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NOTE

The interaction of organosilicon ethers with tungsten hexafluoride

As part of our general study of the reactions of siloxanes and alkoxysilanes with covalent halides, we have extended our work to include WF_6. Very little is known about the chemistry of WF_6[1]. Priest and Schumb[2] report that a violet-brown coloured solution resulted when WF_6 was dissolved in $(C_2H_5)_2O$. A complex of some type was presumably formed, but it was not identified. Although the study was only qualitative, there was no evidence of a chemical breakdown of the ether.

When WF_6 was dissolved in $[(CH_3)_3Si]_2O$ at 0°, there was, at first, no visible sign of an interaction. However, after about a minute the colour of the mixture became pale yellow. After a few more minutes, the yellow colour disappeared and a white precipitate formed. An examination of the mixture after 6 hours of reaction time indicated that a Si–O bond cleavage reaction had occurred, forming $(CH_3)_3SiF$ and the white solid. The amounts of $(CH_3)_3SiF$ formed with various ratios of starting materials are shown in Table 1. These data suggest that the main overall reaction which occurred when $[(CH_3)_3Si]_2O$ and WF_6 were allowed to interact is:

$$2\,[(CH_3)_3Si]_2O + WF_6 \rightarrow 4\,(CH_3)_3SiF + WO_2F_2 \qquad (1)$$

The additional $(CH_3)_3SiF$ formed in expts. 1 and 2 can be attributed to a slow reaction of $[(CH_3)_3Si]_2O$ with the WO_2F_2.

$$[(CH_3)_3Si]_2O + WO_2F_2 \rightarrow 2\,(CH_3)_3SiF + WO_3 \qquad (2)$$

The solid material formed in the reaction was not characterized, but is presumed to be mainly WO_2F_2. It was somewhat volatile, since it would distill into the vacuum line from the reaction vessel. The colour of the material changed from white to greenish-yellow then to blue, when it was allowed to stand for several hours exposed to air and normal lighting conditions. The solid material which distilled into the vacuum line behaved in a similar manner, except the colour change took several days. This may be related to the decomposition of WO_2F_2 forming WO_3 and thence "tungsten blue" in the presence of trace amounts of water and exposure to u.v. light[3]. The dioxydi-

TABLE 1

FORMATION OF $(CH_3)_3SiF$ FROM $[(CH_3)_3Si]_2O$ AND WF_6

Expt.	*Ratio[a] of* $[(CH_3)_3Si]_2O/WF_6$	*Ratio[a] of* $(CH_3)_3SiF/WF_6$
1	4.0	4.5[b]
2	3.0	4.6[b]
3	2.0	3.8
4	1.0	[c]

[a] WF_6 in the ratio is the initial amount of WF_6 used. [b] Excess $[(CH_3)_3Si]_2O$ observed in the products. [c] All the WF_6 did not react. The WF_6 and $(CH_3)_3SiF$ could not be separated in the vacuum line.

fluoride of tungsten has previously been reported[4], but little is known about it.

A reaction similar to that described above took place when $CH_3OSi(CH_3)_3$ was allowed to react with WF_6. Trimethylsilyl fluoride was formed in the reaction; however a dark brown or black solid was the other product. No evidence for any cleavage of the C–O bond was observed. The amounts of $(CH_3)_3SiF$ formed with various ratios of starting materials are shown in Table 2. No unreacted WF_6 or $CH_3OSi(CH_3)_3$ was ever observed in the experiments. It appears that up to four, but not necessarily all four, fluorine atoms of WF_6 can easily be removed on interaction with $CH_3OSi(CH_3)_3$. The solid materials formed in the reactions were not completely characterized, but are presumably polymeric alkoxyfluoro derivatives of tungsten. This material is difficult to characterize, since on brief exposure to air (possibly containing moisture) the material becomes a dark blue paste. Elemental analyses confirmed the presence of carbon and hydrogen in the samples (*i.e.* the CH_3 groups), but did not help to identify the exact nature of the material.

TABLE 2

FORMATION OF $(CH_3)_3SiF$ FROM $CH_3OSi(CH_3)_3$ AND WF_6

Expt.	*Ratio of* $(CH_3)_3SiOCH_3/WF_6$	*Ratio of* $(CH_3)_3SiF/WF_6$
1	6.1	4.3
2	4.2	3.8
3	3.0	3.0
4	2.0	2.0
5	1.0	1.0

The reaction of $CH_3OSiH(CH_3)_2$ with WF_6 was carried out in order to ascertain the stability of the Si–H bond in the cleavage reaction. Conditions used were the same as those previously described, with a $CH_3OSiH(CH_3)_2/WF_6$ ratio at 2.9. A black solid was formed in the reaction, and the volatile products were: H_2 (trace amount), $(CH_3)_2SiHF$, and $(CH_3)_2SiF_2$. The $(CH_3)_2SiHF$ (purified)/WF_6 ratio was found to be a 2.6. It can be concluded that the Si–H bond in $CH_3OSiH(CH_3)_2$ is attacked to a small extent in the cleavage reaction. Since $(CH_3)_2SiH_2$ was not observed in the products, it is unlikely that the $(CH_3)_2SiF_2$ came from the disproportionation of $(CH_3)_2SiHF$.

Experimental

All work was carried out in a Pyrex glass high vacuum system. Apparatus and techniques used were identical to those previously described[5].

Materials. Commercial WF_6 and $[(CH_3)_3Si]_2O$ were purified by low temperature fractionation (purities confirmed by their infrared spectra[6,7]). Methoxytrimethylsilane (mol. wt. found 104.4, calcd. 104.2; purity confirmed by its mass spectrum[8]) and $CH_3OSiH(CH_3)_2$ (mol. wt. found 90.5, calcd. 90.2; purity confirmed by its mass spectrum) were prepared by the reaction of CH_3OH with $[(CH_3)_3Si]_2S$ and $[(CH_3)_2SiH]_2S$ respectively. Details of the preparations will be published in a separate communication.

Reactions. All reactions of $[(CH_3)_3Si]_2O$, $CH_3OSi(CH_3)_3$, and $CH_3OSiH(CH_3)_2$ with WF_6 were carried out at 0° in approximately 15 cc all-glass tubes fitted with break-seals. At lower temperatures (*e.g.* −78°) for a similar time period or longer (10 h) the reactions were not complete. Trimethylsilyl fluoride was identified by its molecular weight and/or infrared spectrum[9]. Unreacted WF_6 and $[(CH_3)_3Si]_2O$, present in certain experiments, were identified by their infrared spectra[6,7]. A small amount of SiF_4 (identified by its infrared spectrum[10]) was observed in several (but not all) of the experiments. It was easily removed from the products by low temperature fractionation. Four reactions of $[(CH_3)_3Si]_2O$ and WF_6, and five reactions of $CH_3OSi(CH_3)_3$ and WF_6 were carried out with different mole ratio quantities of reactants in each particular system. Only one reaction of $CH_3OSiH(CH_3)_2$ with WF_6 was carried out. The volatile products of this reaction were identified by their infrared* and mass spectra. One typical reaction (expt. 1, Table 1) is described below; the other reactions were essentially identical except for suitable adjustments of quantities and the nature of the solid material formed in the reaction. Results of all experiments are given in Tables 1, 2, and the discussion section.

Hexamethyldisiloxane (3.95 mmole) and WF_6 (0.973 mmole) were combined and allowed to react under conditions described above. No non-condensable material was formed in the reaction. The volatile products were removed from the reaction vessel and allowed to distill through traps held at −64°, −112°, and −196°. Unreacted $[(CH_3)_3Si]_2O$ remained in the −64° trap, while $(CH_3)_3SiF$ (contaminated with a small amount of $[(CH_3)_3Si]_2O$) remained in the −112° trap. No unreacted WF_6 was observed in the −196° trap. Pure $(CH_3)_3SiF$ (4.45 mmole) was obtained by several additional distillations. The yellowish-white solid material which remained in the reaction vessel was not characterized. In the $CH_3OSi(CH_3)_3$ and $CH_3OSiH(CH_3)_2$ experiments, the solid material had a dark brown or black colour. Results of carbon-hydrogen analyses** (By Schwarzkopf Microanalytical Laboratory, Woodside, New York) on some of these dark solids are: solid in expt. 1 (Table 2): C, 9.08; H, 2.49 %; solid in expt. 2 (Table 2): C, 8.92; H, 1.78 %. These analyses do not fit any simple methoxyfluoro derivative of tungsten; they are given for qualitative purposes only, to indicate the presence of carbon and hydrogen in the samples.

In several of the reactions which involved $CH_3OSi(CH_3)_3$, a trace amount of CH_3OH (identified by its infrared spectrum[12]) was observed in the products. Pretreatment of the reaction vessel with a separate sample of WF_6, or an extremely dry vessel prevented the CH_3OH formation.

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* The infrared spectrum of $(CH_3)_2SiHF$ was compared to the spectrum of a separate sample of $(CH_3)_2SiHF$ prepared from $[(CH_3)_2SiH]_2O$ and BF_3[11].

** Samples for analysis were opened in a dry-box.

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