Mechanism of the Thermal Decomposition of Tetra-aryltellurium Species

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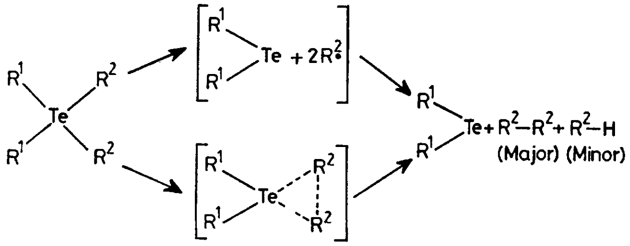
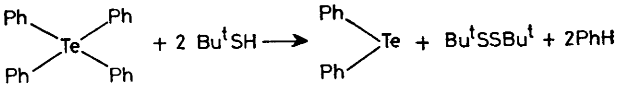
Summary Tetra-aryltellurium compounds decompose thermally to biaryls and diaryl tellurides *via* a concerted pathway which is preceded by a rapid ligand exchange process on Te^{IV} species; diaryl tellurides do not undergo ligand exchange under comparable conditions.

Tetra-aryltellurium compounds decompose on melting to give diaryl tellurides and biaryls as the major products (Scheme 1, R^1=R^2=aryl).[1,2] Alkyl containing species (R^1=alkyl or aryl, R^2=alkyl) decompose similarly.[1,2]

Tetraphenyltellurium,[2] prepared from tellurium tetrachloride and lithium halide-free phenyl-lithium, was decomposed under a variety of conditions (Table 1). Noticeably the yields of biphenyl and diphenyl telluride, on decomposition at 140 °C in toluene, triethylsilane, furan, or styrene, did not differ significantly from the neat reaction. There is little aryl radical trapping. Tetraphenyltellurium reacted exothermically with Bu^tSH at room temperature, where it is stable thermally, to produce benzene, diphenyltelluride, and di-t-butyl disulphide quantitatively (Scheme 2), but we consider that this is a heterolytic and not a radical reaction. Only traces of polymer were formed from decomposition in styrene, although by comparison, thermolysis of equimolar dibenzoyl peroxide gave 77% polymeric material.[3]



Scheme 1



Scheme 2

Since thermolysis of tetraphenyltellurium in toluene and furan at 80 °C afforded similar results to those at 140 °C (Table 1), we were able to compare its decomposition with

Table 1. Decomposition of Ph_4Te at 140 °C in a sealed tube.

Reaction	C_6H_6 (±2%)	Conversion/%[a] Ph_2Te (±5%)	Ph–Ph (±3%)
No solvent (*in vacuo*)	10	92	89
PhMe (N_2)	11	96	101
Et_3SiH (N_2)	—	80	90
Furan (N_2)	16	94	85
Styrene[b] (N_2)	—	103	95
Bu^tSH[c] (N_2)	114[d]	105	0

[a] G.l.c. determination of benzene (squalane on chromosorb P 80—100 mesh), diphenyl telluride, and biphenyl (Fluorosilicone oil on chromosorb W 80—100 mesh) were on a Perkin-Elmer F11 gas chromatograph with F.I.D. [b] Equivalent amounts of polymeric material were formed with or without tetraphenyltellurium. [c] Reaction carried out at room temperature. [d] Larger error limits to this determination.

phenylazotriphenylmethane (PAT), a known source of phenyl radicals at 80 °C. Thus decomposition of PAT in toluene (2 × concentration used in tetraphenyltellurium reactions) gave triphenylmethane (38%), benzene (56%), diphenylmethane (19%), *o*-phenyltoluene (8·5%), and *p*-phenyltoluene (4·5%). Clearly, this result suggests that phenyl radicals are not common to both decompositions.

Table 2. Decomposition of $(p\text{-}MeC_6H_4)_4Te$.

Reaction[a]	Toluene/%	Bitolyl : Ditolyltellurium
Tol_4Te (N_2)	15	0·83 : 1
Tol_4Te + 1,4-Dihydrobenzene (N_2)	12·5	0·94 : 1

[a] Tol = $p\text{-}MeC_6H_4$.

Tetrakis(4-methylphenyl)tellurium likewise decomposed on melting (124—127 °C) to give only bis(4-methylphenyl) telluride and 4,4′-dimethylbiphenyl together with only a small amount of toluene. The results of thermolysis *in vacuo* and in a 2 : 1 mixture of benzene–1,4-dihydrobenzene (a powerful hydrogen atom transfer reagent[4]) are presented in Table 2.

In contrast, the corresponding decomposition of tolylazotriphenylmethane (TAT) in benzene–1,4-dihydrobenzene gave an 80% yield of toluene and a quantitative amount of triphenylmethane thus demonstrating effective tolyl radical scavenging. The results thus far indicate that decomposition of tetra-aryltellurium compounds does not give radicals that can be trapped. However, these observations are in direct contrast to those of cross-over experiments. Tetrakis(4-methylphenyl)tellurium, decomposed with tetraphenyltellurium *in vacuo* or in toluene under nitrogen, afforded large quantities of mixed biphenyls and mixed diaryltellurides. Similarly, decomposition of tetraphenyltellurium with tetrakis(pentadeuteriophenyl)tellurium gave mixed products.

Since radicals cannot be detected, it is proposed that the mixed products arise by interchange of the aryl groups prior to decomposition. Analogous exchange reactions have been reported for organo-lead and -mercury compounds.[5] Based upon the statistical mole fractions of the possible mixed tetravalent tellurium species from the random exchange of phenyl and tolyl groups (or pentadeuteriophenyl), and the assumption that decompositions to form mixed or symmetrical diaryl tellurides and biaryls are equivalent processes, the theoretical mole fractions of biaryls and tellurides can be calculated (Table 3). The experimental results are in reasonable agreement with calculated values. The easy exchange of organic groups does not occur between diaryl tellurides. However, mixed telluride and biphenyl were obtained when tetratolyltellurium was decomposed in the presence of diphenyl telluride.

We conclude that tetra-aryltellurium compounds exchange ligands by a fast non-radical process prior to decomposition to diaryltellurium and biaryl. The decomposition process itself is concerted, does not involve radicals, and represents an interesting procedure for the formation of carbon–carbon bonds.

Table 3. Decomposition of mixtures of Ph_4Te and $(p\text{-}MeC_6H_4)_4Te$, and $(C_6H_5)_4Te$ and $(C_6D_5)_4Te$.

Reaction		$R^1=R^2=Ph$	$R^1=Ph,R^2=Tol$[a]	$R^1=R^2=Tol$[a]
Ph_4Te + Tol_4Te (*in vacuo*)	R^1TeR^2	0·27	0·45	0·26
	Calc.	0·38	0·42	0·19
	R^1–R^2	0·43	0·43	0·12
Ph_4Te + Tol_4Te (in toluene under N_2)	R^1TeR^2	0·21	0·52	0·26
	Calc.	0·32	0·43	0·24
	R^1–R^2	0·31	0·49	0·19
		$R^1=R^2=Ph$	$R^1=C_6D_5,R^2=Ph$	$R^1=R^2=C_6D_5$
Ph_4Te + $(C_6D_5)_4Te$ (*in vacuo*)	R^1TeR^2	0·33	0·47	0·19
	Calc.	0·40	0·42	0·18
	R^1–R^2	0·41	0·42	0·15

[a] Tol = $p\text{-}MeC_6H_4$.

We thank the South African Council for Scientific and Industrial Research and the S.R.C. for financial assistance (to S.A.G.).

(*Received* 16*th February* 1977; *Com.* 138.)

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