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ORGANOTELLURIUM COMPOUNDS

I. SYNTHESIS AND SOLID STATE CHARACTERIZATION OF TRIPHENYLTELLURONIUM PSEUDOHALIDES

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Summary

Previously unreported triphenyltelluronium pseudohalides, $(C_6H_5)_3TeX$ ($X = CN, N_3, NCO, NCS, NCSe$), are synthesized metathetically by reaction of triphenyltelluronium chloride and excess alkali pseudohalide. Triphenyltelluronium azide, the first organotellurium azide synthesized, is stable to detonation by heat, shock or light. Solid state infrared absorption and Raman data suggest the presence of more than one structural type of pseudohalide group in each compound. The number of pseudohalide groups indicated is consistent with recent X-ray structural results which indicate oligomeric solid state structures for these compounds.

Introduction

Triorganotelluronium salts, R_3TeX , have been known for nearly one hundred years, and examples of trialkyl, triaryl and mixed alkyl-aryl derivatives containing many different anions are plentiful [1,2]. Our knowledge of these telluronium salts, however, differs from that of other main-group element 'onium' compounds in two noticeable respects. Firstly, few physicochemical investigations have been carried out with these species, and therefore, the solid salts and their solutions remain largely uncharacterized. Secondly, although many telluronium compounds are known with a large variety of anions, those formed with the common nitrogen-containing pseudohalide ions, such as cyanide, azide, and the chalcogenocyanates, have not been reported. More generally, little is known of Group VI organometallic pseudohalides as compared to other main-group organometallic pseudohalides [3].

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We have undertaken a study to synthesize and characterize the triorgano-telluronium and selenonium pseudohalides and report here the synthesis and solid state characterization of the triphenyltelluronium pseudohalides Ph_3TeX ($\text{X} = \text{CN}, \text{N}_3, \text{NCO}, \text{NCS}, \text{NCSe}$).

Results and discussion

Triphenyltelluronium pseudohalides were prepared metathetically by reaction of triphenyltelluronium chloride and excess alkali pseudohalide. Variances in the procedures, as discussed in the Experimental section, were used to optimize yields by taking advantage of several physical and chemical factors. Analytical data for the compounds are given in Table 1. The compounds analyze for the general formula $\text{C}_{18}\text{H}_{15}\text{TeX}$ ($\text{X} = \text{CN}, \text{N}_3, \text{NCO}, \text{NCS}, \text{NCSe}$) and are stable at ordinary temperatures. The crystalline compounds are diamagnetic, transparent and colorless, except for the selenocyanate which possesses a slight tan coloration possibly due to trace impurities.

Differential thermal analyses (DTA) of the compounds show the expected endothermic peak associated with melting. A typical curve, exemplified by Ph_3TeN_3 , is presented in Fig. 1a. The cyanide, however, which decomposes just before melting, exhibits an exothermic DTA signal (Fig. 1b). Thermal gravimetric analyses (TGA) of the compounds show that they decompose smoothly. This result is somewhat surprising for the telluronium azide since, typically, many inorganic and organic azides show catastrophic decomposition upon heating. The two known tellurium azides that have been reported, $\text{TeCl}_2(\text{N}_3)_2$ and TeCl_3N_3 , are both unpredictably shock and heat sensitive [4]. The TGA curve for the triphenyltelluronium azide is typical of the series and is illustrated in Fig. 1c. We note that no particular curve increment is correlatable solely to nitrogen evolution.

TABLE 1
ANALYTICAL DATA

Compound	m.p. (°C)	Analysis found (calcd.)(%)				
		C	H	N	Te	Cl, S, Se
$\text{Ph}_3\text{Te}(\text{CN})$	183–184 ^a	59.17 (59.28)	3.80 (3.93)	3.61 (3.64)	33.32 (33.15)	
Ph_3TeN_3	155.5–156.5	53.82 (53.92)	3.87 (3.77)	10.46 (10.48)	31.89 (31.83)	
$\text{Ph}_3\text{Te}(\text{NCO})$	151–152	56.83 (56.92)	3.83 (3.77)	3.47 (3.49)	32.08 (31.83)	
$\text{Ph}_3\text{Te}(\text{NCO}) \cdot \frac{1}{2} \text{CHCl}_3$	140 ^a	50.82 (50.85)	3.38 (3.39)	3.00 (3.04)	27.72 (27.70)	11.51 (11.54)
$\text{Ph}_3\text{Te}(\text{NCS})$	165–166	54.35 (54.73)	3.60 (3.63)	3.30 (3.36)	30.71 (30.60)	7.70 (7.69)
$\text{Ph}_3\text{Te}(\text{NCSe})$	164.5–165.5	49.21 (49.19)	3.16 (3.26)	3.16 (3.02)	27.48 (27.50)	16.98 (17.02)

^a Decomposition occurs just before or upon melting.

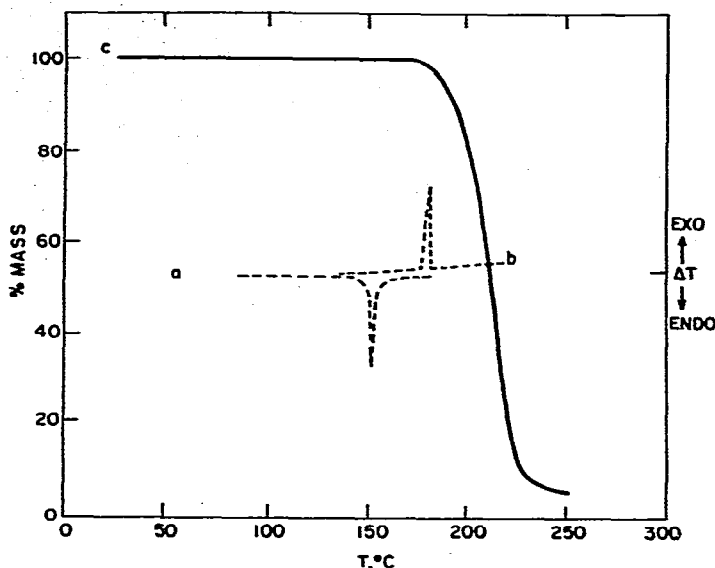


Fig. 1. (a) DTA curve (right ordinate) for Ph_3TeN_3 ; (b) DTA curve for $\text{Ph}_3\text{Te(CN)}$; (c) TGA curve (left ordinate) for Ph_3TeN_3 .

This compound is the first reported organometallic azide of tellurium and is stable to detonation by heat, shock or light.

Although there are no reported systematic investigations of the thermal decomposition of telluronium salts, it is known that triorganotelluronium halides are thermally cleaved to the organohalide and diorganotelluride. Triorganoselenonium salts also thermally decompose to form selenides [5]. The triphenyltelluronium pseudohalides decompose most likely in a similar manner to form diphenyltelluride and the phenyl pseudohalides as shown in eq. 1, which is consistent with the TGA data for the compounds which suggest almost total loss of material and no formation of elemental tellurium. Mass spectral data for the compounds also support decomposition via reaction 1 [6]. In this respect, it is interesting to note that the azide does not decompose by cleavage of the N—N bond, a decomposi-



tion mode typical of organic and some organometallic [3] azides.

Triphenyltelluronium cyanate has a very high propensity for solvent retention upon crystallization and is very difficult to obtain solvent free. $\text{Ph}_3\text{Te(NCO)}$, for instance, retains chloroform to form $\text{Ph}_3\text{Te(NCO)} \cdot \frac{1}{2} \text{CHCl}_3$ which is stable to 140°C. At this temperature, evolution of chloroform occurs and is accompanied by a lattice change as evidenced by a change in the X-ray powder pattern of the compound [7].

Infrared and Raman data are given in Table 2. The infrared spectra of the compounds in the range 4000 to 600 cm^{-1} (KBr) are similar with principal bands at 1575, 1480, 1440, 1060, 1015, 995, 740 and 690 cm^{-1} . Below 600 cm^{-1} (polyethylene matrix) principal bands occur at 465 and 280 cm^{-1} . Of particular interest in the solid state infrared absorption spectra of the compounds is the pseudo-

TABLE 2

Ph₃TeX PSEUDOHALIDE VIBRATIONAL FREQUENCIES (CM⁻¹)^a

Compound	$\nu(\text{cm}^{-1})$	Solid ^b	Solid ionic KX ^c
Ph ₃ Te(CN)	$\nu(\text{CN})$	2065 w	2080
Ph ₃ TeN ₃	$\nu_a(\text{NNN})$	2040 (2025 2002)d	2041
	$\nu_s(\text{NNN})$	Raman (1322 1216)	(1352)
Ph ₃ Te(NCO)	$\nu(\text{NCO})$	2168 (2139 2132)d	2165
	$\nu_s(\text{NCO})$	Raman (1314 1304)	(1254)
Ph ₃ Te(NCO) · $\frac{1}{2}$ CHCl ₃	$\nu_a(\text{NCO})$	2168 (2148 2134)d	—
Ph ₃ Te(NCS) ^d	$\nu(\text{CN})$	2070 2064 2058	2053
		Raman (2067 2062 2053)m	
Ph ₃ Te(NCSe)	$\nu(\text{CN})$	2080 2065	2070
		Raman (2078 2061)m	

^a Table notations; d, doublets; m, medium relative intensity and w, weak relative intensity. ^b IR data from KBr matrix (pressed pellet). ^c See ref. 10. ^d IR data from fluorolube (Hooker) mull.

halide stretching region between 1900 and 2200 cm⁻¹ which is shown in Fig. 2. Each of the compounds has unexpectedly more than one band in this region. In the telluronium thiocyanate spectrum (Nujol or Fluorolube) three distinct bands appear at frequencies higher than that for the NCS ion in KNCS (2053 cm⁻¹). In the telluronium azide, cyanate and selenocyanate spectra (KBr or Nujol) at least two bands are present in this region. The highest frequency band in the spectra of the azide and cyanates in Fig. 2 is attributed to the formation of KN₃ and KNCO, respectively, via a solid state reaction of the telluronium compound with KBr. These bands are at the respective X⁻ asymmetric stretching frequency, they vary in intensity in the KBr spectra and do not appear in the Nujol spectra. We also note that between the solvated and solvent-free cyanate, only the bands associated with the tellurium NCO groups shift.

Raman data (Table 2) for the pseudohalides corroborate the infrared data. The CN stretching frequency of the thiocyanate and selenocyanate compounds in the 2000 cm⁻¹ region are observed as medium intensity bands and their number coincides with the number of infrared bands in the same region. Additionally, two bands in the 1300 cm⁻¹ region are observed for both the azide and cyanate compounds and are assigned to the symmetric stretches (ν_s) of the respective pseudohalide.

The CN stretch in triphenyltelluronium cyanide (KBr) gives rise to a weak broad band at 2065 cm⁻¹ in the infrared, about 15 cm⁻¹ lower in frequency than that of KCN. In terms of valence bond notation this observation suggests some contributions from the Te—C≡N: and $\text{Te}^+=\text{C}=\ddot{\text{N}}:$ structures, consistent with the weak electrolyte behavior of this compound in solution [6]. The number of bands present, however, is not discernible.

The multiplicity of bands for the pseudohalide stretching modes clearly indicates a complex situation for the solid state structure of the compounds and rules out earlier simplistic ionic structural models for the salts, consisting of omnidirectionally interacting discrete Ph₃Te⁺ and X⁻ ions. The number of observed infrared and Raman bands attributable to the pseudohalide stretching is consis-

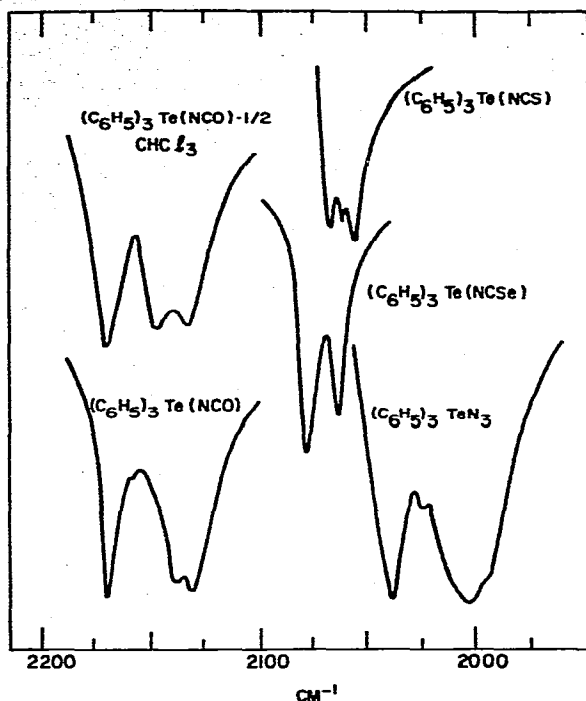


Fig. 2. Infrared spectra (KBr), 1900–2200 cm^{-1} , of triphenyltelluronium pseudohalides; thiocyanate is in Nujol.

tent with recent X-ray crystallographic data for the compounds [7] which show the number of formula units per unit cell to be an even whole number multiple of the number of observed bands. Recently, Titus et al. [8] have determined the structure of the cyanate and thiocyanate compounds from three dimensional X-ray data. The structures consist of discrete oligomeric units made up of centrosymmetric X-bridged Ph_3TeX tetramers, and additionally in the case of the thiocyanate, a centrosymmetric X-bridged Ph_3TeX dimer. Accordingly, there are two crystallographically independent NCO moieties in the cyanate unit cell (four formula units/unit cell) which give rise to the two observed bands at 2139 and 2132 cm^{-1} in the solvent free compound and 2148 and 2134 cm^{-1} in the solvated derivative, and three crystallographically independent NCS moieties in the thiocyanate unit cell (six formula units/unit cell) which give rise to the three observed bands at 2070, 2064 and 2058 cm^{-1} .

Crystallographic cell data for the azide and selenocyanate show them to contain eight and sixteen formula units per cell respectively [7] and at least two crystallographically independent groups appear present from infrared and Raman data. In view of the overall similarity of the spectra of these compounds and of their general behavior it is not unreasonable to suggest that the azide and selenocyanate also possess oligomeric structures in the solid state similar to those found for the cyanate and thiocyanate. In the case of the selenocyanate the crystal lattice is primitive and of the point group mmm [7]. Therefore, eight asymmetric units are present, and, consistent with two bands in the infrared and Raman spectra, the unit cell may consist of either four centrosymmetric tetramers similar to the

thiocyanate and cyanate, or eight non-centrosymmetric dimers. Crystallographic, infrared and Raman data for the azide are consistent with the presence of tetrameric or octameric units in the solid state. Our physicochemical data for the azide do not support a polymeric type solid state structure for this compound. Although the frequencies of the asymmetric stretches of the selenocyanate and azide groups indicate more ionic than covalent character for the group, the nature of the oligomeric unit cannot be ascertained since the frequencies give no indication of the degree of interaction between the azide [9] or selenocyanate and the tellurium.

Discussion of the interesting and complex solution chemistry of these compounds will appear in a subsequent publication.

Experimental section

Reagent grade chemicals were used except where noted otherwise. Triphenyltelluronium chloride was used as received from Orgmet Inc., E. Hampstead, N.H. 03826. Melting points were determined both by the capillary method and on a DuPont 900 thermal analyzer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. Infrared data were determined on a calibrated Beckman IR12 spectrophotometer. Raman spectra were obtained on a Spex instrument with an Argon laser source (5145 Å).

Compound preparations

$\text{Ph}_3\text{Te}(\text{CN})$ Twenty grams of Baker CGA-541 resin were treated with excess aqueous NaCN to replace exchangeable chloride ion. After gradual elution with ethanol/water mixtures of increasing ethanol content, the column was covered with 95% ethanol. A solution of 0.1 g (0.25 mmol) Ph_3TeCl in 60 ml 95% ethanol was passed slowly through the column followed by elution with 200 ml of the same solvent. The eluent was evaporated and the oily residue triturated with ethyl acetate. After several minutes fine colorless needles separated. These were collected, washed with ethyl acetate and dried in vacuum. Yield 85%.

Ph_3TeN_3 A 100 ml H_2O solution of 40 mmol of NaN_3 was shaken for 30 min. with 200 ml of a CHCl_3 solution containing 2 g (5 mmol) of Ph_3TeCl . The CHCl_3 layer was separated, dried over MgSO_4 , concentrated to 40 ml and chilled. Cold petroleum ether (b.p. 30–60°C) was added slowly and the flask swirled. Fine needles precipitated and were filtered. Yield 75–85%. Ph_3TeN_3 may be recrystallized from 2-propanol, chloroform or toluene. The last solvent yielded well-formed, clear, colorless needles.

$\text{Ph}_3\text{Te}(\text{NCO})$ One mmol (0.15 g) of AgOCN (Eastman) was dissolved in 0.85 l of boiling H_2O and 0.394 g (1 mmol) of Ph_3TeCl , dissolved in 50 ml of hot H_2O , were added. AgCl precipitated immediately. The mixture was stirred for several minutes, cooled and filtered. The 900 ml solution was concentrated to 5 ml by vacuum evaporation then cooled to about 5°C. The cool solution was filtered and after standing open to the atmosphere for 48 h, yielded large colorless crystals. The crystals were crushed and then dried in vacuum (24°C, P_2O_5) for 48 h. Yield 90%. $\text{Ph}_3\text{Te}(\text{NCO})$ is soluble in most polar solvents, benzene and toluene, and has a high propensity for solvent retention upon crystallization. Recrystallization from CHCl_3 yields $\text{Ph}_3\text{Te}(\text{NCO}) \cdot \frac{1}{2} \text{CHCl}_3$.

Ph_3TeX ($\text{X} = \text{NCS}, \text{NCSe}$) Approximately 20 mmol of NaNCS or KNCSe (Alfa) were dissolved in 10 ml of warm water and added to 100 ml of hot H_2O containing 2 g (5 mmol) of dissolved Ph_3TeCl . Immediate precipitation occurred. The mixture was stirred for a few minutes, then filtered. The filtrate was washed with water and then dried in vacuum. Yield 90–95%. Recrystallization from 2-propanol yielded clear, colorless prisms of the thiocyanate and platelets of the selenocyanate.

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