

Reactions of Some Phenyltellurium(IV) Compounds with Metal Halides

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Reactions between triphenyltelluronium halides and mercury(II) halides in alcoholic solutions give crystalline compounds which are shown by infrared spectroscopy to correspond to the formulation $\text{Ph}_3\text{Te}\cdot\text{HgX}_3$ or $(\text{Ph}_3\text{Te})_2\cdot\text{HgX}_4$. Conductivity, ^1H n.m.r. and molecular weight determinations are consistent with their dissociation in dilute solution as Ph_3Te^+ and HgX_3^- or Ph_3Te^+ and $\text{Ph}_3\text{Te}\cdot\text{HgX}_4^-$ units. Diphenyltelluroxide acts a ligand with transition metal halides whereas reactions with some main group halides follow different routes to give diphenyltellurium(IV) dihalides.

Introduction

Addition compounds of the type $\text{R}_2\text{Te}\cdot\text{HgX}_2$ (R = alkyl or aryl; X = halogen) have been known for many years and their chemistry has been recently reviewed [1, 2]. In contrast, the adducts of triorganotelluronium halides appear to be less well understood and have received significantly less attention in contemporary studies [3–9].

Similarly, although the diaryltelluroxides are well documented compounds [10–13], with structures which have been described [14] as being similar to the corresponding selenoxides there is an apparent sparcity of data by which their fundamental chemistry can be described. It is especially interesting that despite the large number of complexes of dimethyl sulphoxide [15] there appear to be no reports of the analogous compounds of diaryltelluroxides.

In order to clarify and expand this area of organotellurium chemistry we have prepared and examined some products from reactions of triphenyltelluronium halides with mercury(II) halides and from reactions of diphenyltelluroxide with both transition- and main group-metal halides.

Experimental

Triphenyltelluronium Complexes of Mercury(II) Halides

Triphenyltelluronium chloride was prepared according to the method reported in the literature [16]. The corresponding -bromide and -iodide derivatives were obtained by halogen exchange reactions using potassium -bromide and -iodide in hot water.

Materials of composition $\text{Ph}_3\text{Te}\cdot\text{HgX}_3$ and $(\text{Ph}_3\text{Te})_2\cdot\text{HgX}_4$ (X = Cl or Br) were obtained from mixtures of the required proportions of triphenyltelluronium halide and mercury(II) halide in saturated ethanolic solution. The white crystalline solids were recrystallised from acetone and chloroform respectively. The corresponding iodine compounds were obtained as yellow solids from similar reactions between the appropriate iodides in methanolic solutions. Analytical data are reported in Table I.

Reactions of Diphenyltelluroxide and Metal Halides

Diphenyltelluroxide was prepared by alkaline hydrolysis of diphenyltellurium(IV) dibromide [10–12].

Reactions between ethanolic solutions of diphenyltelluroxide and metal halides in ice baths gave products at 5 °C (24 h) which were recrystallised from ethanol. Analytical data for the diphenyltelluroxide complexes of transition metal halides are given in Table II.

Conductance measurements were performed under dry conditions in nitrobenzene, acetone and acetonitrile solution at 25 ± 1 °C using a conductance bridge and dip type cell with smooth platinum electrodes. Molecular weights were determined cryoscopically in nitrobenzene. (Tabulated molar conductance and molecular weight data are deposited with the Editor).

TABLE I. Analytical Data for Triphenyltelluronium Complexes of Mercury(II) Halides.

Compound	M.p. (°C)	Found (%)				Molecular formula	Calcd. (%)				
		C	H	Hal	Hg		C	H	Hal	Hg	
$\text{Ph}_3\text{TeHgCl}_3$	149-150	32.60	1.90	15.97	18.54	$\text{C}_{18}\text{H}_{15}\text{Cl}_3\text{TeHg}$	32.45	2.25	16.00	19.17	30.13
$\text{Ph}_3\text{TeHgBr}_3$	142-144	28.20	1.69	29.76	15.96	$\text{C}_{18}\text{H}_{15}\text{Br}_3\text{TeHg}$	27.03	1.87	30.00	15.97	25.10
$\text{Ph}_3\text{TeHgI}_3$	142-144	22.80	1.39	40.36	13.43	$\text{C}_{18}\text{H}_{15}\text{I}_3\text{TeHg}$	22.98	1.59	40.50	13.57	21.34
$(\text{Ph}_3\text{Te})_2\text{HgCl}_4$	198-200	40.70	2.60	13.44	23.57	$\text{C}_{36}\text{H}_{30}\text{Cl}_4\text{Te}_2\text{Hg}$	40.76	2.82	13.40	24.08	18.92*
$(\text{Ph}_3\text{Te})_2\text{HgBr}_4$	212-214	35.20	2.30	25.70	20.41	$\text{C}_{36}\text{H}_{30}\text{Br}_4\text{Te}_2\text{Hg}$	34.91	2.42	25.83	20.62	16.21
$(\text{Ph}_3\text{Te})_2\text{HgI}_4$	218-220	30.10	1.90	34.85	18.01	$\text{C}_{36}\text{H}_{30}\text{I}_4\text{Te}_2\text{Hg}$	30.30	2.10	35.61	17.90	14.07

TABLE II. Analytical Data for Diphenyltelluroxide Complexes of Transition Metal Halides.

Compound	M.p. (°C)	Found (%)				Molecular formula	Calcd. (%)			
		C	H	Hal	Hal		C	H	Hal	Hal
$(\text{Ph}_2\text{TeO})_3\text{CrCl}_3$	230-232	42.47	3.08	10.58	10.58	$\text{C}_{36}\text{H}_{30}\text{Cl}_3\text{O}_3\text{Te}_3\text{Cr}$	41.49	2.86	10.11	10.11
$(\text{Ph}_2\text{TeO})_2\text{MnCl}_2$	246-247	40.79	2.83	8.00	8.00	$\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_2\text{Te}_2\text{Mn}$	39.95	2.77	9.84	9.84
$(\text{Ph}_2\text{TeO})_2\text{FeCl}_3$	137-139	37.43	2.80	14.07	14.07	$\text{C}_{24}\text{H}_{20}\text{Cl}_3\text{O}_2\text{Te}_2\text{Fe}$	38.05	2.64	14.03	14.03
$(\text{Ph}_2\text{TeO})_2\text{FeBr}_3$	197-199	32.98	2.46	27.70	27.70	$\text{C}_{24}\text{H}_{20}\text{Br}_3\text{O}_2\text{Te}_2\text{Fe}$	32.34	2.24	27.77	27.77
$(\text{Ph}_2\text{TeO})_3\text{CoCl}_2$	179-181	43.28	3.26	6.60	6.60	$\text{C}_{36}\text{H}_{30}\text{Cl}_2\text{O}_2\text{Te}_3\text{Co}$	42.27	3.26	6.60	6.60
$(\text{Ph}_2\text{TeO})_2\text{NiCl}_2$	239-241	40.59	2.81	9.49	9.49	$\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_2\text{Te}_2\text{Ni}$	39.76	2.75	9.79	9.79
$(\text{Ph}_2\text{TeO})_2\text{ZnBr}_2$	206-208	35.83	2.78	19.17	19.17	$\text{C}_{24}\text{H}_{20}\text{Br}_2\text{O}_2\text{Te}_2\text{Zn}$	35.13	2.43	19.46	19.46

TABLE III. Far Infrared and Raman Data for Triphenyltelluronium Complexes of Mercury(II) Halides.

Assignment	Ph ₃ TeHgCl ₃		Ph ₃ TeHgBr ₃		Ph ₃ TeHgI ₃		(Ph ₃ Te) ₂ HgCl ₄		(Ph ₃ Te) ₂ HgBr ₄		(Ph ₃ Te) ₂ HgI ₄	
	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman	Infrared	Raman
$\nu(\text{Te}-\text{C}) \text{ cm}^{-1}$	275(s)	276(w) 266(m)	275(sh) 270(s)	274(w) 266(m)	262(s)	264(m)	268(s)	269(s)	270(s) 263(s)	274(w) 263(s)	262(s)	266(vs)
$\nu(\text{Te}-\text{Hg}) \text{ cm}^{-1}$	105(vs)	105(s)		106(s)		105(vs)		105(m)		104(w)		107(m)
$\nu(\text{Hg}-\text{X}) \text{ cm}^{-1}$	282(s)	289(s)	192(m)	181(s)	127(m)	121(vs)		286(m)	192(m)	199(w)	127(m)	125(vs)

¹H n.m.r. spectra were recorded in *d*-acetonitrile using tetramethylsilane as an internal reference. Infrared spectra were recorded using samples in the form of KBr pellets or nujol mulls. Raman spectra of the solids were recorded using the 4880 Å exciting line of an argon ion laser.

Results and Discussion

Triphenyltelluronium Complexes of Mercury(II) Halides

Analyses of the products from the reactions of triphenyltelluronium halides with mercury(II) halides (Table I) are consistent with the formation of addition compounds. Thin layer chromatography confirmed the isolation of only one product from each reaction. Although complex formation between similar reactants has been reported in the literature [3–9] there appears to be some confusion as to whether halogen transfer occurs and, for example, whether the adducts should be represented as R₃TeX·HgX₂ or R₃Te·HgX₃. In this respect it is significant that the compounds give infrared and Raman spectra (Table III) which show absorptions corresponding to those recently assigned [17] to $\nu(\text{Te}-\text{Hg})$ but an apparent absence of any modes which may be attributed to $\nu(\text{Te}-\text{X})$ [17–20]. The observations are therefore consistent with the formation of complexes involving direct tellurium–mercury bonds and the loss of halogen by the triphenyltelluronium species. Given that boron tribromide acts as an acceptor [21, 22] to the anion released from telluronium halides it would not be unreasonable to expect similar behaviour by the mercury(II) halides. Since mercury is commonly surrounded by four or six ligands and given the dependence of the compositions of the materials reported here on the stoichiometric ratios of the reactants, we suggest that the complexes are best described by the formulations Ph₃Te·HgX₃ or (Ph₃Te)₂·HgX₄.

The infrared spectra of the complexes showed bands in the region 260–280 cm⁻¹ similar to those attributed to $\nu(\text{Te}-\text{C})$ in other phenyl derivatives of tellurium [17–20]. This is particularly interesting since the donation of electrons from tellurium to mercury in the formation of an adduct might be expected to modify the carbon–tellurium infrared frequencies, indeed, it appears significant that the $\nu(\text{Te}-\text{C})$ assignments in these complexes are not significantly different from those reported for the free diphenyltelluride unit [18]. Although the extent of back bonding from platinum to tellurium in diorganotelluride complexes of platinum(II) is unclear [23, 24] it is quite reasonable that some degree of back donation of *dπ* electrons from mercury into empty tellurium *d* orbitals does occur. The $\nu(\text{Hg}-\text{X})$ bands were assigned according to the analyses of other spectra of mercury halides [17, 25, 26].

The crystalline triphenyltelluronium complexes of mercury(II) halides are stable in air and soluble in acetone, acetonitrile, alcohol, chloroform and nitrobenzene with 2:1 adducts being less soluble than their 1:1 analogues.

The molar conductance data for all the compounds except $(\text{Ph}_3\text{Te})_2 \cdot \text{HgI}_4$ were within the range expected [27] for 1:1 electrolytes containing *ca.* 10^{-3} M of solute. It might be expected that materials of the type $\text{Ph}_3\text{Te} \cdot \text{HgX}_3$ dissociate as either Ph_3Te^+ and HgX_3^- or $\text{Ph}_3\text{Te} \cdot \text{HgX}_2^+$ and X^- pairs, whilst complexes of composition $(\text{Ph}_3\text{Te})_2 \cdot \text{HgX}_4$ dissociate as either Ph_3Te^+ and $\text{Ph}_3\text{Te} \cdot \text{HgX}_4^-$ or $(\text{Ph}_3\text{Te})_2 \cdot \text{HgX}_3^+$ and X^- species. In this respect it is significant that the ^1H n.m.r. spectra from the complexes formulated as $\text{Ph}_3\text{Te} \cdot \text{HgX}_3$ showed similar phenyl proton signals which were independent of the halogen and therefore consistent with dissociation as Ph_3Te^+ and HgX_3^- . However, the spectra from materials of the type $(\text{Ph}_3\text{Te})_2 \cdot \text{HgX}_4$ suggested the presence of two types of phenyl proton signals the positions of which appeared to depend on the electron withdrawing nature of the halogen and indicative of dissociation as Ph_3Te^+ and $\text{Ph}_3\text{Te} \cdot \text{HgX}_4^-$ units. The complex $(\text{Ph}_3\text{Te})_2 \cdot \text{HgI}_4$ gave conductance data which suggested dissociation properties intermediate between those of 1:1 and 1:2 electrolytes.

The low molecular weights of the complexes at low solute concentrations were consistent with the conductance data, however, at higher solute concentrations the molecular weights resembled the formula weights suggesting the existence of molecular species.

Reactions of Diphenyltelluroxide with Metal Halides

Diphenyltelluroxide reacted with electron accepting transition metal halides to give complex compounds (Table II). Given that the coordination chemistry of triphenylphosphine oxides [28–31] and triarylsarsine oxides [32–36] with a variety of acceptors is well established it might be expected that diphenyltelluroxide would exhibit similar electron donor properties. Indeed, a large number of complexes of dimethyl sulphoxide have been reported [15] in which oxygen frequently acts as the donor atom and, given the relatively high dipole moment of di-*p*-tolyl telluroxide [37] which suggests that the tellurium–oxygen bond in these compounds is quite polar, it is not unreasonable that the diphenyltelluroxide complexes of transition metal halides should involve similar coordination.

Reactions of diphenyltelluroxide with the halides of aluminium, carbon, silicon and phosphorus in ethanol were quite different in that crystalline diphenyltellurium(IV) dihalides were formed. Presumably such reactions involve the solvolysis of the main

group halides by ethanol and subsequent halogenolysis of diphenyltelluroxide by the hydrogen halide.

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