoO_2F_2 + Xe + Cl_2 \qquad (2)$$

The product does not melt or sublime at temperatures up to 310 °C *in vacuo* and is insoluble in MeCN, $CHCl_3$, $ClF_2{\cdot}CCl_2F$, and propylene carbonate. It is soluble in SO_2ClF and slightly soluble in HF. *X*-Ray powder photography showed that the material is not MoO_3, MoO_2, MoO_2Cl_2, or $MoOF_4$ and elemental analyses suggested the empirical formula MoO_2F_2.

The dominant species in the mass spectrum is $MoO_2F_2^+$ and the main fragmentation pathway is *via* MoO_2F^+, $MoOF^+$, and MoO^+ to Mo^+. The only species observed which were of greater mass than MoO_2F_2 were due to traces of MoO_2FCl^+ (*m/e* 178—188) and $Mo_2O_3F_4^+$ (*m/e* 309—320), the latter suggesting that MoO_2F_2 may be polymeric. This is further supported by the lack of solubility and volatility mentioned earlier.

The i.r. spectrum also evidences a possible polymeric formulation. Features at 993s and 1007w,sh cm^{-1} are identical in shape with the band envelope for the symmetric and asymmetric stretching modes of the MoO_2 unit in gas-phase spectra of MoO_2X_2 (X = F, Cl, or Br)[4] and the frequencies correlate well with data for solid CrO_2F_2,[5] MoO_2Cl_2, and MoO_2Br_2.[6] The broad absorption at 835s cm^{-1} can be assigned to bridging Mo · · · OMo stretching vibrations by comparison with related bands in MoO_3[7] and MoO_2Cl_2.[8] Terminal Mo–F stretching modes at 670s and 695w,sh cm^{-1} and bridging Mo · · · F stretches at 587s and 522w,sh cm^{-1} are similar in frequency to bands in $MoOF_4$.[9]

^{19}F N.m.r. spectra of solutions of MoO_2F_2 in HF and SO_2ClF–HF mixtures show a broad singlet, width 130 Hz at half-height, at −131·5 p.p.m. relative to $CFCl_3$. These compare with signals at −146 and −140 p.p.m. for $MoOF_4$ and $MoOF_5^-$ respectively.

Stoicheiometric quantities of H_2O in anhydrous HF were distilled on to WOF_4 at −196 °C in pre-seasoned FEP tubes. In each case the reactor was warmed slowly by consecutively immersing it in each of a series of low temperature baths at −160, −139, −119, −98, −78, −63, −42, −23, and 0 °C for 30—45 min. Finally, the reactants were brought briefly to room temperature before recooling to −78 °C and slowly removing the HF under reduced pressure [equation (3)].

$$WOF_4 + H_2O \xrightarrow{HF} WO_2F_2 + 2HF \qquad (3)$$

Vibrational spectra of the unstable, off-white solid were poor but demonstrated the absence of WOF_4. The mass spectrum is similar to that of MoO_2F_2, the main fragmentation pathway being $WO_2F_2^+ \rightarrow WO_2F^+ \rightarrow WOF^+ \rightarrow WO^+$. The parent ion of WOF_4 is totally absent whilst WOF_3^+ is less abundant than both $WO_2F_2^+$ and WO_2F^+.

Reaction of stoicheiometric quantities of solid MoO_2F_2 or WO_2F_2 with equimolar quantities of XeF_2 in anhydrous HF gave the tetrafluoride oxides. With excess of XeF_2 the $XeF_2{\cdot}MoOF_4$ and $XeF_2{\cdot}WOF_4$ adducts were formed.[10]

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