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Triphenyltelluronium Halo (mixed) Titanates (IV)

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The paper reports the synthesis and properties of triphenyltelluronium halo (mixed) titanates (IV). 1 : 1, $Ph_3TeX.TiX'_4$ and 2 : 1, $2Ph_3TeX.TiX'_4$ (where X, X'=Cl, Br, I) type products are obtained by reactions of Ph_3TeX with TiX'_4. Conductivity, molecular weight determinations and ^1H nmr are consistent with their dissociation in dilute solution as Ph_3Te^+ and TiX'_4X^- or Ph_3Te^+ and $TiX'_4X^2_2{}^-$ units. The absence of Te–Ti and Te–X vibrations in the far i.r. spectra of these compounds reflects the transfer of halogen atom from Ph_3TeX to TiX'_4 thus resulting in the formation of halo (mixed) titanate (IV) ions.

INTRODUCTION

Triphenyltelluronium halides are known[1,2] to form adducts with BBr_3, $ZnCl_2$, HgX_2 etc., but such type of compounds have received significantly less attention. Characteristics of only a few adducts of triphenyltelluronium halides, those with HgX_2[3,4], TiX_4[5] and $SnCl_4$[6] have been reported. We report here the synthesis of adducts of Ph_3TeX with TiX'_4 (X, X'_4 = Cl, Br, I) and describe some of their physical and spectroscopic properties.

EXPERIMENTAL

Tellurium tetrachloride used was of Riedel (Germany) and was purified before use by a standard method.[7] Triphenyltelluronium chloride was prepared by the method reported in literature.[8] The corresponding bromide and –iodide derivatives were obtained by halogen exchange reactions using KBr and KI (BDH, AnalR quality) in hot water. Titaniumtetrachloride used was of Riedel, Germany and titanium tetrabromide and –tetraiodide were of Fluka-Switzerland.

Preparations

(i) Adducts of Ph_3TeCl with $TiBr_4$ and TiI_4

(a) Triphenyltelluronium chlorotetrabromotitanate (IV): $[Ph_3Te][TiBr_4Cl]$

A solution of Ph_3TeCl (3.95 g, 10 m mol) in about 20 ml of dry chloroform was added to a solution of $TiBr_4$ (3.68g, 10m mol) in about 20 ml of dry chloroform, dropwise and with constant stirring. The resultant clear solution was shaken for *ca.* 3 hrs. The brown crystalline solid thus obtained was filtered, washed with a mixture of chloroform and benzene

(1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca* 75%, m.pt. 124–125° (dec.).

(*b*) *Triphenyltelluronium dichlorotetrabromotitanate* (*IV*): $[Ph_3Te]_2[TiBr_4Cl_2]$

A solution of $TiBr_4$ (1.84 g, 5 m mol) in about 10 ml of dry chloroform was added to the solution of Ph_3TeCl (3.95 g, 10 m mol) in about 20 ml of dry chloroform, dropwise and with constant stirring. The resultant clear solution was shaken for about 2 hrs. The light brown product thus obtained was filtered, washed with chloroform and dried over P_4O_{10} in vacuo. Yield *ca* 65%; m.pt. 160–161° (dec.).

(*c*) *Triphenyltelluronium chlorotetraiodotitante* (*IV*): $[Ph_3Te][TiI_4Cl]$

A solution of Ph_3TeCl (1.97 g, 5 m mol) in about 10 ml of dry chloroform was added to the solution of TiI_4 (2.78 g, 5 m mol) in 10 ml of dry chloroform dropwise and with constant stirring. The resultant clear solution was concentrated under vacuum to about 10 ml and left overnight in a vacuum desiccator. A brownish black product was obtained which was filtered, washed with benzene and dried over P_4O_{10} in vacuo. Yield *ca* 80%; m.pt. 144–145° (dec.)

(*d*) *Triphenyltelluronium dichlorotetraiodotitanate* (*IV*): $[Ph_3Te]_2[TiI_4Cl_2]$

A solution of TiI_4 (2.78 g, 5 m mol) in 10 ml of chloroform was added to the solution of Ph_3TeCl (3.59 g, 10 m mol) in chloroform (20 ml), dropwise and with constant stirring. The resultant clear solution was concentrated under vacuum to about 10 ml and left in a vacuum desiccator overnight. This resulted in separation of a brown product which was filtered, washed with benzene and dried over P_4O_{10} in vacuo. Yield *ca* 70%, m.pt. 164–165° (dec.).

(*ii*) *Adducts of* Ph_3TeBr *with* $TiCl_4$ *and* TiI_4

(*a*) *Triphenyltelluronium tetrachlorobromotitanate* (*IV*): $[Ph_3Te][TiCl_4Br]$

A suspension of Ph_3TeBr (4.38 g, 10 m mol) in about 20 ml of dry chloroform was added to the solution of $TiCl_4$ (1.9 g, 10 m mol) in dry chloroform (10 ml) dropwise and with constant stirring. The contents were filtered immediately to remove any unreacted Ph_3TeBr and the filtrate was shaken for *ca* 5 hrs. Reddish product thus obtained was filtered, washed with chloroform and dried over P_4O_{10} in vacuo. Yield *ca.* 90%; m.pt. 149–150° (dec.).

(*b*) *Triphenyltelluronium tetrachlorodibromotitanate* (*IV*): $[Ph_3Te]_2[TiCl_4Br_2]$

A solution of $TiCl_4$ (0.95 g, 5 m mol) in about 10 ml dry chloroform was added to the suspension of Ph_3TeBr (4.38 g, 10 m mol) in chloroform (20 ml) dropwise and with constant stirring. The contents were filtered immediately to remove any Ph_3TeBr left unreacted. The clear solution obtained after filtration was then shaken for *ca.* 6 hrs. The yellow product thus separated was filtered, washed with chloroform and dried over P_4O_{10} in vacuo. Yield *ca.* 80%; m.pt. 134–135° (dec.).

(*c*) *Triphenyltelluronium bromotetraiodotitanate* (*IV*): $[Ph_3Te][TiI_4Br]$

A suspension of Ph_3TeBr (2.19 g, 5 m mol) in *ca.* 10 ml of dry chloroform was added to the solution of TiI_4 (2.78 g, 5 m mol) in 20 ml of dry chloroform dropwise and with constant stirring. The contents were filtered immediately to remove any Ph_3TeBr left unreacted and the clear filtrate solution was concentrated under vacuum to about 10 ml. Then a little dry carbon tetrachloride was added to it and shaken for *ca.* 2 hrs. which resulted in separation of a dark brown solid which was filtered, washed with carbon tetrachloride and dried over P_4O_{10} in vacuo. Yield *ca.* 80%; m.pt. 89–90° (dec.).

(*d*) *Triphenyltelluronium dibromotetraiodotitanate* (*IV*): $[Ph_3Te]_2[TiI_4Br_2]$

A solution of TiI_4 (1.39g, 2.5m mol) in 10 ml of dry chlhoroform was added to the suspension of Ph_3TeBr (2.19g, 5m mol) in chloroform (10 ml) dropwise and with constant stirring. The resultant clear solution obtained after filtration was concentrated under vacuum to about 10 ml. A little dry carbon tetrachloride was added to this and then was shaken for *ca.* 2 hrs. The brownish black product thus obtained was filtered, washed with a mixture of chloroform and carbon tetrachloride (1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca.* 80%; m.pt. 109–110° (dec.).

(*iii*) *Adducts of Ph_3TeI with $TiCl_4$ and $TiBr_4$*

(*a*) *Triphenyltelluronium tetrachloroiodotitanate* (*IV*): $[Ph_3Te][TiCl_4I]$

A suspension of Ph_3TeI (2,43 g, 5 m mol) in 10 ml of chloroform was mixed with the solution of $TiCl_4$ (0.95 g, 5 m mol) in 10 ml of dry chloroform, dropwise and with constant stirring. The contents were filtered immediately to remove any Ph_3TeI left unreacted and then the clear filtrate solution was shaken for *ca.* 3 hrs. along with the addition of dry carbon tetrachloride. The dark brown product thus obtained was filtered, washed with mixture of chloroform and carbon tetrachloride (1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca.* 90%, m.pt. 89–90° (dec.).

(*b*) *Triphenyltelluronium tetrachlorodiiodotitanate* (*IV*): $[Ph_3Te]_2[TiCl_4I_2]$

A solution of $TiCl_4$ (0.95 g, 5 m mol) in about 10 ml of dry chloroform was added to the suspension of Ph_3TeI (4.86 g, 10 m mol) in about 20 ml of dry chloroform, dropwise and with constant stirring. The resultant clear solution obtained after immediate filtration was shaken for about 3 hrs. alongwith addition of a little carbon tetrachloride. A light brown product thus obtained was filtered, washed with a mixture of chloroform and carbon tetrachloride (1 : 1) and dried over P_4O_{10} in vacuo. Yield *ca.* 70%; m.pt. 162–163° (dec.).

(*c*) *Triphenyltelluronium tetrabromoiodotitanate (IV)*: $[Ph_3Te][TiBr_4I]$

A suspension of Ph_3TeI (2.43 g, 5 m mol) in about 10 ml of dry chloroform was mixed with the solution of $TiBr_4$ (1.84 g, 5 m mol) in dry chloroform (10 ml), dropwise and with constant stirring. The contents were filtered immediately to remove any Ph_3TeI left unreacted. Then the clear filtrate was shaken for *ca.* 4 hrs. The light brown product thus obtained filtered, washed with chloroform and dried over P_4O_{10} in vacuo. Yield *ca.* 80%; m.pt. 124–125° (dec.).

(*d*) *Triphenyltelluronium tetrabromodiiodotitanate (IV)*: $[Ph_3Te]_2[TiBr_4I_2]$

A solution of $TiBr_4$ (1.84 g, 5 m mol) in about 10 ml of dry chloroform was added to the solution of Ph_3TeI (4.86 g, 10 m mol) in about 20 ml of dry chloroform, dropwise and with constant stirring. The resultant clear solution obtained after immediate filtration was then shaken for *ca.* 4 hrs. The brown product was filtered, washed with chloroform and dried over P_4O_{10} in vacuo. Yield *ca.* 85%; m.pt. 144–145° (dec.).

The compounds were recrystallized from chloroform/acetonitrile. The purity of the compounds was checked by TLC. Tellurium contents were determined volumetrically[9] and titanium gravimetrically[9] after decompesing the compound with HNO_3. Halogen contents were estimated potentiometrically[10] after fusing the compound with $Na_2CO_3/NaOH$. The analytical data are compiled in Table 1.

RESULTS AND DISCUSSION

The reactions of Ph_3TeX with TiX'_4 (X, X′ = Cl, Br, I) give both 1 : 1 as well as 2 : 1 type of adducts. In these adducts Ph_3TeX transfers its halogen atom to TiX'_4 to give TiX'_4X^- or $TiX'_4X_2^{2-}$ species. These adducts are crystalline solids, which are fairly stable in dry atmosphere, but get hydrolysed in moist air. The compounds are soluble in polar organic solvents, but insoluble in nonpolar solvents. The adducts triphenyltelluronium halides with TiI_4 have relatively more solubility as compared to others.

The molar conductance data in nitrobenzene, acetonitrile and nitromethane reflect the electrolytic behaviour of these adducts. Λ_M values for 1 : 1 adducts are within or close to the expected[11] ranges for 1 : 1 electrolytes containing *ca.* 10^{-3}M of solute and reflect the likely formation in

TABLE 1

ANALYTICAL DATA FOR ADDUCTS OF Ph_3TeX WITH TiX'_4

Compounds	Analysis found (Calculated)						
	Te	Ti	C	H	Cl	Br	I
$[Ph_3Te][TiBr_4Cl]$	16.18 (16.75)	6.12 (6.28)	28.17 (28.35)	1.95 (1.96)	4.02 (4.66)	41.89 (42.01)	—
$[Ph_3Te]_2[TiBr_4Cl_2]$	21.93 (22.07)	4.13 (4.14)	37.14 (37.36)	2.61 (2.59)	6.04 (6.14)	27.12 (27.67)	—
$[Ph_3Te][TiI_4Cl]$	13.34 (13.43)	4.98 (5.04)	22.92 (22.74)	1.53 (1.57)	3.46 (3.73)	—	53.11 (53.49)
$[Ph_3Te]_2[TiI_4Cl_2]$	18.73 (18.99)	3.46 (3.56)	32.32 (32.14)	1.10 (1.11)	5.18 (5.28)	—	37.68 (37.80)
$[Ph_3Te][TiCl_4Br_2]$	20.21 (20.30)	7.49 (7.62)	34.23 (34.36)	2.21 (2.38)	22.43 (22.59)	12.59 (12.72)	—
$[Ph_3Te]_2[TiCl_4Br_2]$	23.74 (23.91)	4.32 (4.48)	40.39 (40.48)	2.67 (2.81)	13.19 (13.30)	14.87 (14.99)	—
$[Ph_3Te][TiI_4Br]$	12.63 (12.83)	4.53 (4.81)	21.53 (21.72)	1.51 (1.50)	—	7.92 (8.04)	50.98 (51.10)
$[Ph_3Te]_2[TiI_4Br_2]$	17.70 (17.81)	3.18 (3.34)	30.02 (30.15)	2.17 (2.09)	—	11.03 (11.16)	35.31 (35.45)
$[Ph_3Te][TiCl_4I]$	18.63 (18.80)	6.98 (7.09)	31.83 (31.97)	2.31 (2.22)	20.98 (21.02)	—	18.63 (18.80)
$[Ph_3Te]_2[TiCl_4I_2]$	21.69 (21.97)	4.02 (4.12)	37.11 (37.20)	2.61 (2.58)	12.12 (12.22)	—	21.19 (21.87)
$[Ph_3Te][TiBr_4I]$	14.73 (14.95)	5.47 (5.61)	25.07 (25.30)	1.83 (1.75)	—	37.42 (37.50)	14.69 (14.88)
$[Ph_3Te]_2[TiBr_4I_2]$	19.01 (19.06)	3.42 (3.57)	32.17 (32.26)	2.13 (2.25)	—	23.79 (23.90)	18.78 (18.97)

in solution of $[Ph_3Te]^+$ and $[TiX'_4X]^-$ ions. However Λ_M values in nitromethane are generally slightly higher than reported values for 1 : 1 electrolyte. This may be due to partial decomposition of these adducts in this solvent. The Λ_M values for 2 : 1 adducts in acetonitrile are also close to the expected[11] ranges for 2 : 1 electrolytes at *ca.* 10^{-3}M of solute which reflect the likely formation of $2[Ph_3Te]^+$ and $[TiX'_4X_2]^{2-}$ ions in solution. However, in nitrobenzene and in nitromethane, the Λ_M values are slightly lower than expected, which may be due to incomplete dissociation of these compounds in these solvents or interaction of the solvent molecules with the solute ions. The molecular weight data are consistent with the electrolytic nature of compounds as predicted by conductance measurements. This may be mentioned that molecular weight determination could not be carried out to a wide range of concentration because of rather poor solubility of these compounds in nitrobenzene.

^1H nmr spectra of these adducts in $DMSO-d_6/CDCl_3/CD_3CN$ show almost similar and of only one type phenyl proton chemical shifts as broad multiplet centred at around δ 7.63–7.64 ppm, which are independent of the halogen. This reflects the dissociation of these adducts as [Ph$_3$Te]$^+$ and [TiX$_4'$X]$^-$ or [TiX$_4'$ X$_2$]$^{2-}$.

The far ir spectra of these adducts (Table 2) show the absence of

TABLE 2

FAR IR DATA (cm^{-1}) FOR ADDUCTS OF Ph$_3$TeX WITH TiX$_4'$

Compound	Assignments				Skeletal/lattice phenyl modes
	Te-C	Ti-Cl	Ti-Br	Ti-I	
[Ph$_3$Te][TiBr$_4$Cl]	269s 258s	341m 323mb	244w	—	200w 184w 161w
[Ph$_3$Te]$_2$[TiBr$_4$Cl$_2$]	273vs 264vs	340s 313s	241s	—	199m 190m 180m 83s
[Ph$_3$Te][TiI$_4$Cl]	270s 260s	341w 312w	—	196w 190s	180w
[Ph$_3$Te]$_2$[TiI$_4$Cl$_2$]	274s 266s	340m 330m 313m	—	196w	180w 172m 143w 96s 73s
[Ph$_3$Te][TiCl$_4$Br]	264s 256s	344m 336m 314m	235m	—	220w 180w 178w
[Ph$_3$Te]$_2$[TiCl$_4$Br$_2$]	270s	331m 323m 314m 290m	240m	—	226w 193w 184w 176w
[Ph$_3$Te][TiI$_4$Br]	270s 261s	—	241s	188w	160m 140s
[Ph$_3$Te]$_2$[TiI$_4$Br$_2$]	260s	—	241m	185m	230m 220m 163m
[Ph$_3$Te][TiCl$_4$I]	268s 256s	336m 313m	—	201w	184w 173w 160w
[Ph$_3$Te]$_2$[TiCl$_4$I$_2$]	273s	346w 333w 321w	—	192m	234m 203m 175m 72s
[Ph$_3$Te][TiBr$_4$I]	267s	—	241sh	198w	186w 173w
[Ph$_3$Te]$_2$[TiBr$_4$I$_2$]	265s	—	241w	193w	180w 166w 154w

modes which may be assigned as ν_{Te-X}[12-15]. It means that Ph_3TeX transfers its X atom to TiX'_4 resulting in the formation of halo (mixed) titanate ions. So Ph_3TeX acts as halogen donor, whereas TiX'_4 as an acceptor.[16] All these adducts show very strong bands in the region 256–273 cm^{-1}, which are similar to those assigned to ν_{Te-C} in other phenyl derivatives of tellurium.[12-15] The ν_{Te-C} assignments in these compounds are not significantly different from those reported for the free diphenyltelluride unit[13] and the parent Ph_3TeX[5]. This indicates the absence of any Te-Ti bond. On the basis of absence of Te-Ti and Te-X bonds it will be suitable to formulate there adducts as $[Ph_3Te][TiX'_4X]$ or $[Ph_3Te]_2[TiX'_4X_2]$. Thus, the behaviour of these adducts is similar to those of TiX_4^5 and $SnCl_4^6$, but different from those of $HgX_2^{3,4}$ where Te-Hg bond is reported. ν_{Ti-X} vibrations of triphenyltelluronium halo (mixed) titanates are similar to those given in literature[17] for $[TiX'_4X]$ and $[TiX'_4X_2]$ type species.

Since a number of phenyl modes[12,13] and skeletal bending modes[17] are also expected in the region 230–165 cm^{-1}, the Ti-X may in some cases be mixed with these. In addition to these some lattice modes may also be present due to their ionic character. The $[TiX'_4X_2]^{2-}$ ions in these adducts most probably have *cis*-octahedral structures which are considered relatively more stable.[17,18]

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