

The Solvolysis of Orthotelluric Acid in HF

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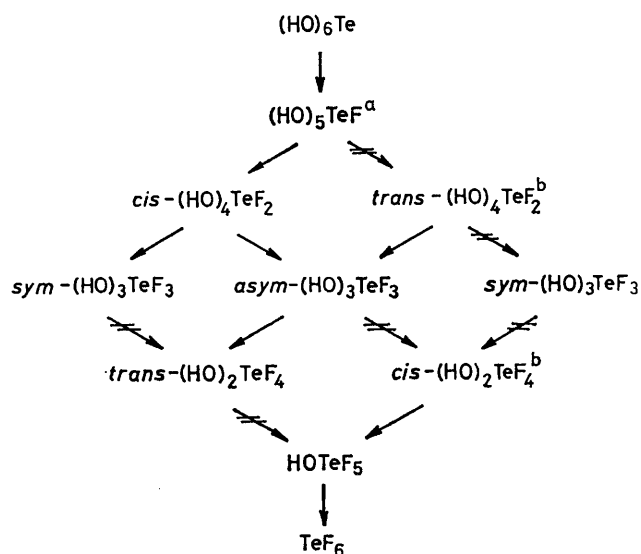
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Summary The stereochemistry of the solvolysis of orthotelluric acid in hydrogen fluoride has been followed up by ^{125}Te n.m.r. spectroscopy for each individual step of replacement of a hydroxy-group by fluorine.

THE stereospecificity of the preparative routes for *cis*- and *trans*-(HO) $_2\text{TeF}_4$ ¹ prompted us to re-examine the solvolysis of orthotelluric acid in HF. Previous results indicated the replacement of up to four hydroxy-groups by fluorine in the system (HO) $_6\text{Te}$ -40% aqueous HF.² The identification of the products by paper chromatography, however, did not allow a discernment between possible stereoisomers. From ^{19}F n.m.r. studies of solutions of (HO) $_6\text{Te}$ in aqueous and anhydrous HF the formation of four unknown species and of (HO) $_n\text{TeF}_{6-n}$ ($n = \text{up to } 3$) was deduced.³ Assignment of three singlets to specific isomers was based on n.m.r. systematics. Only *asym*-(HO) $_3\text{TeF}_3$ (AB_2 spin system) was identified unambiguously.

With the aid of ^{125}Te n.m.r. spectroscopy and by isolating most of the intermediate species we were able to follow the stereochemical route of the solvolysis of orthotelluric acid in HF step by step (Scheme).

If (HO) $_6\text{Te}$ is dissolved in aqueous HF, the product exclusively formed is *cis*-(HO) $_4\text{TeF}_2$ and not the expected (HO) $_5\text{TeF}$ which has previously been reported.³ (HO) $_5\text{TeF}$



SCHEME. Solvolysis of orthotelluric acid in HF. Reactions take place along the arrows as indicated by dissolving the starting material in aqueous or anhydrous HF, and warming the solutions to ca. 60 °C for ca. 2 h.

^a Not observed in 48% HF. ^b Hydrolysis products of TeF_6 .

appears to be stable only in the presence of excess of $(\text{HO})_6\text{Te}$. To discern between *cis*- and *trans*- $(\text{HO})_4\text{TeF}_2$ which have identical spin systems in ^{19}F n.m.r. (A_2) and ^{125}Te n.m.r. (A_2X) spectroscopy the corresponding tetramethoxy-derivatives were prepared (equation 1). Owing



to ^{125}Te - ^{19}F - ^1H coupling, *cis*- $(\text{MeO})_4\text{TeF}_2$ was expected to exhibit a triplet of septets of septets which was indeed observed.† *trans*- $(\text{MeO})_4\text{TeF}_2$ would be expected to show a triplet of a 13-line multiplet.

further to give HOTeF_5 and traces of TeF_6 . ^{125}Te -N.m.r. data for the identification of the compounds $(\text{HO})_n\text{TeF}_{6-n}$ are given in the Table.

In contrast with the hydrolysis of TeF_6 , which appears to be governed entirely by kinetics,⁴ the products of the solvolysis of $(\text{HO})_6\text{Te}$ in HF are the thermodynamically favoured isomers. Separate studies of isomerization reactions, which proceed only at elevated temperatures and with a much slower rate than the solvolysis, prove *cis*- $(\text{HO})_4\text{TeF}_2$ and *trans*- $(\text{HO})_2\text{TeF}_4$ to be more stable than *trans*- $(\text{HO})_4\text{TeF}_2$ and *cis*- $(\text{HO})_2\text{TeF}_4$, respectively. The solvolysis of *cis*- $(\text{HO})_4\text{TeF}_2$, the only step in which both of

TABLE. ^{125}Te N.m.r. data for $(\text{HO})_n\text{TeF}_{6-n}$.

	Solvent ^b	Spin system	$\delta(\text{Te})/\text{p.p.m.}^a$	Coupling constants (Hz)	
				$J(\text{TeF}_A)$	$J(\text{TeF}_B)$
$(\text{HO})_6\text{Te}$	i	X	707	—	—
$(\text{HO})_5\text{TeF}$	ii	AX	722	2754	—
<i>cis</i> - $(\text{HO})_4\text{TeF}_2$	ii	A_2X	708	2951	—
<i>trans</i> - $(\text{HO})_4\text{TeF}_2$	ii	A_2X	711	2895	—
<i>sym</i> - $(\text{HO})_3\text{TeF}_3$	iii	A_3X	678	3136	—
<i>asym</i> - $(\text{HO})_3\text{TeF}_3$	iii	AB_2X	671	3315	3253
<i>cis</i> - $(\text{HO})_2\text{TeF}_4$	ii	A_2B_2X	652	3247	3307
<i>trans</i> - $(\text{HO})_2\text{TeF}_4$	ii	A_2X	649	3443	—
HOTeF_5	ii	AB_4X	601	3339	3552

^a Relative to Me_2Te . ^b i, H_2O ; ii, MeCN; iii, ca. 80% aqueous HF.

cis- $(\text{HO})_4\text{TeF}_2$ is the final product of the solvolysis of $(\text{HO})_6\text{Te}$ in 48% aqueous HF. Further fluorination only occurs in anhydrous HF with the formation of *sym*- and *asym*- $(\text{HO})_3\text{TeF}_3$ in ca. 1:1 ratio. By comparison, *trans*- $(\text{HO})_4\text{TeF}_2$, a hydrolysis product of TeF_6 ,⁴ is converted into *asym*- $(\text{HO})_3\text{TeF}_3$ exclusively. Only this acid undergoes further solvolysis to *trans*- $(\text{HO})_2\text{TeF}_4$, which together with *sym*- $(\text{HO})_3\text{TeF}_3$ is the final product of the solvolysis of $(\text{HO})_6\text{Te}$ in anhydrous HF. Interestingly, *cis*- $(\text{HO})_2\text{TeF}_4$, again only a hydrolysis product of TeF_6 ,⁴ reacts

the possible isomers are formed, produces *sym*- and *asym*- $(\text{HO})_3\text{TeF}_3$ in the expected statistical 1:1 ratio. This indicates an identical kinetic barrier for the displacement of a hydroxy-group *trans* to a fluorine atom and *trans* to another hydroxy-group by fluorine in *cis*- $(\text{HO})_4\text{TeF}_2$. Since no isomerization occurs between *sym*- and *asym*- $(\text{HO})_3\text{TeF}_3$ both species must be of comparable thermodynamic stability as well.

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† *cis*- $(\text{MeO})_4\text{TeF}_2$ ($A_2M_6N_6X$): $\delta(\text{Te})$ 698 p.p.m. [$J(\text{TeF})$ 3174, $J(\text{TeH}_M)$ 108, $J(\text{TeH}_N)$ 86 Hz].

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³ U. Elgad and H. Selig, *Inorg. Chem.*, 1975, 14, 140.

⁴ W. Tötsch and F. Sladky, *Angew. Chem.*, in the press.

⁵ A. Engelbrecht and F. Sladky, *Monatsh. Chem.*, 1965, 96, 159.