

Syntheses of Alkoxotellurium(vi) Fluorides, $(RO)_xTeF_{6-x}$: Importance of Intramolecular Electronic Effects on the Value of x

By George W. Fraser* and Gordon D. Meikle, Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL

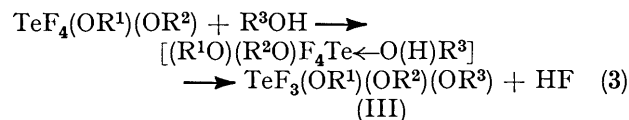
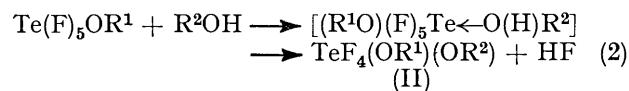
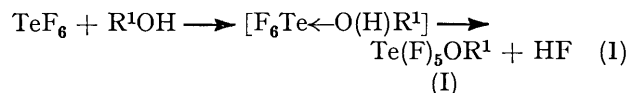
Under similar experimental conditions, tellurium hexafluoride reacts with the alcohols ROH ($R = Me, Et, CH_2=CHCH_2, ICH_2CH_2, MeC(O)CH_2CH_2, MeOC(O)CH_2CH_2, Br[CH_2]_3, PhCH_2CH_2, PhOCH_2CH_2, and Bu^tOCH_2CH_2$) to produce the dialkoxotellurium(vi) tetrafluoride, $TeF_4(OR)_2$; with $R = CF_3CH_2, ClCH_2CH_2, (ClCH_2)_2CH, BrCH_2CH_2, and MeSCH_2CH_2$ to produce the trialkoxotellurium(vi) trifluorides, $TeF_3(OR)_3$; and with $R = NC-CH_2CH_2, MeOCH_2CH_2, and EtOCH_2CH_2$ to produce a mixture of both the di- and tri-alkoxo-compounds. The importance of Taft constants, steric effects, and neighbouring group participation in explaining these differences is discussed.

TELLURIUM HEXAFLUORIDE reacts with methanol to produce the mono- and di-alkoxotellurium(vi) fluorides, $Te(F)_5OMe$ and $TeF_4(OMe)_2$.¹ Recently the reaction has been extended to include other simple primary and secondary alcohols and in all cases only the mono- and di-alkoxo-compounds were obtained.²

In further studies of the TeF_6 -alcohol systems we find that some alcohols containing functional groups behave in a similar manner to those described above, while others react further to form the trialkoxotellurium(vi) trifluorides. In this paper we discuss some of the possible explanations for these variations.

RESULTS AND DISCUSSION

It has been postulated that the reactions of tellurium hexafluoride with alcohols occur *via* the complex intermediates $[F_6Te \leftarrow O(H)R]$ which lose hydrogen fluoride to form the monoalkoxotellurium(vi) pentafluorides.³ Further reactions would be expected to take place similarly to produce the di- and tri-alkoxo-derivatives, as indicated in equations (1)–(3).



¹ A. Clouston, R. D. Peacock, and G. W. Fraser, *Chem. Comm.*, 1970, 1197.

² G. W. Fraser and J. B. Millar, *J.C.S. Dalton*, 1974, 2029.

In view of our evidence that all alcohols can react with TeF_6 to produce the mono- (I) and di-alkoxo-compounds (II) but only a few react further to produce the trialkoxo-compounds (III), trisubstitution must depend upon the nature of the R^1 and R^2 groups in (II) and the R^3 group of the alcohols. The importance of the former can be clearly shown by the observation that (III; $R^1 = R^2 = ClCH_2CH_2, R^3 = Et$) can be prepared from (II; $R^1 = R^2 = ClCH_2CH_2$) and EtOH but not from (II; $R^1 = ClCH_2CH_2, R^2 = Et$) and $ClCH_2CH_2OH$. However, our studies show that the R^3 group attached to the alcohol appears to be of less importance and has only a marginal effect on the formation of (III).

Comparison of the R^1 and R^2 groups in (II) which react according to equation (3) with those that do not shows that, in almost all cases, reactivities of these groups could be correlated with the combined Taft constants, $\Sigma\sigma^*$, of their substituents.^{4,5} Examination of a series of (II) of the type $TeF_4(OCH_2X)(OCH_2Y)$ (IV) showed that when the $\Sigma\sigma^*$ values for X and Y were greater than +1.75, further reaction with alcohols occurred. In contrast, nearly all the compounds in which the $\Sigma\sigma^*$ values for X and Y were less than +1.75 did not react with alcohols. Thus, (IV; X = Y = $ClCH_2$) has a combined value of σ^* of +2.10 and reacts with alcohols according to equation (3) but (IV; X = Y = ICH_2), which has $\Sigma\sigma^* = +1.70$, does not. Similarly (IV; X = H, Y = NCC_2), which has $\Sigma\sigma^* = +1.79$, reacts with alcohols whereas (IV; X = Me, Y = $ClCH_2$), $\Sigma\sigma^* = +1.05$, does not. A list of the Taft

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

⁴ R. W. Taft, in 'Steric Effects in Organic Chemistry,' ed. M. S. Newman, Wiley, New York, 1956, ch. 13.

⁵ P. R. Wells, *Chem. Rev.*, 1963, **63**, 171.

constants $\Sigma\sigma^*$ and the products of the reactions are given in the Table.

While the Taft constants $\Sigma\sigma^*$ provide a useful guide to the reactions of (II) with alcohols, the number of atoms between the X and Y groups and the tellurium atom in (IV) means that the transmission of a negative inductive ($-I$) effect through these atoms must be limited. Ingold states that the transmission of the $-I$ effect through one carbon-carbon bond reduces it by a factor of *ca.* 2.8.⁶ Therefore, the transmission of the $-I$ effect through both the oxygen and carbon atoms in (IV) must be very small and cannot be the most

that other effects may also be important. Bohme⁸ found that the compound $\text{ClCH}_2\text{CH}_2\text{SEt}$ hydrolysed 10^4 times more rapidly than $\text{ClCH}_2\text{CH}_2\text{OEt}$ and these results have been interpreted⁹ using the neighbouring group participation effect. This theory can be applied to the examples of (II) given above; interaction could occur between the oxygen or the sulphur atom and the tellurium atom as shown. Electron density can be donated from the oxygen atom or the sulphur atom to the tellurium atom, resulting in a weakening of the tellurium-fluorine bonds and possibly lowering the activation energy for reaction (3) to proceed. The

Reactions represented by equation (3)

R ¹	R ²	R ³	$\Sigma\sigma^*$ ^a for X + Y	Product
CF_3CH_2	CF_3CH_2	CF_3CH_2	$\sim 6.2^a$	(III)
$(\text{ClCH}_2)_2\text{CH}$	$(\text{ClCH}_2)_2\text{CH}$	$(\text{ClCH}_2)_2\text{CH}$	~ 3.8	(III)
NCCH_2CH_2	NCCH_2CH_2	NCCH_2CH_2	2.6	(II) + (III)
ClCH_2CH_2	ClCH_2CH_2	ClCH_2CH_2	2.1	(III)
ClCH_2CH_2	ClCH_2CH_2	Et	2.1	(III)
BrCH_2CH_2	BrCH_2CH_2	BrCH_2CH_2	2.0	(II)
ClCH_2CH_2	$\text{PhOCH}_2\text{CH}_2$	$\text{PhOCH}_2\text{CH}_2$	~ 1.9	(II)
$(\text{ClCH}_2)_2\text{CH}$	Et	Et	1.9	(III)
NCCH_2CH_2	Me	Me	1.8	(III)
ICH_2CH_2	ICH_2CH_2	ICH_2CH_2	1.7	(II)
$\text{PhOCH}_2\text{CH}_2$	$\text{PhOCH}_2\text{CH}_2$	$\text{PhOCH}_2\text{CH}_2$	1.7	(II)
$\text{MeOC(O)CH}_2\text{CH}_2$	$\text{MeOC(O)CH}_2\text{CH}_2$	$\text{MeOC(O)CH}_2\text{CH}_2$	~ 1.4	(II)
$\text{MeC(O)CH}_2\text{CH}_2$	$\text{MeC(O)CH}_2\text{CH}_2$	$\text{MeC(O)CH}_2\text{CH}_2$	1.2	(II)
ClCH_2CH_2	C_2H_5	ClCH_2CH_2	1.1	(II)
$\text{MeOCH}_2\text{CH}_2$	$\text{MeOCH}_2\text{CH}_2$	$\text{MeOCH}_2\text{CH}_2$	1.0	(II) + (III)
$\text{EtOCH}_2\text{CH}_2$	$\text{EtOCH}_2\text{CH}_2$	$\text{EtOCH}_2\text{CH}_2$	$\sim 1.0^a$	(II) + (III)
$\text{Bu}^t\text{OCH}_2\text{CH}_2$	$\text{Bu}^t\text{OCH}_2\text{CH}_2$	$\text{Bu}^t\text{OCH}_2\text{CH}_2$	$\sim 1.0^a$	(II)
Me	Me	Me	1.0	(II)
$\text{MeSCH}_2\text{CH}_2$	$\text{MeSCH}_2\text{CH}_2$	$\text{MeSCH}_2\text{CH}_2$	$\sim 0.9^a$	(II)
$\text{Br}[\text{CH}_2]_3$	$\text{Br}[\text{CH}_2]_3$	$\text{Br}[\text{CH}_2]_3$	~ 0.7	(II)
$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_2=\text{CHCH}_2$	$\text{CH}_2=\text{CHCH}_2$	$\sim 0.7^a$	(II)
PhCH_2CH_2	PhCH_2CH_2	PhCH_2CH_2	0.4	(II)
Et	Et	Et	0	(II)
Et	Et	ClCH_2CH_2	0	(II)
Pr^n	Pr^n	Pr^n	-0.2	(II)

^a Our estimate.

important effect which influences whether the reaction represented by equation (3) takes place. In addition, compounds (IV; X = Y = MeOCH_2 , EtOCH_2 , and MeSCH_2) form the corresponding product (III) whereas (IV; X = Y = Bu^tOCH_2 and PhOCH_2) do not, although the combined σ^* values are *ca.* +1.0 in all cases.

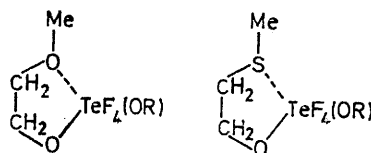
Although the transmission of the $-I$ effect through the bonds is probably not significant, the transmission of the $-I$ effect through space may be more important. Roberts⁷ found that the reactivity of 4-substituted bicyclo[2.2.2]octane-1-carboxylic acid derivatives was influenced by the nature of the group in the 4 position although it was four atoms away from the reaction site. The results have been interpreted⁶ as a through space transmission of the inductive and field effects represented by σ^* . The reactivities of [II; R¹ = R² = CF_3CH_2 , ClCH_2CH_2 , $(\text{ClCH}_2)_2\text{CH}$, and NCCH_2CH_2] may be explained in this way.

The different reactivities of (II; R¹ = R² = $\text{MeOCH}_2\text{CH}_2$) and (II; R¹ = R² = $\text{MeSCH}_2\text{CH}_2$) suggest

⁶ C. K. Ingold, in 'Structure and Mechanism in Organic Chemistry,' Bell, London, 1969, 2nd edn., ch. 16.

⁷ J. D. Roberts and W. J. Moreland, jun., *J. Amer. Chem. Soc.*, 1953, **75**, 2167.

greater polarisability, electron donation, and anchimeric assistance of the sulphur atom relative to the oxygen



atom means that (III; R¹ = R² = R³ = $\text{MeSCH}_2\text{CH}_2$) is formed more readily than (III; R¹ = R² = R³ = $\text{MeOCH}_2\text{CH}_2$).

Steric effects also appear to be important as (II; R¹ = R² = $\text{Bu}^t\text{OCH}_2\text{CH}_2$, $\text{PhOCH}_2\text{CH}_2$, and ICH_2CH_2) do not react according to equation (3), yet on the basis of the factors described so far, might be expected to do so. The sizes of the tellurium and fluorine atoms in tellurium(vi) fluorides means that steric hindrance will occur when bulky groups such as Bu^tO , PhO , or I are involved in the neighbouring group participation discussed above. In these cases, interaction between

⁸ H. Bohme and K. Sell, *Chem. Ber.*, 1948, **81**, 123.

⁹ E. S. Gould, in 'Mechanism and Structure in Organic Chemistry,' Holt, Rinehart, and Winston, London, 1969, ch. 14.

the oxygen or the iodine atom and the tellurium atom will be limited and consequently the degree of anchimeric assistance will be reduced.

In summary, it appears that many factors contribute to the degree of substitution of alkoxy-groups into tellurium hexafluoride but the most important appear to be through-space inductive effects, steric effects, and neighbouring group participation.

EXPERIMENTAL

The synthesis of some dialkoxotellurium(vi) tetrafluorides, $\text{TeF}_4(\text{OR}^1)_2$ and $\text{TeF}_4(\text{OR}^1)(\text{OR}^2)$, has been described previously. A similar procedure was followed,

using excess of the alcohol, pyridine (to remove hydrogen fluoride), and chloroform (as solvent). The products were extracted from water-chloroform, dried (Na_2SO_4), and the majority purified by distillation under reduced pressure. The constitution of the products was confirmed by microanalyses and by ^{19}F n.m.r. spectroscopy, the dialkoxo-derivatives exhibiting A_2B_2 (when $\text{R}^1 = \text{R}^2$) or A_2BC (when $\text{R}^1 \neq \text{R}^2$) spectra and the trialkoxo-compounds giving AB_2 spectra together with a single line, indicating that the stereochemistry of the products is *cis*- $\text{TeF}_4(\text{OR}^1)(\text{OR}^2)$ and both *mer*- and *fac*- $\text{TeF}_3(\text{OR}^1)(\text{OR}^2)(\text{OR}^3)$.

We thank the S.R.C. for a research studentship (to G. D. M.).

[4/1789 Received, 29th August, 1974]