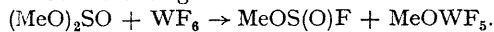


Methoxypentafluorotungsten(VI)

By A. M. NOBLE and J. M. WINFIELD*

(Chemistry Department, The University, Glasgow, W.2)

ALTHOUGH compounds containing the pentafluorosulphur-(VI) group are well known,¹ the only corresponding tungsten compound appears to be WF_5Cl .² The preparation of alkylfluorosulphites from the reactions of WF_6 with dialkyl sulphites³ suggests that alkoxy-pentafluorotungsten compounds should be capable of existence. This has been confirmed by the formation of methoxypentafluorotungsten-(VI) from the reaction between WF_6 and $(MeO)_2SO$ at low temperatures. A quantitative reaction occurs within 10 min. at -30° according to



$MeOWF_5$ is a white solid m.p. $\sim 85^\circ$ which has been characterised by elemental analysis and its mass spectrum. It sublimes readily at 25° (10^{-4} mm.) and decomposes slowly on standing, significant amounts of WOF_4 and MeF being observable after 7 days. At 135° , decomposition is rapid and complete. The thermal stability of $MeOWF_5$ is intermediate between those of $MeOPF_4$, which is stable only below room temperature,⁴ and $EtOTiF_3$ which decomposes at 215° and is polymeric in the solid state and in benzene.⁵

$MeOWF_5$ is soluble in C_6F_6 without decomposition to give a yellow solution; presumably the colour is due to charge transfer. Its ^{19}F n.m.r. spectrum in C_6F_6 is typical of an AX_4 system with F_X at -118.5 , F_A at -89.5 p.p.m. (both from CCl_3F internal), $J(F_A F_X)$ 66 and $J(F_X^{183}W)$ 43 c./sec. The signals due to F_X and the methoxy-group, at -5.60 p.p.m. (from Me_4Si internal) have fine structure due to HF_X coupling of 1 c./sec. The ^{19}F nuclei are more

shielded than those in WF_6 , as expected when fluorine is replaced by the less electronegative methoxy-group,⁶ but the ^{19}F chemical shifts² in WF_5Cl and recent studies of complex fluoro-anions⁷ suggest that other factors are important in the shielding of ^{19}F nuclei. Similar spectra are observed in WF_6 solution and in a partially decomposed melt, indicating that in each case $MeOWF_5$ is monomeric with a square-pyramidal arrangement of fluorine atoms about tungsten. The Raman and i.r. spectra of the solid contain peaks attributable to methoxy- and W-F groups. While the Raman spectrum in C_6F_6 is similar to that of the solid, the present data do not afford an unambiguous determination of the structure of the solid.

In most of the reactions of $MeOWF_5$ that we have studied WOF_4 is produced, although it may be present either as an isolatable complex (*e.g.* with Et_2O) or weakly complexed in solution [*e.g.* by $(MeO)_2SO$]. Methyl fluoride is produced in these reactions, but in the presence of a suitable substrate (*e.g.* benzene), $MeOWF_5$ behaves as a methylating agent. As expected, analogous reactions do not occur with pyridine or C_6F_6 .

Formation of $ROWF_5$ from reactions of WF_6 with sulphite esters appears to be general. $EtOWF_5$ is thermally less stable than $MeOWF_5$ and has been obtained only mixed with WOF_4 , while $PhOWF_5$ is stable at 20° .

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