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Reaction of Tellurium Hexafluoride with Silanols

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Summary Tellurium hexafluoride reacts with trimethyl- and triphenyl-silanol to form the corresponding fluorosilane and pentafluoro-orthotelluric acid.

IT has been reported that in the reaction of alcohols with tellurium hexafluoride, the O–H bond is cleaved and the alkoxy derivatives $ROTeF_5$ and $(RO)_2TeF_4$ are formed.[1] We have investigated the reaction of trimethylsilanol with tellurium hexafluoride in a sealed tube at room temperature and find that the Si–O bond rather than the O–H bond is cleaved, the reaction proceeding according to equation (1).

$$TeF_6 + Me_3SiOH \longrightarrow TeF_5OH + Me_3SiF \qquad (1)$$

The products were identified by their vapour-phase i.r.[2,3] and ^1H and ^{19}F n.m.r. spectra.[4]

When the reaction was carried out at low temperature in the presence of pyridine, a white solid was deposited which, on removal of the volatile materials, was identified by micro-analysis and its i.r. spectrum[5] as pyridinium pentafluoro-orthotellurate, $C_5H_5NH^+TeF_5O^-$. The 56·4 MHz ^{19}F n.m.r. spectrum of a solution of the pyridinium salt in methanol was analysed as a typical AB_4 system, consistent with the TeF_5O^- ion, with δ_A $+28{\cdot}9$, δ_B $+43{\cdot}3$ p.p.m. (relative to $CFCl_3$) J_{AB} 175 Hz. The volatile products were trimethylfluorosilane and traces of hexamethyldisiloxane. The reaction therefore proceeds according to equation (2).

$$TeF_6 + Me_3SiOH + C_5H_5N \longrightarrow C_5H_5NH^+TeF_5O^- + Me_3SiF \qquad (2)$$

Triphenylsilanol and tellurium hexafluoride react similarly to give triphenylfluorosilane and pentafluoro-orthotelluric acid or its pyridinium salt.

The differences in the reactions of tellurium hexafluoride with alcohols and silanols can be explained by examining the charge distribution of the intermediates formed. Since tellurium hexafluoride is reported[6] to be a weak Lewis acid, its reactions with both alcohols and silanols are likely to involve the intermediates $TeF_6 \leftarrow O(H)R$. In the silanol reactions, the Si–O bonds are likely to be more polarised than the H–O bonds on the basis of their relative electronegativities, so that in the intermediates the silicon atoms would be the most electrophilic centres and trimethylfluorosilane would be formed. However, in the reactions with alcohols, the H–O bonds would be more polarised than the C–O bonds and in these cases, hydrogen fluoride would be produced.

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[1] A. Clouston, R. D. Peacock, and G. W. Fraser, *Chem. Comm.*, 1970, 1197.
[2] H. Bürger, *Z. Anorg. Chem.*, 1968, **360**, 97.
[3] V. H. Kriegsmann, *Z. Anorg. Chem.*, 1958, **294**, 113.
[4] P. Bladon, D. H. Brown, K. D. Crosbie, and D. W. A. Sharp, *Spectrochim. Acta*, 1970, **26**A, 2221.
[5] A. Engelbrecht and F. Sladky, *Inorg. Nuclear Chem. Letters*, 1965, **1**, 15.
[6] E. L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, 1957, **79**, 2975.