Hydrolysis of Tellurium Hexafluoride

By GEORGE W. FRASER* and GORDON D. MEIKLE
(*Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow* G1 1XL)

Summary The hydrolysis of tellurium hexafluoride produces the fluoro-orthotelluric acids, $TeF_n(OH)_{6-n}$, $n = 1$—4, which undergo complete hydrolysis to orthotelluric acid only over a long period of time.

IN 1906, Prideaux reported[1] that TeF_6 was completely hydrolysed by water in 24 h, producing TeO_3 and HF. Since that date, the comparison of the reactions of SF_6 and TeF_6 with water has been used to show the importance of steric factors in inorganic chemistry and, as such, has been widely quoted and discussed.[2]

Our investigations into the chemistry of TeF_6 have led us to question the accuracy of the above work, since hydrolysis of the TeF_5O^- ion[3] produced the *cis*-$TeF_4O_2^{2-}$ ion and this was found to be stable in aqueous solution for several days. In addition, the fluoro-orthotelluric acids, $TeF_x(OH)_{6-x}$, which would be expected to be intermediates in the hydrolysis of TeF_6, have all been prepared and studied.[4,5] Therefore, we have re-investigated the reaction of TeF_6 with water by following the reaction by ^{19}F n.m.r. spectroscopy and by paper chromatography and, also, by measuring the pressure of unchanged TeF_6 at regular intervals. A number of reactions were carried out in glass and metal vessels, which were shaken continuously to obtain maximum mixing between the gas and the liquid.

Complete absorption of the TeF_6 in 24 h only occurred when small quantities of the hexafluoride (2 g) were shaken with large volumes of water (50 ml). Under different conditions (*e.g.*, 5 g TeF_6 and 5 ml water), unchanged TeF_6 could still be detected, by its i.r. spectrum, in both types of reaction vessel after 6 days. Regular examinations of the solutions by ^{19}F n.m.r. spectroscopy showed that, after 24 h, the main products in the aqueous solution were HF and *cis*-tetrafluoro-orthotelluric acid [A_2B_2 pattern, $\delta_A + 31$ p.p.m.; $\delta_B + 42$ p.p.m. (w.r.t. $CFCl_3$); J_{AB} 153 Hz]. Small quantities of two other compounds were also found to be present ($\delta + 36$ and $+30$ p.p.m.) and as the intensity of these signals increased with time at different rates, they are believed to be due to $TeF_3(OH)_3$ and $TeF_2(OH)_4$, respectively. No pentafluoro-orthotelluric acid which has a characteristic ^{19}F n.m.r. spectrum[6] could be detected at any stage of the reaction. After 6 days, the intensities of the A_2B_2 signals of the *cis*-tetrafluoro-orthotelluric acid had greatly diminished; the two signals mentioned above had greatly increased intensities and a new signal, $\delta + 22$ p.p.m., appeared, which was probably due to $TeF(OH)_5$. Unfortunately, as the reaction proceeded, a white solid was steadily deposited and the signals associated with the fluoro-orthotelluric acids subsequently decreased. However, paper chromatography of the mixture after 10 days showed that the tetra-, tri-, di-, and mono-fluoro-orthotelluric acids as well as the fully hydrolysed orthotelluric acid were present,[5] indicating that hydrolysis was still not complete.

In a similar series of reactions using aqueous NaOH instead of water, the ^{19}F n.m.r. spectrum of the solution after several days showed the presence of the *cis*-$TeF_4O_2^{2-}$ ion (A_2B_2 pattern, $\delta_A + 14$ p.p.m.; $\delta_B = + 36$ p.p.m.; J_{AB} 142 Hz). Therefore, the above results show that the hydrolysis of TeF_6 is much slower than previously reported and the fluoro-orthotelluric acids formed during the hydrolysis undergo further, complete hydrolysis only over a long period.

(*Received, 6th June* 1974; *Com.* 658.)

[1] E. B. R. Prideaux, *J. Chem. Soc.*, 1906, 316.

[2] P. W. Wiggars, *Educ. in Chem.*, 1973, 178; Open University Film S25/11, 'Fluorine and Its Compounds'; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' 3rd edn., Interscience, 1972, p. 440.

[3] G. W. Fraser and J. B. Millar, *J.C.S. Chem. Comm.*, 1972, 1125.

[4] F. Sladky and H. Kropshofer, *J.C.S. Chem. Comm.*, 1973, 600.

[5] L. Kolditz and I. Fitz, *Z. anorg. Chem.*, 1967, **349**, 175.

[6] P. Bladon, D. H. Brown, K. D. Crosbie, and D. W. A. Sharp, *Spectrochim. Acta*, 1970, **26A**, 2221.