

The Deaction of Tellurium Hexafluoride with Methyl Alcohol

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Summary The reaction of tellurium hexafluoride with methyl alcohol leads to the formation of $\text{TeF}_5(\text{OMe})$ and $\text{TeF}_4(\text{OMe})_2$.

ALTHOUGH tellurium hexafluoride has been known for over 60 years, very few of its simple chemical reactions have been studied. We find that methyl alcohol reacts at 25° with excess of tellurium hexafluoride according to the equation $\text{TeF}_6 + \text{MeOH} \rightarrow \text{HF} + \text{TeF}_5(\text{OMe})$. The reaction proceeds cleanly in a sealed tube in the presence of sodium fluoride, which combines with the hydrogen fluoride produced.

Methoxytellurium(vi) pentafluoride, $\text{TeF}_5(\text{OMe})$, forms a colourless liquid, m.p. below -78°; with a vapour pressure of 159 mm Hg at 20° and 754 mm at 64°. The molecular weight of the vapour at 25° is 257 (calc. 253), and the mass spectrum shows the parent ion TeF_5OMe^+ , (the parent ion appears only in small proportion, the major peak is associated with $\text{TeF}_5\text{OCH}_2^+$) and fragments. The 56.4 MHz ^{19}F n.m.r. spectrum is consistent with a typical AB_4 system, with J_{AB} 188 Hz, δ_{A} +43.2, δ_{B} +56.6 p.p.m. (relative to CFCl_3), calculated by the method of Harris and Packer.¹ The compound (which may be regarded as an ester of the acid TeF_6OH)² is stable up to ca. 150°.

Disubstitution is possible if conditions are varied.

Tellurium hexafluoride reacts with excess of methyl alcohol in the presence of sufficient pyridine to combine with the free hydrogen fluoride formed, according to the equation $\text{TeF}_6 + 2\text{MeOH} \rightarrow 2\text{HF} + \text{TeF}_4(\text{OMe})_2$.

Dimethoxytellurium(vi) tetrafluoride is a colourless liquid, m.p. below -90°, which is much less volatile than the monosubstituted derivative. The mass spectrum shows the parent ion, $\text{TeF}_4(\text{OMe})_2^+$, (again in small proportion) and fragments, and the 56.4 MHz ^{19}F n.m.r. spectrum is consistent with a typical A_2B_2 system expected for the *cis*-isomer, with J_{AB} 151 Hz, δ_{A} +51.1, δ_{B} 61.5 p.p.m.

Attempts to prepare a trisubstituted derivative have so far resulted in complete decomposition of TeF_6 , but it should be noted that an orthotelluric ester, $\text{Te}(\text{OMe})_6$,³ is reported in the early literature.

Preliminary experiments indicate that tellurium hexafluoride undergoes similar reactions with ethanol, *t*-butyl alcohol, and ethylene glycol.

These methoxy-derivatives are much more thermally stable than the dialkylaminotellurium(vi) fluorides.⁴ They have, when pure, a not unpleasant odour, and are hydrolysed only slowly by concentrated alkali at 60°, with the intermediate formation of the *cis*- $\text{TeF}_4\text{O}_2^{2-}$ anion in solution.

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² A. Engelbrecht, W. Loreck, and V. Nehoda, *Z. anorg. Chem.*, 1968, 360, 88.

³ N. V. Sidgwick, "The Chemical Elements and their Compounds," vol. II, Oxford University Press, Oxford, 1950, p. 984.

⁴ G. W. Fraser, R. D. Peacock, and P. M. Watkins, *Chem. Comm.*, 1967, 1248.