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STUDIES OF DIORGANOTELLURIUM DIISOTHIOCYANATES AND OF A TRIORGANOTELLURIUM ISOTHIOCYANATE IN THE SOLID STATE AND IN SOLUTION

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Summary

The synthesis of the first diorganotellurium dithiocyanates is reported. It is argued that the tellurium interacts more strongly with the nitrogen than with the sulphur atom of the NCS group. Two structural classes are noted: (a) $R_2Te(NCS)_2$ ($R = Ph, p\text{-}CH_3O \cdot C_6H_4$) in which interaction of tellurium with the two NCS groups is equal and in which intermolecular association via long Te—S bonds probably occurs; (b) $[R_2Te(NCS)](NCS)$ ($R = p\text{-}C_2H_5O \cdot C_6H_4$) in which the tellurium interacts unequally with the two NCS groups to give a structure with some "telluronium salt" character.

The chemistry of $MePh_2Te(NCS)$ is studied. In solvents of reasonable polarity (e.g. DMSO), and probably in the solid state, it behaves as an essentially ionic telluronium salt $[MePh_2Te](NCS)$. However, in $CDCl_3$ solution it exists in a covalent form, $MePh_2Te(NCS)$, from which reductive elimination of, exclusively, methyl thiocyanate occurs. The mechanism of the decomposition is not simple: initially it is probable that a free radical pathway dominates, but after approximately 100 min the rate of decomposition increases. There is evidence that the second rate process is catalysed by diphenyltelluride. Other salts, $[MePh_2Te]X$ ($X = BF_4, PF_6$) are reported for comparison.

Introduction

The recent literature contains several papers which indicate a growing interest in organotellurium pseudohalides. For example, a range of triphenyltellurium pseudohalides have been prepared [1] and studied crystallographically [2]. The crystal and molecular structures of $(Ph_3Te)(NCO) \cdot \frac{1}{2}\ CHCl_3$ [3] and of $(Ph_3Te)(NCS)$ [4,5] are particularly interesting since they show association to tetramers in the isocyanate and to both dimers and tetramers in the thiocyanate. The association within the oligomers seems to be predominantly ionic. A further interesting structure is that of $(Ph_2TeNCS)_2O$ [6] in which the tellurium is located in a distorted square based pyramidal environment.

We recently communicated the synthesis of the first reported examples of diorganotellurium diisocyanates [7] and, in this paper, we give further details of that work. In addition we report on the solution behaviour of $Ph_2MeTe(NCS)$ which parallels in some respects the behaviour of Ph_2MeTeX (X = Cl, Br, I) which was the subject of a recent detailed study [8].

Experimental

Diphenyltelluride [9], di-(*p*-methoxyphenyl)telluride [10], di-(*p*-ethoxyphenyl)-telluride [10] and thiocyanogen [11] were prepared following the literature.

Preparations

Diorganotellurium diisothiocyanates. Two methods of preparation were developed.

(a) The appropriate telluride (5×10^{-3} mol) was dissolved in carbon tetrachloride (25 cm^3) and cooled to 0°C. A solution of thiocyanogen (20 cm^3, 0.1 *M*) was added to the telluride solution under dry dinitrogen. Crystals were deposited overnight which were filtered and washed with carbon tetrachloride.

(b) e.g. Di-(*p*-ethoxyphenyl)tellurium dichloride (2 g) and ammonium thiocyanate (0.6 g) were refluxed in methanol (25 cm^3) for 4 h. Ether (10 cm^3) was added to the cooled solution to precipitate ammonium chloride (IR) which was removed by filtration. Water (50 cm^3) was then added to concentrate the tellurium compound in the ether layer. The ether layer was separated and dried, after which removal of the solvent afforded the product.

An attempted reaction between dibutyltindiisothiocyanate and the diaryltellurium dichloride afforded only unreacted starting materials.

Triorganotellurium salts. Diphenylmethyltelluronium iodide was prepared by Lederer's method [12] and recrystallised from water to m.p. 123—124°C (lit. [12] 123—124°C).

Methyldiphenyltelluronium thiocyanate. An aqueous solution of silver nitrate (1.5 g) was added to an aqueous solution of potassium thiocyanate (1.5 g) to afford a curdy white precipitate of silver thiocyanate. To this mixture was added an aqueous solution (200 cm^3) of methyldiphenyltelluronium iodide (1.5 g). The mixture was stirred for 1 h at room temperature, then heated under reflux for 4 h. The reaction mixture was then concentrated and the precipitate of silver iodide removed. On further concentration and cooling white crystals of the product appeared, m.p. 125°C.

Methyldiphenyltelluronium tetrafluoroborate. Silver tetrafluoroborate was obtained by crystallising the solution resulting from the neutralization of tetrafluoroboric acid with silver oxide. The above method was then followed using Ph_2MeTeI (0.5 g) and $AgBF_4$ (0.23 g). The product was obtained as white crystals, m.p. 135°C.

Methyldiphenyltelluronium hexafluorophosphate. IRA 400 resin (30 g), exchanged with PF_6^-, was added to an aqueous solution (200 ml) of methyldiphenyltelluronium iodide (0.2 g). The mixture was gently warmed and stirred for 4 h. The resin was removed and the solution concentrated to afford white crystals of m.p. 135°C.

Physical measurements. IR spectra were measured using Perkin—Elmer 457 (4000—250 cm^{-1}) and 225 (600—200 cm^{-1}) spectrophotometers. ^{1}H NMR measurements were made on a Perkin—Elmer R14 instrument using DMSO(d_6) or $CDCl_3$ as solvents. For kinetic studies the tube was thermostated at 35°C in the spectrometer. Conductivity measurements were obtained with a Henelec bridge using a dip cell. Mass spectra were measured with an AE1 MS9 mass spectrometer.

Results and discussion

Analytical data are presented in Table 1, relevant IR data in Table 2 and ^{1}H NMR data for methyldiphenyltelluronium salts in Table 3. The results of conductivity measurements are included in Table 1.

Diaryltellurium diisothiocyanates

These compounds have been the subject of a preliminary communication [7] and only brief amplification need be given here. The synthesis, by oxidative addition of thiocyanogen to a diaryltelluride, was preferred, in the practical sense, to that involving metathesis of $(aryl)_2TeCl_2$ and NH_4NCS. Both methods do, however, give the same product.

IR spectroscopy has been much used to differentiate coordination of the thiocyanate group via sulphur (thiocyanato-) or nitrogen (isothiocyanato-). Thus, for complexes of palladium(II), ν(CN) is said to be sharp and above 2100 cm^{-1} for the thiocyanato- complex, but below 2100 cm^{-1} and broad for the N-bonded case [13]. Indeed, there are also many examples known where isothiocyanato- groups coordinated to harder acids than palladium(II) will give ν(CN) between 2000 and 2100 cm^{-1}. Bridging of the group between two acceptor centres also tends to raise the frequency of ν(CN) [14]. Rather ambiguous conclusions may often be drawn from the position of ν(CS) [15] or of δ(NCS)

TABLE 1

ANALYTICAL AND CONDUCTIVITY DATA FOR SOME NEW ORGANOTELLURIUM COMPOUNDS

Compound	Analysis (%)						Molar conductivity (Λ_M: 10^{-3} *M* soln.)
	Found			Calculated			
	C	H	X	C	H	X	
$Ph_2Te(NCS)_2$	42.7	2.50		42.3	2.53	7.04 [a]	Insoluble
$(p\text{-}MeO \cdot C_6H_4)_2Te(NCS)_2$	41.6	3.30		42.0	3.08	6.12 [a]	61 ($MeNO_2$)
$(p\text{-}EtO \cdot C_6H_4)_2Te(NCS)_2$	44.27	3.48	5.62	44.5	3.73	5.76 [a]	106 ($MeNO_2$)
$Me \cdot Ph_2TeNCS$	47.2	3.70	3.54	47.4	3.69	3.95 [a]	95 (DMF) 27 (DMSO)
$Me \cdot Ph_2TeBF_4$	40.4	3.67		40.7	3.42		34 (DMSO)
$Me \cdot Ph_2TePF_6$	35.3	2.93	6.38	35.3	2.97	7.01 [b]	36 (DMSO)

[a] % N. [b] % P.

TABLE 2

INFRARED DATA (FREQUENCIES IN WAVENUMBERS) FOR SOME NEW ORGANOTELLURIUM COMPOUNDS

Compound	Solid state. ν(CN) thiocyanate and anion bands	Solution, $CHCl_3$	ν(Te—Me) (solid)
$Ph_2Te(NCS)_2$	2060s, 2050s		
$(p\text{-}MeO \cdot C_6H_4)_2Te(NCS)_2$	2060(sh), 2040s		
$(p\text{-}EtO \cdot C_6H_4)_2Te(NCS)_2$	2040s(sharp), 1980s (u.br.)		
$MePh_2TeNCS$	2078s (assymm. to bw wavenumber)	Time = 0, 2059s(br) Time > 0, 2059 (assym. to low wavenumber, diminishing), 2161 (sharp, growing)	536w
MeSCN		2161s, sharp	
$MePh_2TeBF_4$	1088 1060 } ν_3 (BF_4^-) 1038	insoluble	520w
$MePh_2TePF_6$	880 860 } ν_3 (PF_6^-) 840	insoluble	
	556 ν_4 (PF_6^-)		masked

[14], but these regions are obscured by the rich contribution to the spectrum of the aromatic groups.

In the light of the above paragraph, we conclude that the NCS groups are bonded via nitrogen to tellurium(IV) in the case of the phenyl- and *p*-methoxyphenyl- compounds. This would be expected if we take the usual view that in compounds R_2TeX_2 the more electronegative X will take an axial position in the pseudo-trigonal bipyramid and thereby be better able to accommodate the electron density within the non-bonding molecular orbital associated with the axial bonds. Clearly this is a role more suited to nitrogen than to sulphur. However, the overall structure is probably not well described by the term "pseudo-trigonal bipyramidal". The ν(CN) vibration is split in $R_2Te(NCS)_2$ for both

TABLE 3

^1H NMR DATA FOR TELLURONIUM SALTS IN DMSO(d_6), $CDCl_3$ OR MIXED SOLVENTS

Compound	Solvent	Methyl group resonance (δ from TMS in ppm)	
		Resonance 1	Resonance 2
$MePh_2TeNCS$	DMSO(d_6)	2.73, $J(^{125}Te—^1H) = 24$ Hz	
	$CDCl_3$	2.90 (diminishing), $J(^{125}Te—^1H) = 25$ Hz	2.56 (growing)
MeSCN	EtOH		2.60
$MePh_2TePF_6$	DMSO(d_6)/benzene (50 : 50)	2.68, $J(^{125}Te—^1H) = 25$ Hz	
	DMSO(d_6)/$CDCl_3$ (50 : 50)	2.72 (diminishing slowly)	3.01 (growing slowly)
MeCl	$CDCl_3$	—	2.96
$MePh_2TeBF_4$	DMSO(d_6)	2.71, $J(^{125}Te—^1H) = 24$ Hz	

R = Ph and R = p-MeOC$_6$H$_4$—. This may imply a non-linear N—Te—N arrangement, but more probably hints at some molecular association via weakly bridging thiocyanate groups in which the sulphur atoms form long bonds to tellurium in a neighbouring molecule, thus giving the tellurium a distorted six-coordinate environment. The Te—S interaction possibly explains the yellow colour of these two compounds and the poor solubility of the diphenyl compound.

By contrast, the IR spectrum of (p-EtO · C$_6$H$_4$)$_2$Te(NCS)$_2$ is rather different in the ν(CN) region and is characterised by a broad band at 1980 cm^{-1} which implies a much stronger covalent interaction of one group than of the other (ν(CN) = 2040 cm^{-1}). As previously argued, a reasonable interpretation is that a telluronium compound, [(p-EtO · C$_6$H$_4$)$_2$Te(NCS)](NCS), provides a better model. Even in this case it is likely that some degree of oligomerisation occurs within the solid, but the tellurium does not interact symmetrically with the two NCS groups. The energy balance between the two structural classes that appear to exist is probably delicate. Thus we argue that the change occurs as a result of the influence of the *para*-substituent (H, MeO or EtO) on the relative lattice energies of the two structures, rather than as a consequence of any electronic effect at tellurium.

The p-methoxy- and p-ethoxy- compounds were sufficiently soluble in nitromethane to enable conductivity studies to be undertaken. Both gave appreciably conducting solutions at concentrations of 10^{-3} M and plots of Λ_M against (concentration)$^{1/2}$ were markedly non-linear. Values of Λ_M extrapolated to infinite dilution implied that, under such conditions, the dissociation of the thiocyanate groups was essentially complete, thus it would seem that the behaviour may be represented as follows:

$$R_2Te(NCS)_2 \rightleftharpoons R_2Te(NCS)^+ + NCS^-$$

$$R_2Te(NCS)^+ \rightleftharpoons R_2Te^{2+} + NCS^-$$

(R = p-MeO · C$_6$H$_4$— or p-EtOC$_6$H$_4$—)

Thus, the p-methoxyphenyl- compound shows properties intermediate between those of the phenyl- and p-ethoxyphenyl- compounds, resembling the former in the solid state and the latter in solution. Unfortunately, all attempts made by ourselves, and others [16], to grow crystals of (p-EtO · C$_6$H$_4$)$_2$Te(NCS)$_2$ suitable for structural investigation have, to date, failed.

The mass spectra of the three diisothiocyanates were measured. The diphenyl-compound showed a weak parent ion at m/e 488 ($^{12}C_{18}{}^{1}H_{18}{}^{14}N_2{}^{16}O_2{}^{32}S_2{}^{130}Te^+$), together with a major peak at m/e 372 (p-EtO · C$_6$H$_4$)$_2$Te$^+$). No parent ion could be detected from (p-MeOC$_6$H$_4$)$_2$Te(NCS)$_2$, but $(SCN)_2^{\dot{+}}$ was identified (m/e = 116). Ph$_2$Te(NCS)$_2$ afforded a weak parent ion at m/e = 400 ($^{12}C_{14}{}^{1}H_{10}$-$^{14}N_2{}^{32}S_2{}^{130}Te^+$) together with fragments showing stepwise loss of NCS i.e. Ph$_2$Te(NCS)$^+$ (m/e = 342) and Ph$_2$Te$^+$ (m/e = 284). Thus some differences are observed in the behaviour of these materials in the mass spectrometer. As is often the case with such organometallic compounds, the fragmentation pattern observed probably arises from a combination of thermolysis (reductive elimination of thiocyanogen which dominates in the case of (p-MeOC$_6$H$_4$)$_2$Te(NCS)$_2$) and volatilisation to monomeric species in the vapour phase. We may usefully conclude that the spectra do confirm that the structural building blocks for the solids are indeed $R_2Te(NCS)_2$.

Methyldiphenyltelluronium thiocyanate and other telluronium salts

We have recently demonstrated [8] that methyldiphenyltelluronium salts undergo dissociation in deuterochloroform solution, to telluride and alkyl halide, with a rate which is halogen dependent:

i.e. $Cl < Br < I$

Further we were able to show that the dissociation occurred from a covalent, rather than from an ionic, form. Thus the following equilibria were shown to be shifted to right or left by selecting solvents of differing polarity:

$Ph_2MeTe^+X^- \rightleftharpoons Ph_2MeTeX \rightleftharpoons Ph_2Te + MeX$

"ionic" "covalent"

We decided to extend the study to include $X^- = NCS^-$. In this case it was of interest to establish whether MeSCN or MeNCS might be eliminated (or a mixture of both), and also we wished to obtain more kinetic data on these systems with a view to ultimately establishing the mechanism of the reductive elimination reaction.

Crystalline methyldiphenyltelluronium thiocyanate was conveniently prepared by the metathesis of methyldiphenyltelluronium iodide and silver(I) thiocyanate. The compound $[MePh_2Te](NCS)$ gives conducting solutions in DMSO and DMF, the value of the molar conductivity in each case being consistent with the presence of a 1 : 1 electrolyte.

The solid state IR spectrum has been recorded. We find that $\nu(CN)$ is insensitive to the sampling technique, thus in a KBr matrix it is located at 2080 cm^{-1}, and in a Nujol mull the position is 2078 cm^{-1} (Table 2). The band differs in frequency from that in a typically ionic thiocyanate e.g. KCNS has $\nu(CN)$ at 2053 cm^{-1}; on the other hand the complexity observed for $Ph_3Te(NCS)$ is not duplicated here. We therefore consider that there could well be a weak, essentially ionic, association in the solid and suggest that the nitrogen atom of NCS may interact with tellurium more strongly than does the sulphur atom. Other diagnotic regions are masked.

In chloroform solution the initial spectrum consists of a broad band due to $\nu(CN)$ centred on 2059 cm^{-1}, and this decays with time to be replaced by an extremely sharp band at 2161 cm^{-1}. A solution of methylthiocyanate in chloroform gave $\nu(CN)$ as a sharp band at 2161 cm^{-1}. Thus, there is good evidence that, over a period of about 3 h, the telluronium salt is decomposing to MeSCN and, presumably, Ph_2Te (subsequently confirmed by ^1H NMR). Although the maximum of $\nu(CN)$ in the initial solution is close to the free ion value, we believe that in fact the thiocyanate group is coordinated, as an isothiocyanato-ligand, to tellurium(IV). The considerable breadth of the band would appear to us to indicate some covalent interaction ($\Gamma_{1/2} = 62$ cm^{-1}). Since we had previously found ^1H NMR spectroscopy to be useful in the investigation of the reductive elimination of an alkyl halide from Ph_2MeTeX ($X = Cl, Br, I$) [8], we decided to examine the NMR spectrum of $Ph_2MeTe(NCS)$ in solvents of differing polarity.

In DMSO(d_6) a simple spectrum is obtained with a single methyl resonance at $\delta = 2.73$ (relative to TMS) with satellites due to coupling of ^{125}Te ($J(^{125}\mathrm{Te}{-}^1\mathrm{H}) = 24$ Hz). Clearly this is the resonance of the methyl group of the telluronium ion and the chemical shift is closely similar to those obtained from solutions of $[\mathrm{MePh_2Te}]\mathrm{PF_6}$ and $[\mathrm{MePh_2Te}]\mathrm{BF_4}$ (Table 3). In $\mathrm{CDCl_3}$, the methyl resonance is initially located at $\delta = 2.90$ ($J(^{125}\mathrm{Te}{-}^1\mathrm{H}) = 25$ Hz), identical with that for $\mathrm{MePh_2TeBr}$ [8]. As time passes, the initial methyl resonance decays to be replaced by a new resonance at $\delta = 2.56$, reasonably assigned to MeSCN (Table 3). The relative rates of dissociation of $\mathrm{MePh_2TeX}$ in $\mathrm{CDCl_3}$ are then:

$\mathrm{X = I > NCS \simeq Br > Cl}$

and appear to parellel the electronegativity of the groups. We have previously argued [8] that a "covalent" form of the telluronium compound exists in deuterochloroform solution, hence, from the IR data, we postulate that the dissociation occurs from the isothiocayanato species $\mathrm{MePh_2Te(NCS)}$.

The total integrated intensity of the methyl resonances remained constant throughout the reaction, thus, within the sensitivity of the continuous wave NMR technique, no other methyl-containing products than methyl thiocyanate were formed. By monitoring the ^{1}H NMR spectrum at time intervals over the course of the reaction we were able to construct pseudo first order rate plots from the data. A typical result is shown in Fig. 1. Over a period of 90 min a linear plot is obtained, however the rate then changes and the slope alters. A further linear plot is then obtained. It would therefore appear that there were two mechanisms operative, the second of which becomes dominant during the latter stages of the reaction. The most probable mechanism for the initial stage of the reaction is one involving loss of a methyl radical in a rate-determining step:

$\mathrm{MePh_2TeNCS} \xrightarrow{\text{slow}} \dot{\mathrm{M}}\mathrm{e} + \mathrm{Ph_2\dot{T}eNCS}$

followed by a sequence of fast steps.

e.g. $\dot{\mathrm{M}}\mathrm{e} + \mathrm{(SCN)TePh_2Me} \rightarrow \mathrm{MeSCN} + \mathrm{\dot{T}ePh_2Me}$

$\mathrm{\dot{T}ePh_2Me} \rightarrow \mathrm{Ph_2Te} + \dot{\mathrm{M}}\mathrm{e}$

$\dot{\mathrm{M}}\mathrm{e} + \mathrm{(SCN)\dot{T}ePh_2} \rightarrow \mathrm{MeSCN} + \mathrm{Ph_2Te}$.

Some evidence that radicals may be involved comes from studies of $[\mathrm{MePh_2Te}]$-$\mathrm{PF_6}$ in DMSO(d_6)/$\mathrm{CDCl_3}$ and DMSO(d_6)/benzene. In the presence of chloroform, the very slow growth of a second methyl resonance is noted ($\delta = 3.01$, Table 3) which is assigned to MeCl which must arise from attack at chloroform. The use of benzene rather than chloroform results in a time-independent spectrum (Table 3). (N.B. $[\mathrm{MePh_2Te}]\mathrm{PF_6}$ is insufficiently soluble in $\mathrm{CDCl_3}$ or benzene for the pure solvent to be used). These results suggest that methyl radicals can be released and may attack chlorinated solvents in a slow reaction, however, our results for the thiocyanate system clearly eliminate the possibility of products originating from the solvent.

If the above speculation is accepted, it is reasonable to postulate that a material whose concentration grows during the reaction may exercise some catalytic

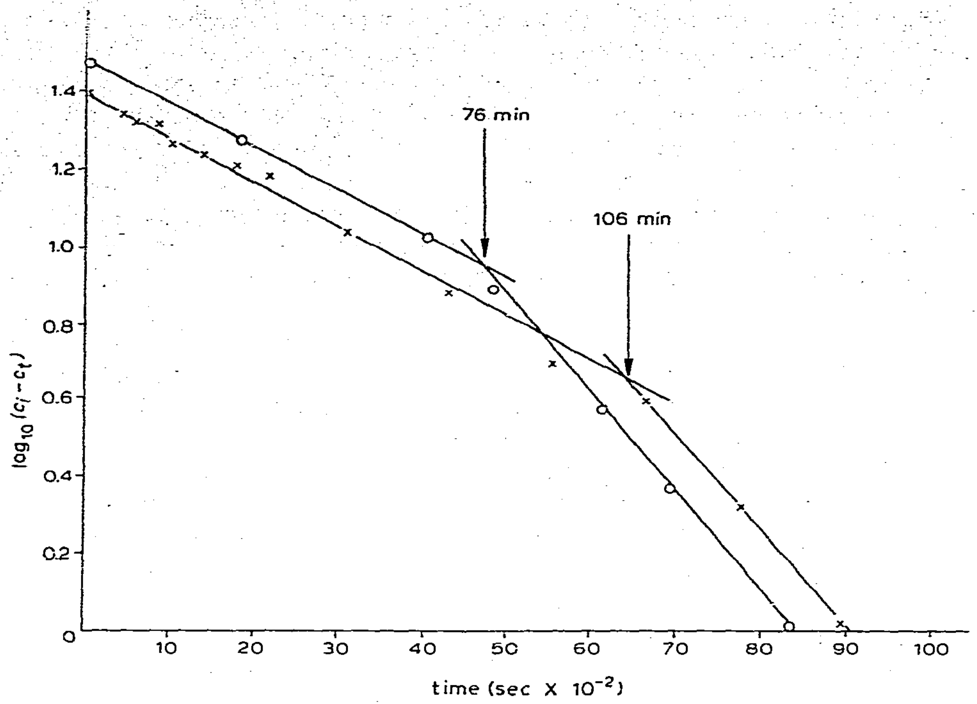


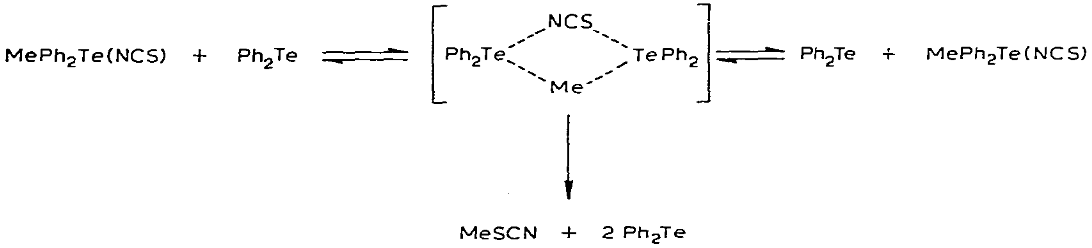
Fig. 1. Plot of $\log_{10}(C_i - C_t)$ against time (sec X 10^{-2}) for decomposition of $MePh_2Te(NCS)$ in $CDCl_3$ solution. Concentrations were obtained from the integrated intensity of the methyl resonance in the ^1H NMR spectrum; C_i = initial concentration, C_t = concentration at time *t*. Data set (*A*) (x) refers to $MePh_2Te(NCS)$ alone in $CDCl_3$, data set (*B*) (o) to the case where $MePh_2Te(NCS) : Ph_2Te = 1 : 1.5$ initially.

influence. The two candidates are Ph_2Te and MeSCN. Methyl thiocyanate has been shown to be inert under these conditions, hence a role for diphenyltelluride is possible. An alternative explanation is that a concerted mechanism may become dominant. Barton [18] has shown that the thermolysis of tetraphenyltellurium proceeds by a concerted mechanism, but the suggestion seems less likely to be true here. Given that dissociation occurs from an isothiocyanato-species, $MePh_2Te(NCS)$, it would be expected that methyl isothiocyanate would be formed. However, methyl thiocyanate is the exclusive product, hence we regard the concerted mechanism as unlikely in the light of data presently available.

A further possibility is that diphenyltelluride, the concentration of which increases during the reaction, may play some catalytic role. We therefore repeated the kinetic experiments in the presence of an initial concentration of diphenyl telluride. Also illustrated in Fig. 1 is the result of an experiment for which, initially, $Ph_2Te : MePh_2Te(NCS) = 1.5 : 1$. The initial rates of decomposition agree well, and the major influence of the excess telluride is to advance the onset of the faster stage of the reaction. As with the initial stage, rates for the later stage are the same within experimental error.

The interpretation of these results requires care. In our earlier studies of methyldiphenyltelluronium halides, diphenyltelluride behaved as a solvent intermediate in polarity between $CDCl_3$ and DMSO, thus dilution of $CDCl_3$ with Ph_2Te might begin to favour the ionic form of the telluronium salt and hence slow the reductive elimination reaction i.e. if the role of Ph_2Te is purely dielectric, kinetic effects opposite to those observed might be anticipated. The ^1H NMR chemical shift of the methyl-group of MeSCN shows some degree of solvent dependence. Thus in $CDCl_3$, $\delta = 2.56$ ppm; in EtOH, $\delta = 2.60$ ppm; and in $CDCl_3/Ph_2Te$, $\delta = 2.42$ ppm. Although the variation in δ is small, some change of solvation is implied. However, apart from the changes illustrated in Fig. 1, this was the only difference noted for the system in the presence of excess diphenyltelluride.

The evidence available indicates that the mechanism of reductive elimination of MeSCN from $MePh_2Te(NCS)$ is not simple. There is support for the view that diphenyltelluride has a catalytic role. We speculate that the initial stage of the reaction is a radical process and suggest that as diphenyltelluride concentration builds up, interaction between Ph_2Te and unreacted $MePh_2Te(NCS)$ may occur:



This is however pure speculation and it must be emphasised that no concrete evidence is available to indicate the precise role of diphenyltelluride.

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