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Aspects of the Chemistry of Diarylditellurides and Related Compounds containing Tellurium to Tin Bonds.

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ABSTRACT

The examination of mixtures of two ditellurides by mass and ¹H nmr spectroscopies provides the first evidence for the existence of unsymmetrical diarylditellurides, RTe-TeR′. Possible mechanisms for the redistribution reaction are discussed and it is noted that no positive support for a radical mechanism is obtained. Appearance potential measurements on the ion (aryl)Te$^+$ derived from a number of organotellurium compounds suggest that tellurium extrusion may be a low energy pathway for the decomposition of diarylditellurides. A new series of compounds, Ph_3Sn-Te(aryl) is reported and they are examined by ^{119}Sn and ^{125}Te Mössbauer spectroscopies. Attempts are made to interpret the Mössbauer data in terms of orbital populations, and it is demonstrated that only an s-p bonding model gives a self-consistent interpretation of the combined tin and tellurium Mössbauer data.

INTRODUCTION

We originally became interested in the diarylditellurides through their vibrational spectra[1]. During the study we commented that we were unable to substantiate an earlier claim by Farrar[2] that diphenylditelluride was appreciably dissociated into radicals in solution. Further there is no evidence from vibrational spectroscopy[1] or ^{125}Te Mössbauer spectroscopy[3] that the Te-Te bond is particularly weak in these compounds. It may also be noted that Morgan and Drew[4] with $(p\text{-}EtOC_6H_4)_2Te_2$ and Morgan and Kellett[5] with $(p\text{-}MeOC_6H_4)_2Te_2$ obtained values for the molecular weights in freezing benzene which were in close agreement with expected values for undissociated molecular ditellurides. Farrar[2], however, reported a molecular weight for Ph_2Te_2 in freezing camphor of 318 rather than the required 409. One possible explanation is that decomposition to telluride and tellurium had occurred but the work of Petragnani and De Moura Campos[6] suggests that thermal decomposition should not be significant at the m.p. of camphor. Thus the evidence for significant dissociation of ditellurides, at

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least in solution under 100°C, is slight.

We also failed, in our earlier study[1], to obtain unsymmetrical ditellurides RTe-TeR′ using preparative routes which should, if $R\dot{T}e$ radicals were involved in the reactions , have afforded mixtures of R_2Te_2, R'_2Te_2 and RTe-TeR′. In this study we return to this problem and also examine the mass spectra of ditellurides in more detail. We also include a study of some new compounds of the type Ph_3Sn-TeR by ^{125}Te and ^{119}Sn Mössbauer spectroscopy.

EXPERIMENTAL

The diarylditellurides used in this work were synthesised by literature methods viz. Ph_2Te_2[2], $(p\text{-}CH_3.C_6H_4)_2Te_2$[7], $(p\text{-}MeO.C_6H_4)_2Te_2$[5], $(p\text{-}EtO.C_6H_4)_2Te_2$[4], $(p\text{-}PhOC_6H_4)_2Te_2$[8] and $(C_6F_5)_2Te_2$[9]. All materials had satisfactory melting points and spectra (i.r., ^1H n.m.r.). Other organotellurium compounds required for mass spectrographic work were prepared following the methods indicated in table 2. The following new compounds containing tin to tellurium bonds were also prepared:

Phenyl(triphenylstannyl)telluride. Diphenylditelluride (2.05g, 0.005 mole) was added to triphenyltin hydride[10] (3.5g, 0.01 mole) and warmed to 60-70°C. When evolution of dihydrogen ceased, a further quantity of Ph_3SnH was added and the temperature maintained until the mixture was completely decolourised. The mixture was cooled and the product was extracted from hexaphenylditin with a mixture of ether and 40-60 petroleum ether and crystallised to give 50-70% Ph_3Sn-TePh. A similar procedure was adopted for Ph_3Sn-TeR (R = $p\text{-}MeO.C_6H_4$–, $p\text{-}EtO.C_6H_4$–, $p\text{-}PhO.C_6H_4$–) but when tri-n-butyltin hydride replaced Ph_3SnH in the method above, a red oil was formed which decomposed under vacuum or when chromatographed. However, the mass spectrum of the crude material showed P^+ for $^nBu_3Sn$-TePh. Analytical data are given in table 1.

Table 1

	FOUND		CALCULATED		
	%C	%H	%C	%H	m.p. (°C)
Ph_3Sn - TePh	53.5	3.77	52.0	3.63	91-93
Ph_3Sn - $Te(C_6H_4.OMe)$	52.2	3.79	51.4	3.79	76-77
Ph_3Sn - $Te(C_6H_4.OEt)$	54.3	4.20	52.2	4.04	77-78
Ph_3Sn - $Te(C_6H_4.OPh)$	56.4	3.68	55.7	3.74	86-88

Physical Measurements. Mass spectra were recorded with an AEI MS9 instrument. Appearance potentials of RTe^+ were measured by the method of Warren[11] based on extrapolated voltage difference using argon as calibrant gas. Replicate determinations showed results to be reproducible to within ± 0.2eV (1eV = 96.5 kJ mol^{-1}). Measurements were carried out on ^{130}Te which is the isotope of largest mass number and highest relative abundance thus eliminating the danger of measuring (R-H)Te^+. However measurements on other isotopes, and the study of isotopic spread, indicated very little (R-H)Te^+ formation when R = Ph. Results are presented in table 2 for a range of organotellurium compounds.

^{1}H n.m.r. spectra were measured with a Varian spectrometer at 100 MHz. The Raman spectrum of $(C_6F_5)_2Te_2$ was recorded on a Cary 81 laser Raman spectrometer at the University of Nottingham (we thank Dr. G. Davidson for access to this instrument). Far infra-red spectra were measured using an FS 720 interferometer.

Mössbauer spectra were recorded for some compounds. The ^{125}Te data quoted were measured with the ^{125}Sb/Cu source at 80K and the absorbers at 4.2K as reported previously[13]. ^{119}Sn spectra were obtained via the PCMU service with a $Ba^{119m}SnO_3$ source with absorbers at 80K. The sign of the ^{119}Sn quadrupole splitting was determined experimentally to be negative for Ph_3Sn-TePh. Mössbauer data are given in table 3.

RESULTS AND DISCUSSION

Mass Spectroscopic Data. The ion RTe^+ may be readily identified in the mass spectrum of R_2Te_2 and probably arises by both of the routes shown in the scheme (some curvature was noted on plots used to measure the appearance potential, A.P., of this ion in ditelluride spectra). Alternatively, thermolysis of the ditelluride to telluride may occur prior to vapourisation. Whilst we may not completely exclude the latter possibility, we note that Ph_2Te^+ which is a prominent fragment in the mass spectrum of Ph_2Te_2, gives an A.P. of 10.0eV whereas the A.P. of Ph_2Te^+ from Ph_2Te is 8.75 eV. Presumably, if R_2Te arose mainly from thermolysis of the ditelluride on the probe of the mass spectrometer these figures would be more nearly equal. The A.P.s for Ph_2Te^+ together suggest that extrusion of tellurium from $R_2Te_2^+$ requires approximately 120 kJ mol^{-1} whereas, assuming an ionisation potential of ∿10eV for Ph_2Te_2 (probably an upper limit), the data of table 2 suggest the strength of Te-C and Te-Te in $R_2Te_2^+$ to be of the order of 3eV i.e. ∿290 kJ mol^{-1}. Thus extrusion of tellurium appears to be a low energy pathway for the decomposition of the parent ion. We note that differences in the A.P.s of $PhTe^+$ derived from PhTe-R (R = Ph, $-C_6H_4OMe$, $-C_6H_4OEt$, $-C_6H_4OPh$) are as likely to arise from differences in the ionisation potentials as from

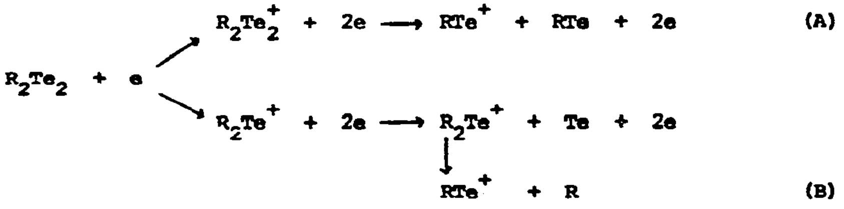


Table 2

Appearance potential of RTe^+ for some organotellurium compounds

(R = Ph or p-$CH_3.C_6H_4$-).

Compound	$A(PhTe^+)$[a]	Ref.[b]	Compound	$A(PhTe^+)$[a]	Ref.[b]
Ph_2Te_2[c]	13.6 ± 0.2	2	PhTe(p-PhO.C_6H_4)	13.2 ± 0.2	14
Ph_2Te[d]	13.35 ± 0.1	12	Ph_2Te_2 + $(C_6F_5)_2Te_2$	14.15 ± 0.2	-
PhTe-$SnPh_3$	13.55 ± 0.1	this work	Ph_2Te_2 + (p-MeO.$C_6H_4)_2Te_2$	13.0 ± 0.2	-
(p-$CH_3.C_6H_4)_2Te_2$	13.3 ± 0.2[e]	7	Ph_2Te_2 + (p-EtO.$C_6H_4)_2Te_2$	13.0 ± 0.2	-
(p-$CH_3.C_6H_4)_2Te$	13.35 ± 0.2[e]	13	PhTe(p-MeO.C_6H_4)	12.7 ± 0.2	14
(p-$CH_3.C_6H_4$)Te-$SnPh_3$	13.05 ± 0.2[e]	this work	PhTe (p-EtO.C_6H_4)	12.7 ± 0.2	14

[a] in eV [b] reference to preparation, [c] appearance potential of Ph_2Te^+ from same spectrum = 10.0 eV, [d] appearance potential of Ph_2Te^+ = 8.75eV, [e] refers to (p-$CH_3.C_6H_4)Te^+$

Table 3 Mössbauer spectroscopic data for some organotellurium compounds

Compound.	^{119}Sn data		^{125}Te data	
	δ^*(mm sec^{-1}) ± 0.03	Δ(mm sec^{-1}) ± 0.03	δ^+(mm sec^{-1}) ± 0.08	Δ(mm sec^{-1}) ± 0.1
$Ph_3Sn - TePh$	1.40	-1.31	0.15	9.2
$Ph_3Sn - Te(C_6H_4.CH_3)$	1.40	1.17	-	-
$Ph_3Sn - Te(C_6H_4.OMe)$	1.40	1.15	0.10	9.0
$Ph_3Sn - Te(C_6H_4.OEt)$	1.40	1.09	0.24	9.3
$Ph_3Sn - SePh$[a]	1.37	1.43	-	-
$Ph_3Sn - SPh$	1.39[b]	1.49[b]	-	-
$Ph_3Sn - OPh$	1.34[c]	2.27[c]	-	-
PhTe - TePh	-	-	0.37[d]	10.7[d]
$(p\text{-}MeOC_6H_4)_2Te_2$	-	-	0.42[d]	10.1[d]
$(p\text{-}EtOC_6H_4)_2Te_2$	-	-	0.28[d]	10.6[d]
Ph_4Sn[e]	1.22	0.0		

[a] Prepared following ref. 15, [b] data from ref. 16,

[c] data from ref. 16, [d] data from ref. 3. [e] data from ref. 17

[*] Chemical isomer shift relative to barium stannate

[+] Chemical isomer shift relative to I/Cu.

any difference of Te-C bond strengths in $PhTeR^+$.

Figure 1 shows a plot of the relative abundance of $Ph_2Te_2^+$, Ph_2Te and $PhTe^+$ as the exciting potential is varied from 12eV to 70eV. The results indicate that at low potentials Ph_2Te^+ is a dominant ion consistent with the dominance of route (B) and with the arguements above. Figure 1 is also consistent with the view that route (A) makes a greater contribution as the exciting potential is increased.

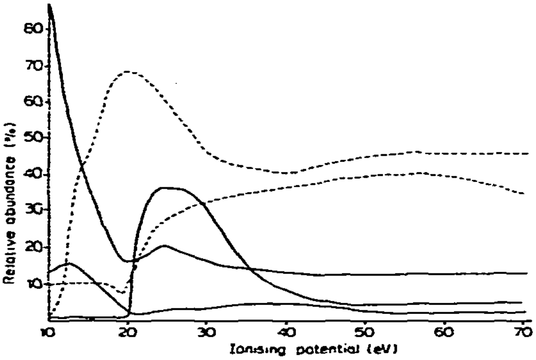


Fig. 1. Plot of the relative abundance against the ionising potential of $Ph_2Te_2^+$, Ph_2Te and $PhTe^+$.

A feature of table 2 is the remarkable consistency (with few exceptions) of the A.P.s of $PhTe^+$ from whatever source (the same is true for the p-tolyl-compounds measured). However, the similar A.P.s for RTe^+ (R = Ph, p-$CH_3.C_6H_4$-) from R_2Te_2 and RTe-SnP_3 need not reflect similar Te-Te and Te-Sn bond strengths, since in addition to RTe-$SnPh_3^+$ the spectra of the tin compounds sometimes show $Ph_6Sn_2^+$ which can only arise from thermolysis. Hence RTe^+ may arise via the ditelluride as well as via the parent ion of the triphenylstannyl-derivative.

When the spectra of mixtures of ditellurides are measured e.g. Ph_2Te_2 + (p-$PhOC_6H_4)_2Te_2$ it is possible to observe both parent ions $(Ph_2Te_2)^+$ and (p-$PhOC_6H_4)_2Te_2^+$) but, in addition, PhTe-Te$C_6H_4OPh^+$ is seen. Also, as well as Ph_2Te^+ and (p-$PhOC_6H_4)Te_2^+$ the parent ion of the mixed telluride is noted, $PhTe(C_6H_4OPh)^+$. Similar observations are made when intimate mixtures of other ditellurides are examined. Furthermore the measured A.P. for $PhTe^+$ shows more fluctuation on replicate determination for different mixtures supporting the contention that route (C) contributes significantly to its formation:

$$\begin{tikzcd}
\mathrm{PhTeTeR} + e \arrow[r] & \mathrm{PhTeTeR}^{+} + 2e \arrow[d] & & \\
 & \mathrm{PhTeR}^{+} + \mathrm{Te} \arrow[r] & \mathrm{PhTe}^{+} + \mathrm{R} & \text{(C)}
\end{tikzcd}$$

These observations confirm that unsymmetrical ditellurides can exist, yet all attempts to separate such mixtures via fractional crystallisation or by chromatography resulted in the isolation of the original symmetrical species.

Examination of the infra-red spectra of mixtures of two ditellurides showed bands due to the two symmetrical materials and some modification to vibrations in the 200–260 cm^{-1} region in which skeletal motions are expected[1]. This would be consistent with the view that new species were present. In order to ascertain if the unsymmetrical species existed in solution (from which separation was generally attempted), the problem was examined further by nuclear magnetic resonance spectroscopy.

^{1}H nmr Investigation of Solutions of Two Ditellurides. The system selected for study was $(C_6F_5)_2Te_2$ + $(p\text{-}MeO.C_6H_4)_2Te_2$ because the ^{1}H nmr spectrum of the p-methoxyphenyl- compound is easy to interpret and is relatively simple, also the choice of the perfluoro- compound is likely to ensure the best chance of different proton chemical shifts for $(p\text{-}MeO.C_6H_4)_2Te_2$ and $(p\text{-}MeO.C_6H_4)Te\text{-}Te(C_6F_5)$. Experiments with a variety of pairs of ditellurides confirmed that this was the easiest system with which to work. Two distinct methyl singlets were seen for a range of mixtures in deuteriochloroform one of which corresponds to $(p\text{-}MeOC_6H_4)_2Te_2$, the other however arises from a new species – reasonably $(p\text{-}MeOC_6H_4)Te\text{-}Te(C_6F_5)$. However there is the possibility that the acceptor power of tellurium is enhanced when bonded to a perfluorophenyl group and that co-ordination of the ether oxygen of the bis (p-methoxyphenyl)ditellurides to one tellurium atom of $(C_6F_5)_2Te_2$ may occur. When the ^{1}H nmr spectrum of phenyl methyl ether is measured in the presence of $(C_6F_5)_2Te_2$, no evidence of co-ordination is obtained, thus we proceed on the assumption that the mixed ditelluride is formed.

Integration of the spectrum enables us to estimate an "equilibrium constant" (K, as defined below) of approximately 4.

$$K = \frac{[(C_6F_5)Te\text{-}Te(C_6H_4OMe)]^2}{[(C_6F_5)_2Te_2]\,[(p.MeO.C_6H_4)_2Te_2]}$$

Furthermore, this was shown to be independent of temperature and hence the reaction is under entropy control and there is the further implication that the Te-Te bond strength is not greatly influenced by the nature of the group R in R_2Te_2.

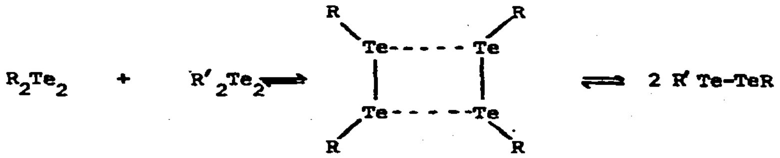
However, Mössbauer data[3] indicated a lower tellurium p-orbital population in bonds to perfluorophenyl-groups than to phenyl-groups and we see from table 2 that the measured appearance potential of PhTe$^+$ from the mixture Ph_2Te_2 + $(C_6F_5)_2Te_2$ (the perfluoro compound in excess to ensure maximum conversion of Ph_2Te_2

to PhTe-Te(C_6F_5)) is significantly greater than that measured from other sources. The Raman spectrum of $(C_6F_5)_2Te_2$ shows two bands to be candidates for ν(TeTe) at $\Delta\nu$ = 173 and 186 cm^{-1}. Both these are within the range observed by Thavornyutikarn hence the Raman data do not suggest that the tellurium-tellurium bond strength is significantly different in the perfluoro- and phenyl- compounds. Thus the appearance potential data more probably reflect an increase in the ionisation potential of the ditelluride on substitution of a perfluorophenyl group. Since the Mössbauer data would argue for a positive charge on tellurium in the Te-C_6F_5 bond, if ionisation is from the lone pair orbital on tellurium, this would seem reasonable.

The mechanism of the redistribution reaction is of interest. It may go via a radical mechanism.

$$R_2Te_2 \rightleftharpoons 2R\dot{T}e$$
$$R'_2Te_2 \rightleftharpoons 2R'\dot{T}e$$
$$R\dot{T}e + R\ Te \rightleftharpoons RTe - TeR'$$

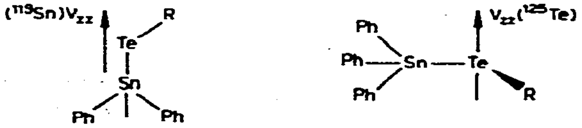
If this is the case, it is surprising that we do not detect other products e.g. R_2Te, R'_2Te and RTeR' and that no tellurium is extruded. A recent study by Gunther et al.[18] on the photochemically and thermochemically induced extrusion of selenium from dibenzyldiselenide emphasises this point. Whilst our evidence does not justify extensive mechanistic speculation, one other possibility should be considered. A dimeric intermediate, similar in type to that recently confirmed for a redistribution reaction between platinum and palladium chloride - tributylphosphine complexes[19],



and which could also account for the formation of R'P-TeR from R'_2P-PR'_2 and R_2Te_2[20]. We attempted to differentiate the possibilities kinetically but, unfortunately, without success. The fact that we could differentiate sharp methyl signals for the symmetrical and unsymmetrical ditellurides indicated that the redistribution reaction was slow on the nmr timescale, hence we raised the temperature in the hope of causing the two methyl resonances to coalesce. Decomposition occurred first. We did however attempt some measurements on the reaction between a ditelluride and triphenyltin hydride (this affords Ph_3Sn-TeR and dihydrogen - see experimental section). Triphenyltin hydride is a radical trap, but we found no reaction at room temperature (whereas the redistribution reaction did occur at this temperature) and, at 78.5°C, the rate, measured by quenching aliquots of the solution in chloroform and monitoring the optical density at the diphenylditelluride visible spectral maximum, was independent of the ditelluride concentration and equal to the rate of thermal decomposition of Ph_3SnH at that temperature. Thus no evidence that ditellurides spontaneously produce $R\dot{T}e$ radicals is obtained and the dimeric intermediate remains a distinct possibility.

^{125}Te and ^{119}Sn Mössbauer Studies. The reaction between triphenyltin hydride and various diarylditellurides affords a new series of triphenylstannyl(aryl) tellurides. These compounds are attractive for Mössbauer studies since the presence of two Mössbauer nuclei in the same molecule should lead to a more self-consistent interpretation of the data, a point made convincingly recently by Drago and his collaborators in their comparative study of $MeSnI_3$ and Me_3SnI[21]. The new compounds give adequate elemental analysis and good mass spectra, in which the parent ion is recognised. They are stable over long periods of time when stored in a refridgerator, but at room temperature they slowly discolour as decomposition to the ditelluride occurs.

The ^{125}Te data were measured by the PCMU at Harwell and at Simon Fraser University. The data were in good agreement and that obtained at Simon Fraser University is tabulated, this being directly comprable to that reported for a wide range of organotellurium compounds[3]. The sign of the ^{119}Sn quadrupole splitting is reasonably assumed to be negative in $Ph_3Sn\text{-}TeR$ and this was confirmed experimentally for R = Ph, thus Vzz, the principal component of the electric field gradient tensor, is positive. Vzz is assumed to be negative at the tellurium nucleus[3]. The relative directions of Vzz at the two Mössbauer nuclei are given in the figure.



The ^{119}Sn isomer shifts (table 3), relative to $BaSnO_3$, for Ph_3SnXPh (X = O,S,Se,Te - we have measured $Ph_3SnSePh$ to complete the series) exhibit the following trend:

$$Ph_4Sn < Ph_3SnOPh < Ph_3SnSPh \sim Ph_3SnSePh \sim Ph_3SnTePh$$

It would appear that the Sn-XPh bonds have greater p-character than the Sn-Ph bond and that this leads to an increased removal of tin 5p electron density which in turn results in an increase in s electron density at tin (and a more positive isomer shift), through deshielding. However, the Sn-XPh bonds must retain significant s character and the relative isomer shifts of $Ph_3Sn\text{-}OPh$ and

Ph_3Sn-TePh argue for the greater covalency of the Sn-Te bond relative to the Sn-O bond. The greater s electron density at the tin nucleus in the Sn-Te bond would then result from a smaller withdrawal of s-p hybrid electron density from tin compared with that in the Sn-O bond.

The sign of the ^{119}Sn quadrupole coupling constant (e^2qQ) in $Ph_3SnTePh$ is negative, thus Vzz, the principal component of the electric field gradient tensor, is positive. Assuming that the micro-symmetry of the tin environment approximates to C_{3v}, Vzz will lie along the Sn-Te bond axis (see figure) and the positive sign implies that the Sn-Te σ-bonding orbital has a smaller occupancy than the Sn-Ph σ-bonding orbital.

In contrast to the isomer shifts, which do not change very much, the ^{119}Sn quadrupole splittings (table 2) span a range of values from 1.09 to 2.27 mm s^{-1}. This is evidence of the changing sp- character of the Sn-XPh and Sn-Ph bonds. Thus while the p orbital imbalance is much greater in Ph_3SnOPh than in $Ph_3SnTePh$ but the values of $|\psi(o)|^2$ are similar in the two compounds.

The ^{125}Te isomer shifts of the compounds Ph_3SnTeR (R = Ph⁻, $pMeOC_6H_4$-, p-$EtOC_6H_4$-) are less positive than those of the diarylditellurides R_2Te_2. This suggests that in the Sn-Te bond there is a greater occupancy of the tellurium 5p orbital than is the case for the Te-Te bond, leading to an increased shielding of the 5s electrons from the tellurium nucleus and a smaller isomer shift. A greater occupancy of the tellurium 5p orbital in the Te-Sn bond than in the Te-Te bond implies a smaller p-orbital imbalance for tellurium in Ph_3Sn-TeR than in RTe-TeR which leads to the observed smaller ^{125}Te quadrupole splittings for the triphenylstannyl compounds than for the ditellurides. Thus both the ^{119}Sn and ^{125}Te Mössbauer data are consistent with the donation of electron density from the tin to the tellurium and this leads to a net increase in $|\psi(o)|^2$ and a positive Vzz at the tin nucleus, and a smaller δ and Δ at the tellurium nucleus in comparison with the values observed for R_2Te_2. It is interesting to note that any significant $5p_\pi(Te) \rightarrow 5d_\pi(Sn)$ overlap would lead to the prediction that the ^{125}Te isomer shift should increase from the ditelluride compound to the tin-tellurium compound. Thus only an s-p bonding model gives a self-consistent explanation of the isomer shift data.

In the past a number of attempts have been made[22-25] to interpret ^{119}Sn Mössbauer data in terms of valence-shell orbital populations and such analyses have also recently been extended to ^{121}Sb[26] and ^{125}Te[3]. It is of interest in the present case to see if the two sets of Mössbauer data (^{119}Sn, ^{125}Te) afford a self consistent picture of the orbital populations in Ph_3Sn-TeR. Only the quadrupole splittings are used here to estimate the σ-bond orbital populations.

For tin in the compound $Ph_3SnTePh$, assuming C_{3v} symmetry with the Sn-Te bond along C_3, in Townes-Dailey theory[27]:

$$e^2qQ = e^2q_0Q \cdot \frac{[1 - 3\cos\alpha]}{[1 - \cos\alpha]} \quad (a-b)$$

where e^2q_oQ is the unit coupling constant taken as +8.6 mm s^{-1} [25], α is the Ph-Sn-Ph bond angle and a and b are the Sn-Te and Sn-Ph orbital populations at tin, respectively. The latter has been estimated[22] as 1.1. If it is assumed that $\alpha = 109.5^\circ$ (i.e. regular tetrahedral geometry), then a is 0.7 and the tellurium contribution to that bond will be 1.3 electrons.

At the tellurium atom, the Te-Ph σ-bond orbital population has been previously estimated as 1.1[3]. The tellurium is bonded to two ligands, Ph_3Sn^- and Ph^-, and has two lone pairs of electrons. In our previous analysis of quadrupole splittings in a large number of compounds of types R_2Te, R_2Te_2, R_2TeX_2, $RTeX_3$ (X = Cl,Br,I) it was found that a consistent explanation of the Δ values in terms of a simple additive model could be obtained by assuming the $5s^2$ electrons to be stereochemically inactive. The present arguements are developed from the same assumption, thus the tellurium is considered to bond the Ph_3Sn- and Ph- ligands through its $5p_y$ and $5p_x$ orbitals, with the $5p_z$ lone pair directed perpendicular to the bonding plane. In Townes-Dailey theory

$$
\begin{aligned}
e^2qQ &= -Up\, e^2q_oQ \\
Up &= -U_z + \frac{U_x + U_y}{2} \\
\text{and} \quad &= \frac{3}{2}\left[\frac{U_x - U_y}{Up}\right] \\
\text{when} \quad \Delta &= \tfrac{1}{2}\, e^2qQ\left(1 + \frac{\eta^2}{3}\right)^{\frac{1}{2}}
\end{aligned}
$$

where the U values are the individual p-orbital populations and η is the asymmetry parameter. Taking $U_x = 1.1$, $U_y = 1.3$ and $U_z = 2.0$, and assuming e^2q_oQ (^{125}Te) = + 24 mm s^{-1} [28], the Δ is calculated as 9.8 mm s^{-1}. The observed value is 9.2 mm s^{-1} and this would correspond to a U_y value (The Te-$SnPh_3$ bond) of ~ 1.4. Given the many approximations in the analysis, the ^{119}Sn and ^{125}Te quadrupole splitting data provide a surprisingly consistent picture of the electron distribution in the Sn-Te bond. The agreement is in part fortuitous, since Δ (^{119}Sn) for the compounds Ph_3SnTeR (R = Ph^-, p-$MeC_6H_4^-$, p-$MeOC_6H_4^-$) ranges from 1.31 to 1.09 mm s^{-1}, corresponding to effective σ-bond orbital populations on tin in the Sn-Te bond of 0.70 to 0.76, while the ^{125}Te quadrupole splittings do not show any significant change. However the variation in Δ(^{119}Sn) would correspond to a variation of Δ(^{125}Te) of only 0.4 mm s^{-1} which is almost within the errors. Moreover, the small variation in Δ(^{119}Sn) may in part be explained by the variations in the relative s-p hybrid character of the Sn-TeR and Sn-Ph bonds as R is varied.

The above analysis is based on an oversimplified model, since it assumes sp^3 hybridisation at the tin and pure p bonding at the tellurium, neither of which can be wholly true. However, such simplifications are characteristic of additive models as generally used in interpreting Mössbauer data, and the assumption of such idealised geometries generally leads to a more consistent explanation of quadrupole splittings than more sophisticated models which attempt to accommodate departures from ideal geometries[22].

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