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Short Communication

Reactions of molybdenum hexafluoride with compounds containing methoxo groups

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The preparation of methoxotungsten(VI) fluorides from tungsten hexafluoride and methylmethoxosilanes or dimethyl sulphite has been reported[1,2]. We now describe some corresponding reactions of molybdenum hexafluoride, which enable comparisons between the two hexafluorides to be made.

MoF_6 reacts with the methylmethoxosilanes $Me_{4-n}Si(OMe)_n$ (n = 1–4) below 0° to give the corresponding fluorosilane, and methyl fluorosulphite is formed from $(MeO)_2SO$ under similar conditions. Solutions of MoF_6 in $Me_{4-n}SiF_n$ or MeOS(O)F are yellow, possibly due to intermolecular charge transfer interactions[3]. Reduction of Mo^{VI}, which occurs when MoF_6 reacts with silicon tetrachloride and other chlorides[4], is not observed, but the identity of the molybdenum-containing products depend on the stoichiometry of the reactions.

An involatile, yellow liquid identified as pentamethoxomolybdenum(VI) fluoride is formed from MoF_6 and a large excess of dimethyldimethoxosilane (reaction 1 in Table 1). Its NMR spectrum (^{19}F, singlet, $\delta = -11.2$ ppm; ^1H doublet relative intensity 4, $\delta = 4.43$ ppm, $J = 1.6$ Hz, and singlet relative intensity 1, $\delta = 4.56$ ppm) is consistent with a monomeric structure. Peaks at 614–512 and 466 cm^{-1} in its IR spectrum, and at 572 and 475 cm^{-1} in its Raman spectrum, are due to Mo–F and Mo–OMe stretching vibrations. The liquid decomposes above 50° to give dimethyl ether, a trace of methyl fluoride and a blue solid.

Reactions of MoF_6 with excess trimethylmethoxosilane or methyltrimethoxosilane (reaction 2) gave only small yields of $MoF(OMe)_5$. The major product is a yellow solid which appears to be predominantly tetramethoxomolybdenum(VI) difluoride. Its ^1H NMR spectrum in C_6F_6 consists of a singlet, $\delta = 4.62$ ppm; its ^{19}F spectrum was not obtained due to its low solubility. A similar product is obtained from MoF_6 and tetramethoxosilane (reaction 3).

The lower members of the series $MoF_{6-n}(OMe)_n$ apparently decompose below 20°. A yellow solid is formed from MoF_6 and $(MeO)_2SO$ (reaction 4) but this decomposes at −20° giving molybdenum oxotetrafluoride and MeF. By analogy with the corresponding reaction of WF_6[2], the solid is believed to be methoxomolybdenum(VI) pentafluoride.

MoF_6 reacts with $Me_{4-n}Si(OMe)_n$ more vigorously than does WF_6, and methoxomolybdenum(VI) fluorides decompose more readily than do their

TABLE 1

REACTIONS OF MoF_6

	Reactants (mmoles)	Reaction conditions	Products (mmoles)	
1	MoF_6(8.9) + $Me_2Si(OMe)_2$ (27.5)	—78° to +20° over 2 d	Me_2SiF_2 (21.4) $MoF(OMe)_5$[a]	Unchanged $Me_2Si(OMe)_2$ (5.6) recovered
2	MoF_6(12.4) + $MeSi(OMe)_3$ (27.8)	—78° to +20° over 2 d	$MeSiF_3$ $MoF_2(OMe)_4$?[b]	Unchanged $MeSi(OMe)_3$ recovered
3	MoF_6(7.1) + $Si(OMe)_4$ (7.0)	—20°, 10 min	SiF_4 (6.9) Me_2O $MoF_2(OMe)_4$?[c]	The solid product was slightly charred
4	MoF_6(4.0) + $(MeO)_2SO$ (12.0)	—50°, 10 min	MeOS(O)F MeF (11.2) $MoOF_4$[d]	Unchanged MoF_6 recovered

[a] Found C, 22.8; H, 5.4; F, 6.6; Mo, 34.1. $C_5H_{15}FO_5Mo$ requires C, 22.6; H, 5.6; F, 7.0; Mo, 35.5%.

[b] Found C, 17.4; H, 4.3; F, 14.1; Mo, 36.3. $C_4H_{12}F_2O_4Mo$ requires C, 18.6; H, 4.7; F, 14.7; Mo, 37.2%.

[c] Found C, 14.6; H, 3.6; F, 16.2; Mo, 38.3%.

[d] Identified by IR spectroscopy, A. J. EDWARDS AND B. R. STEVENTON, *J. Chem. Soc. (A)*, (1968) 2503; Found Mo, 52.0. MoF_4O requires Mo, 51.0%.

tungsten analogues. The average bond energies in MoF_6 and WF_6 are 107 and 121 kcal mole^{-1} respectively[5], and M–F bond energy differences may be partly responsible for the different behaviour observed.

EXPERIMENTAL

Reactions were carried out as described previously[2] in a vacuum system. Careful temperature control was necessary during the initial part of a reaction, otherwise explosions occurred. ^{1}H and ^{19}F NMR spectra were referenced with respect to internal Me_4Si and CCl_3F respectively and a positive δ value corresponds to a low field shift. Volatile products were identified by IR and NMR spectroscopy using authentic samples for comparison. Molybdenum was determined gravimetrically using 8-hydroxoquinoline and microanalyses were by Laboratorium Beller, Göttingen.

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