

Lewis Base Behaviour of Diphenyl Telluroxide

RAM CHAND PAUL, RAJ K. CHADHA*†, B. S. BHANDAL and GURDEV SINGH

Chemistry Department, Panjab University, Chandigarh-160014, India

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Diphenyl telluroxide, (DPTO), reacts with Sn(IV), Ti(IV) and Sb(V) chlorides to give diphenyltellurium dichloride, but with organotellurium trichlorides (R = Me, pMeOPh, pPhOPh) it forms 2:1 addition products. These products have been characterised by elemental analysis and IR spectra. The Te–O vibrations in diaryl telluroxides have been assigned by comparing the IR spectra of diaryl telluroxides, diaryl tellurides and bis(diaryl tellurium chloride)oxides (R = Ph, pMeOPh and pMePh).

Introduction

Jensen [1, 2] has measured the dipole moments of several diaryl telluroxides and found the Te–O bond to be quite polar. Klofutar *et al.* [3] have also showed that basicity increases in the series sulphoxides, selenoxides and telluroxides. Although donor properties of organic sulphoxides and selenoxides have been very well investigated [4–6], there does not seem to be any report concerning the synthesis of adducts of organic telluroxides. The Te–O vibrations in the compounds of the type, tellurinic acids, RTe(O)OH, tellurinic acid halides, RTe(O)X, and tellurinic acid anhydrides, (RTeO)₂O have been reported to appear in the region of 720–300 cm⁻¹ [7]. However, no such assignment has ever been made for Te–O vibrations in well known organic telluroxides. In the present paper, therefore, an attempt has been made to assign Te–O vibrations in a few diaryl telluroxides and to study the coordination ability of a simple diaryl telluroxide, *viz.* DPTO.

Experimental

IR spectra of the compounds were recorded in Nujol mulls on NaCl and polyethylene windows on a Perkin Elmer Grating Spectrophotometer 621

(4000–200 cm⁻¹). Raman spectra were obtained for solid DPTO and liquid Ph₂Te samples with a Cary 81 instrument using laser (He–Ne) excitation. Electric conductance measurements were carried out on nitrobenzene solutions using a Toshniwal conductivity bridge. The organotellurium compounds were prepared by the procedures already described in the literature [8].

Reaction of DPTO with Strong Lewis Acids

Upon the addition of a solution of DPTO in chloroform to a chilled and well stirred solution of Sn(IV), Ti(IV) or Sb(V) chloride in chloroform or carbon tetrachloride (molar ratio 1:1), a compound separated out which was filtered, washed with chloroform and dried in vacuum. The material thus obtained gave negative tests for carbon and hydrogen, but could not be characterised with certainty; though metal and chlorine were detected. Evaporation of the filtrate in all these reactions gave another crystalline compound (in 75–80% yield) which was found to have composition, melting point and IR spectrum identical to those of Ph₂TeCl₂.

Reaction of DPTO with Organotellurium Trichlorides

A chloroform solution of DPTO (2 mol) was added slowly to a chilled and well stirred suspension of methyl, *p*-methoxyphenyl or *p*-phenoxyphenyl tellurium trichloride (1 mol) in the same solvent. The solution became clear. On concentration of the solution under vacuum, a white crystalline material separated out quantitatively whose melting point was entirely different from the starting materials (Table I). Other analytical details and some IR frequencies are also recorded in this table.

Results and Discussion

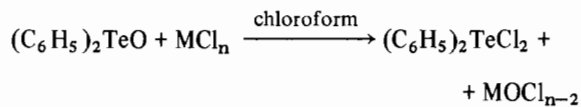
The reaction of DPTO with Sn(IV), Ti(IV) or Sb(V) chloride gives two products, of which only Ph₂TeCl₂ could be identified with certainty. It appears, therefore, that DPTO does not behave as a normal base but reacts with various strong Lewis acids in the following way:

* Author to whom correspondence should be addressed.

† Present address: Department of Chemistry, University of Windsor, Windsor, Ont., Canada N9B 3P4.

TABLE I. Analytical Data^a and IR Spectral Bands (cm⁻¹) of Adducts of Diphenyl Telluroxide DPTO.

Sr. No.	Compound	M. pt. (°C)	Λ_M^b (ohm ⁻¹ cm ² mol ⁻¹)	C (%)	H (%)	Te (%)	Cl (%)	$\nu_{\text{Te=O}}^c$	$\nu_{\text{Te-C}}$	$\nu_{\text{Te-Cl}}$ (<i>trans</i> TeCl ₂)	$\nu_{\text{O-Te}}$
1.	MeTeCl ₃ ·2DPTO	155	0.735	35.09 (35.53)	3.12 (2.72)	45.08 (45.34)	13.02 (12.61)	655s 640s	263s 248sbr	270s	443m
2.	pMeOPhTeCl ₃ ·2DPTO	125	0.311	39.11 (39.73)	2.92 (2.88)	40.23 (40.88)	10.95 (11.37)	655s 613s	264s 239s	273m	417m
3.	pPhOPhTeCl ₃ ·2DPTO	177	0.655	43.50 (43.27)	2.25 (2.90)	37.90 (38.35)	10.02 (10.67)	658s 615s	265sh 255s 245s	275sh	480m

^a Values in parentheses are the calculated ones.^b In nitrobenzene. ^c $\nu_{\text{Te-O}}$ appears at 285 cm⁻¹.

In other words, the metal chlorides are able to chlorinate DPTO to Ph₂TeCl₂. This behaviour of DPTO is similar to dialkyltin oxides, which react with SnX₄ (X = Cl or Br) to give dialkyltin dihalides and SnOX₂ [9]. Metal chlorides like Co(II), Ni(II), and Sn(II) chlorides do not react with DPTO in chloroform or ethanol and the starting materials were recovered as such, even after refluxing the reactants for a long time. These metal chlorides, obviously, could not react as chlorinating reagents. The observed reluctance of formation of adducts by DPTO may be rationalised in terms of O to Te back bonding. The atomic size of tellurium being greater than selenium or sulphur, the pπ-dπ bond strength is weaker in the Te=O bond than in the Se=O or S=O. Consequently, Te=O linkage has more polar character than Se=O or S=O linkage in the organic chalcogenoxides. On the other hand, the lower bond order of Te-O than Se-O or S-O makes telluroxides less stable than selenoxides or sulphoxides, thereby showing the tendency for dimerisation and the reluctance to the formation of addition products by the former.

Organotellurium trihalides are known to be associated in solution and in the presence of a base the tendency towards intermolecular interactions is overcome and molecular complexes are formed [10, 11]. In view of the failure of formation of addition products by DPTO with metal halides, the work has been extended to study its basicity with regards to organotellurium trichlorides, as the grouping Te-O-Te present in DPTO can still persist in its molecular complexes. The attempts in this direction have been successful and we could isolate 1:2 adducts of organotellurium trichlorides with DPTO. These adducts are white in colour, non-hygroscopic and non-electrolytes, as shown by their molar conductance values (Table I). They are highly soluble in chloroform and benzene, while DPTO is moderately soluble in chloroform. The IR spectra of these adducts show a few new bands, besides the bands arising from the starting materials, which also do not appear exactly at the same positions.

The region of Te-O vibrations has been located by the comparison of the IR spectra of diaryl telluroxides (R = Ph, pMeOPh, pMePh) with those of the parent tellurides. Though to consider the normal vibrations of diaryl telluroxide molecule as characteristic group vibrations is undoubtedly an approximation, yet it seems reasonable to assign the new bands arising in the diaryl telluroxide mainly to the Te-O vibrations since the vibrational frequencies of most aryl-tellurium bands are found at nearly the same position in the spectra of telluroxides and tellurides.

TABLE II. Infrared Absorption Frequencies (cm^{-1}) and Proposed Assignments for Various Diaryl Tellurides, Diaryl Telluroxides and Bis(diaryltellurium chloride)oxides.

Ph ₂ Te IR	DPTO		(Ph ₂ TeCl) ₂ O	(pMeOPh) ₂ Te	(pMeOPh) ₂ TeO	[(pMeOPh) ₂ TeCl] ₂ O	(pMePh) ₂ Te	(pMePh) ₂ TeO	Assignments
	Raman	IR							
725s	730s	719s	736s	720w	720s	725w	725w	722s	C-H out of plane defor. Te=O vibr.
688s	690m	683m	691sh 684s	625w	630w	643w	645w 636w	696w	C-H out of plane defor.
652m	654s	653w	657s 611w	625w	630w	643w	645w 636w	634w	unassigned
460m 442m	462s 438s		463s 454s	470w	472w 420s	476s	429m	462w 413s	phenyl ring vibr. + Te=O vibr.
269sh 258s	275sh 253w		285m 264s	403w 331s	406sh 334s	360w 347w	408sh 376w 343m	408sh 328w	pMeOPh and pMePh bands
244m	240s		271s	275m	273s				Te=O vibr.
225w	225s	220s	226s	215sh	215sh	272w	240m	265m	Te=O vibr. Te-C (phenyl) str. (t) Te-Cl str.
				215sh	215sh		240m	246m	Te-C (phenyl) str. (t') phenyl ring vibr.

The vibrational spectra of diaryl telluroxides and their parent tellurides have been recorded in Table II. Comparison of Raman spectra of DPTO and Ph_2Te clearly shows the appearance of a new strong band at 708 cm^{-1} in the former which is obviously due to $\nu_{\text{Te=O}}$. The IR spectra of diaryl telluroxides show two or three additional bands (underlined in Table II) which may be assigned mainly to the Te–O vibrations. A possible explanation for the appearance of more than one band in the IR spectra of diaryl telluroxides having contributions from Te–O vibrations, can be due to the molecular association of telluroxides (*cf.* RTe(O)X , [7]). The molecular weight of DPTO and its *p*-methoxyphenyl analogue in nitrobenzene (450 and 630 respectively) fall in between the values expected for monomers and dimers. This suggests the presence of molecular association. Therefore, out of the additional bands appeared in diaryl telluroxides, the bands at higher frequencies can be assigned to the $\nu_{\text{Te=O}}$ and lower frequencies can be assigned to $\nu_{\text{Te-O}}$. For the assignment of $\nu_{\text{Te=O}}$ and $\nu_{\text{Te-O}}$ in the IR spectrum of diaryl telluroxide, a comparison of the spectrum with that of bis(diaryltellurium chloride)oxide will be helpful. Whereas the former is expected to contain both Te=O and Te–O bonds, the latter contains only Te–O bond. In the IR spectrum of DPTO, three additional bands are observed at 719, 310 and 286 cm^{-1} , while in the IR spectrum of $(\text{Ph}_2\text{TeCl})_2\text{O}$ only one additional band at 285 cm^{-1} is observed. The bands at 719 and 310 cm^{-1} thus have contributions from Te=O and the band at 286 cm^{-1} has a contribution from Te–O. Similar comparison of the IR spectra of *p*-methoxyphenyl analogues shows that the bands at 720 and 420 cm^{-1} have contributions from Te=O and a band at 284 cm^{-1} has contribution from Te–O. The IR spectra of *p*-tolyl analogues can also be interpreted by analogy and bands at 722 and 413 cm^{-1} can be assigned mainly to $\nu_{\text{Te=O}}$. Since the IR spectra of the compounds were obtained in the solid phase (Nujol mulls) and the molecular weight studies were carried out in solution, we cannot base our assignments entirely upon the conclusions from molecular weight studies. There is a possibility that the low frequency additional bands obtained in the IR spectra of diaryl telluroxides may be due to R–Te=O bending modes or phenyl modes which might have become IR active because there is a change of symmetry in going from organic tellurides to telluroxides. Other assignments *viz.*, Te–C (aryl) *etc.* are made in Table II according to McWhinnie and Patel [12].

In the adducts of DPTO, the $\nu_{\text{Te=O}}$ shifts towards lower frequencies and appears as two strong bands in the region $685\text{--}617\text{ cm}^{-1}$ (Table I). This obviously suggests that donation is through oxygen and

probably two ligands are present in the *cis*-positions. The other band at 310 cm^{-1} in DPTO is either missing in the spectrum of the adduct with MeTeCl_3 or has shifted downward to 285 cm^{-1} . However, this band may also be due to $\nu_{\text{Te-O}}$ which appears at 286 cm^{-1} in the free ligand. In the IR spectra of the other two adducts, both these bands (310 and 286 cm^{-1}) do not appear.

The Te–Cl stretching frequencies for MeTeCl_3 and the *para*-substituted aryltellurium trichlorides have been reported to appear in the region $340\text{--}300\text{ cm}^{-1}$ and are said to involve *cis*- TeCl_2 groups [13]. In the IR spectra of adducts, no band is observed in this region, but a single band is observed in the region $275\text{--}270\text{ cm}^{-1}$. This band is, therefore, due to *trans*- TeCl_2 stretching in a six coordinate tellurium with one long Te–Cl bond [14]. It is possible that the absorptions near 265 cm^{-1} are also due to *trans* Cl–Te–Cl stretching rather than Te–C (phenyl) vibrations. Clark and coworkers have obtained a band in the region $265\text{--}215\text{ cm}^{-1}$ associated with S–Te stretching mode of vibration in the adducts of organotellurium trichlorides with tetraethyldithio-oxamide [14]. The similar O–Te stretching frequency, therefore, is expected to appear above this region. A new band which is not seen in the IR spectra of organotellurium trichlorides or DPTO, is observed in the region $480\text{--}417\text{ cm}^{-1}$ in all adducts. The assignment of this band to $\nu_{\text{Te-O}}$, therefore, seems quite reasonable.

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