Lewis-Base Behavior of Methyltellurium(IV) Bromides

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Abstract: To assess the Lewis-base properties of methyl-substituted tellurium(IV) bromides, infrared spectroscopic, electrical conductance, and colligative property measurements have been employed to characterize trimethyltellurium bromide, dimethyltellurium dibromide, methyltellurium tribromide, and the adducts formed by the first two of these substances with boron tribromide. Crystalline trimethyltellurium bromide is ionic, behaves as a strong electrolyte in dimethylformamide solution, and readily forms trimethyltellurium tetrabromoborate with BBr_3. Dimethyltellurium dibromide is a molecular substance and forms a 2:1 adduct, $[(CH_3)_2TeBr_2]_2 \cdot BBr_3$, which is extensively dissociated in benzene and nitrobenzene solutions, the latter having a small electrical conductance. Methyltellurium tribromide displays a concentration-dependent association in benzene solution, with a limiting $\bar{n}$ value of approximately 2. The tribromide is a nonelectrolyte in nitrobenzene and fails to react with BBr_3.

Recently the Lewis-base characteristics of the methyl-substituted selenium(IV) halides, trimethylselenium chloride,[1] dimethylselenium dichloride and dibromide,[2] and methylselenium trichloride,[1] have been described. With boron trichloride as the Lewis acid the trimethyl compound, which is, in fact, an ionic substance in the crystalline state, forms a 1:1 addition compound best formulated as trimethylselenium(IV) tetrachloroborate, $(CH_3)_3Se^+BCl_4^-$. The dihalides, although molecular in the solid state, also form 1:1 addition compounds. These were shown to be composed of halodimethylselenium(IV), $(CH_3)_2SeX^+$, and BX_4^- ions. The trichloride, however, does not react with BCl_3. Of particular interest is the failure of the molecular selenium compounds to employ in a classical donor manner the stereochemically active electron pair associated with the selenium atom. In the present paper the results of studies involving a series of substituted tellurium(IV) bromides are presented.

Experimental Section

Materials. Preparation of Tellurium Compounds. Trimethyltellurium iodide (4.3 g, 14.3 mmoles), prepared according to the Scott method,[3] was ground with excess silver(I) oxide. The resulting mixture was extracted with 100 ml of water, concentrated hydrobromic acid (1.6 ml, 15 mmoles) was added to the extract, and the solution was evaporated to 10 ml. The addition of acetone produced a precipitate, and this was recrystallized from a water–acetone mixture to give 3.5 g of the colorless, crystalline product. This material decomposes above 250°. *Anal.* Calcd for C_3H_9TeBr: Te, 50.5; Br, 31.7. Found: Te, 49.6; Br, 31.8.

α-Dimethyltellurium dibromide[4] was prepared by reaction of $(CH_3)_2TeI_2$ with $AgNO_3$ and HBr. The colorless crystals melted in the 94–95° range (lit.[4] mp 92°). *Anal.* Calcd for $C_2H_6TeBr_2$: Te, 40.3; Br, 50.5. Found: Te, 39.3; Br, 50.2.

Methyltellurium tribromide was prepared by reaction of bromine and dimethyl ditelluride.[7] The greenish yellow crystalline material darkens and decomposes above 140°. *Anal.* Calcd for CH_3TeBr_3: Te, 33.4; Br, 62.8. Found: Te, 33.4; Br, 62.1.

Adduct of Trimethyltellurium Bromide and Boron Tribromide. $(CH_3)_3TeBr$ (1.69 g, 6.69 mmoles) and boron tribromide (15 g, 60 mmoles) were mixed in a vacuum line trap and the system magnetically stirred at room temperature. At certain times the excess BBr_3 was removed by standard vacuum-line means, and the weight gain of $(CH_3)_3TeBr$ was determined. The BBr_3 which had been removed was then returned to the reaction vessel and the procedure repeated. After 8 hr the weight increase corresponded to a 1:1.01 mole ratio of $(CH_3)_3TeBr$ to BBr_3, and this ratio remained effectively constant thereafter; experiments were run as long as 8 days. The colorless product, which darkens at 180° and decomposes rapidly at 215°, is slightly soluble, with reaction, in dimethylformamide but insoluble in benzene. *Anal.* Calcd for $C_3H_9TeBBr_4$: Te, 25.4; Br, 63.6. Found: Te, 24.9; Br, 63.6.

Adduct of Dimethyltellurium Dibromide and Boron Tribromide. (a) From Benzene Solution. $(CH_3)_2TeBr_2$ (1.65 g, 5.2 mmoles) and BBr_3 (6.5 g, 26 mmoles) were dissolved in benzene (10.5 g) in a vacuum-line vessel. After standing overnight at 0° the solution contained a quantity of long, colorless, needle-like crystals. This material was recrystallized from 10 ml of a benzene solution of BBr_3 (19 mmoles), and the vessel containing the product at room temperature was subjected to evacuation until a vapor pressure of less than 1 mm was observed. Spectroscopic examination of the vapor above the solid showed it to be BBr_3 exclusively. The colorless solid (1.19 g) melts in the 57–58° range. *Anal.* Calcd for $C_4H_{12}Te_2BBr_7$: Te, 28.9; Br, 63.3. Found: Te, 27.4; Br, 62.1.

In a related experiment benzene and the major portion of excess BBr_3 were first removed from the reaction vessel by pumping. Thereafter, with continued pumping, the decrease in weight gained (compared to the original weight of $(CH_3)_2TeBr_2$) with time was followed by periodic weighing of the reaction vessel. Graphic representation of these data showed a sharp break in the plot of weight gain *vs.* time at a mole ratio of $(CH_3)_2TeBr_2$ to BBr_3 equal to 2.04:1. Continued evacuation of the system for 4 days removes all BBr_3, and the $(CH_3)_2TeBr_2$ starting material is recovered.

(b) *Via* Direct Reaction. This experiment, similar to that described above for preparing the adduct of $(CH_3)_3TeBr$, employed 1.39 g of $(CH_3)_2TeBr_2$ (4.4 mmoles) and 19.0 g of BBr_3 (76 mmoles). A plot of weight gain *vs.* reaction time showed a rapid weight increase during the first 8 hr, but a relatively constant value of total weight gain thereafter. The constant value corresponded to a mole ratio of $(CH_3)_2TeBr_2$ to BBr_3 equal to 1.98:1. *Anal.* Calcd for $C_4H_{12}Te_2BBr_7$: Te, 28.9. Found: Te, 29.4.

Attempted Reaction of Methyltellurium Tribromide and Boron Tribromide. CH_3TeBr_3 was mixed with excess BBr_3, both in benzene solution and in the absence of solvent. In no case was any evidence of reaction observed; unchanged CH_3TeBr_3 was quan-

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(2) K. J. Wynne and J. W. George, *J. Am. Chem. Soc.*, 87, 4750 (1965).

(3) A. Scott, *Proc. Chem. Soc.*, 20, 156 (1904).

(4) R. H. Vernon, *J. Chem. Soc.*, 117, 86 (1920), first reported this compound and found that it exists in two forms. These are the α form, which is used in the work described in this paper, and the β form, which is a bright orange powder melting at 142° and later predicted[5] to be a salt-like material, $(CH_3)_3Te^+CH_3TeBr_4^-$. Recently, X-ray crystallographic investigation[6] has shown the corresponding β-diiodide to be the ionic substance $(CH_3)_3Te^+CH_3TeI_4^-$.

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(6) F. Einstein, J. Trotter, and C. Williston, *ibid.*, *A*, 2018 (1967).

(7) M. T. Chen and J. W. George, *J. Organometal. Chem.* (Amsterdam), 12, 401 (1968).

Table I. Electrical Conductance Data for Solutions of Methyl-Substituted Tellurium(IV) Bromides, the Boron Tribromide Adduct of Dimethyltellurium Dibromide, and Comparison Solutes

Solute	Solvent	Temp, °C	Concn, mM	Molar conductance, cm^2 ohm^{-1} mole^{-1}
$(C_2H_5)_4NBr$	$C_6H_5NO_2$	24.0 ± 0.5	5.75	26.5
			1.70	31.7
			0.55	33.4
CH_3TeBr_3	$C_6H_5NO_2$	24.0 ± 0.5	7.37	0.38
			1.74	0.60
			0.56	1.43
$(CH_3)_2TeBr_2$	$C_6H_5NO_2$	26.0 ± 0.5	15.0	0.015
			3.0	0.029
			0.12	0.48
$[(CH_3)_2TeBr_2]_2BBr_3$	$C_6H_5NO_2$	24.0 ± 0.5	8.95	0.81
			2.24	2.14
			0.56	5.12
			0.14	6.50
KBr	DMF	26.0 ± 0.5	1.56	70
			0.39	77
			0.10	84
$(CH_3)_3TeBr$	DMF	26.0 ± 0.5	6.6	44
			1.65	59
			0.41	72

titatively recovered, and infrared examination of the volatile material showed only absorptions for BBr_3 and, when used, solvent.

Miscellaneous Chemicals. Standard methods were employed to purify boron tribromide (K and K Laboratories) and reagent grade solvents prior to use. Nitrobenzene used in conductance measurements had specific conductances in the 0.5–2.5 × 10^{-7} ohm^{-1} cm^{-1} range; the corresponding value for dimethylformamide was 5.2 × 10^{-7} ohm^{-1} cm^{-1}.

Physical Measurements. Electrical conductance measurements, the results of which are presented in Table I, were carried out on nitrobenzene and dimethylformamide solutions using glass cells with platinum electrodes and a General Radio Co. 1650A impedance bridge. Infrared spectroscopic data, Table II, were obtained using Perkin-Elmer Model 21 and Infracord and Beckman IR 10 and IR 11 spectrometers. Solid samples were examined as mineral oil mulls between KBr or polyethylene disks. The solution spectrum was obtained using a polyethylene cell of 1-mm path length. Molecular weights or, where association of the species of interest occurred, average degree of association, $\bar{n}$, were determined cryoscopically in benzene and nitrobenzene, and in benzene using a Mechrolab Model 301A vapor-pressure osmometer. These results are presented in Table III. A Varian A-60 spectrometer was employed to obtain proton resonance data for CCl_4 solutions of each of the following (chemical shift values in parts per million *vs.* tetramethylsilane internal standard): $(CH_3)_2Te$, 1.88; $(CH_3)_2TeBr_2$ 3.33; CH_3TeBr_3, 7.36. In each case a single, sharp peak is found. $(CH_3)_3TeBr$ was insufficiently soluble in CCl_4 to obtain a spectrum.

Analyses. Bromine was determined using standard gravimetric technique.[8] Tellurium analyses were initiated by a 3-hr sodium peroxide fusion at 240° in a sealed glass tube. After cooling and opening the tube the contents was dissolved in water, the excess peroxide destroyed by evaporation, and the solution acidified with concentrated hydrochloric acid. Saturation with sulfur dioxide and treatment with hydrazonium hydrochloride gave elementary tellurium which, after washing and drying, was weighed.

Discussion

Characterization of Methyl-Substituted Tellurium(IV) Bromides. The general nature of these compounds is readily discernible from the data given in Tables I–III. The 1:1 electrolyte behavior of $(CH_3)_3TeBr$ in DMF is demonstrated by the similarity of molar conductance values for this solution with those of KBr in the same solvent. That an ionic formulation is appropriate to crystalline $(CH_3)_3TeBr$ is established by the lack of infrared absorption in the Te–Br stretching frequency region.[9–11] Further, the weak absorption at 534 cm^{-1} and the broad, strong absorption at 78 cm^{-1} are readily assigned to the Te–CH_3 stretching frequency[12] and crystal lattice mode, respectively. The ionic character of $(CH_3)_3TeBr$ is parallel to that known for $(CH_3)_3SeCl$,[1] $(CH_3)_3SeI$,[13] and $(CH_3)_3SI$.[14]

Table II. Infrared Absorption Frequencies (cm^{-1}) and Proposed Assignments for Dimethyl Telluride, Trimethyltellurium Bromide, Dimethyltellurium Dibromide, Methyltellurium Tribromide, and Boron Tribromide Adducts[a]

$(CH_3)_2Te$[b]	$(CH_3)_3TeBr$	$(CH_3)_3TeBr \cdot BBr_3$	$(CH_3)_2TeBr_2$	$[(CH_3)_2TeBr_2]_2$-BBr_3	CH_3TeBr_3	CH_3TeBr_3 in C_6H_6	Proposed assignment
1227 m	1233 w	1262 w	1239 w	1234 w		*c*	–CH_3 deformation
1208 m	1212 w	1237 w	1219 w	1211 w			
	967 wm	971 w	976 w	977 w			
875 s	905 m	912 s	908 m	912 w			–CH_3 rocking
837 s	829 m	833 w	855 m	857 w, sh	858 s		
				848 vs			Free BBr_3?
				812 vs			
		606 vs		608 m			BBr_4^-
528 s	534 w	538 m	538 w	535 w	524 vw		Te–CH_3 stretch
			185 s	188 s	226 vs	220 s	Te–Br stretch
			148 s	149 s	202 s	200 s	
					133 s, br	120 s, br	Te–Br bridge stretch?
			103 s	102 s	105 m, br	104 vw	Br–Te–Br deformation
			98 s	98 s			
	78 s, br	40 m, br					Lattice mode

[a] vs, very strong; s, strong; m, medum; w, weak; br, broad; sh, shoulder. [b] Data for liquid sample taken from ref 12. [c] 500–1200-cm^{-1} region not examined.

Dimethyltellurium dibromide is clearly monomeric in either benzene or nitrobenzene solution. Since the conductance data indicate it to be a nonelectrolyte, the infrared spectrum is interpreted within the framework of a trigonal bipyramidal molecule having an electron

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Table III. Colligative Property Data for Methyltellurium Tribromide, Dimethyltellurium Dibromide, and the Boron Tribromide Adduct of Dimethyltellurium Dibromide in Benzene and Nitrobenzene Solution

Substance[a]	Method	Solvent	Concn, *M*	Exptl mol wt	Av deg of association, $\bar{n}$
$(CH_3)_2TeBr_2$ (317)	Osmometry	C_6H_6	0.054	316	
	Cryoscopy	$C_6H_5NO_2$	0.196	331	
$[(CH_3)_2TeBr_2]_2BBr_3$ (886)	Osmometry	C_6H_6	0.0184	308	
			0.0288	331	
	Cryoscopy	C_6H_6	0.0446	320	
		$C_6H_5NO_2$	0.0562	345	
CH_3TeBr_3 (383)	Osmometry	C_6H_6	0.0087		1.45
			0.0154		1.70
			0.0295		1.84
			0.0526		1.94
			0.0705		1.98

[a] Formula weight in parentheses.

pair in one of the equatorial positions. The molecule is thus similar in general form to related selenium compounds whose infrared spectra have been discussed in some detail.[2] The two infrared-active Te–Br stretching frequencies occur at 185 and 148 cm^{-1}, and Br–Te–Br bending motions are associated with the well-resolved doublet at 100 cm^{-1}. The configuration of the dibromide thus corresponds to that of the analogous dichloride, the structure of which has been determined by X-ray crystallographic means.[15]

The colligative properties of methyltellurium tribromide solutions evidence association increasing to a limiting $\bar{n}$ value of 2 with increasing concentration. The infrared spectroscopic results, although very similar in the low-frequency range for crystalline CH_3TeBr_3 and for benzene solutions of the substance, are indecisive in distinguishing between various models for the molecule. In each instance a minimum of three absorptions which may be associated with Te–Br stretching frequencies appear; two of these, at 226 and 202 cm^{-1} for the crystalline material, are higher in frequency than the Te–Br modes in $(CH_3)_2TeBr_2$, and the other, at 133 cm^{-1}, is lower. This latter frequency could be due to a Te–Br bridging mode in an associated species. No significant differences in absorption frequency or relative intensity were observed for 10 and 60 m*M* benzene solutions of CH_3TeBr_3.

Comparing the methyl proton resonance values of 3.33 and 7.36 ppm for the di- and tribromide, respectively, with the value of 1.88 ppm found for dimethyl telluride demonstrates the expected downfield shift with increasing bromine content of the molecule.

Adduct Formation with Boron Tribromide. Two of the above compounds, $(CH_3)_3TeBr$ and $(CH_3)_2TeBr_2$, form addition compounds with BBr_3. The 1:1 adduct of the former is too insoluble in benzene or nitrobenzene to permit either molecular weight or electrical conductance measurements to be carried out, and when the adduct was added to DMF a white precipitate, identified as $(CH_3)_3TeBr$, was formed. This observation may be correlated with the strong Lewis-base character of DMF; thus

$$(CH_3)_3TeBr \cdot BBr_3 + DMF = (CH_3)_3TeBr + DMF \cdot BBr_3$$

The infrared spectrum of $(CH_3)_3TeBr \cdot BBr_3$, however, provides strong evidence for an ionic formulation, $(CH_3)_3Te^+BBr_4^-$. The strong band at 606 cm^{-1} is in a position characteristic of the antisymmetric stretching frequency, ν_3, of the BBr_4^- ion.[16] Frequencies of BBr_3 in "–$XBBr_3$" species are found in the 670–700-cm^{-1} range,[17,18] and the possibility of a tellurium-to-boron bond is therefore unlikely. The absorption at 40 cm^{-1}, assigned to a lattice mode, is significantly lower than the corresponding vibration of $(CH_3)_3TeBr$, as would be expected.

The BBr_3 adduct of dimethyltellurium dibromide is of lower thermal stability than that of trimethyltellurium bromide and exhibits a small vapor pressure of BBr_3 at room temperature. It is soluble in benzene and nitrobenzene, but cryoscopic and osmometric measurements are in accord with extensive dissociation. This conclusion is supported by the spectroscopic detection of BBr_3 in the vapor phase over the solution. The low conductance values for nitrobenzene solutions of the adduct suggest that the tendency to form ions in solution is less favored than the decomposition to $(CH_3)_2TeBr_2$ and BBr_3. The infrared spectrum of the solid adduct differs from a composite spectrum of a mixture of $(CH_3)_2TeBr_2$ and free BBr_3 only in the presence of the absorption at 608 cm^{-1}. Considering the low thermal stability of the adduct it appears probable that at least partial decomposition occurs in the infrared beam. In view of the interesting 2:1 composition of this adduct it is unfortunate that decomposition and the possible overlapping of absorptions results in a spectrum not useful in structural characterization.[19]

Finally, the possibility that the 2:1 composition may be the result of transformation[4] of α-$(CH_3)_2TeBr_2$ to the β form, and subsequent reaction of BBr_3 with either $(CH_3)_3Te^+$ or $CH_3TeBr_4^-$ ion, is considered unlikely in view of the colorless nature of the adduct. As noted earlier, $CH_3TeBr_4^-$ displays a bright orange color, and the presence in the adduct of any significant amount of this ion, whether free or complexed, should be readily observable.

Lewis-Base Characteristics of Methyltellurium Tribromide. The failure of CH_3TeBr_3 to react with BBr_3

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finds a parallel in a similar lack of reaction between CH_3SeCl_3 and BCl_3.[1] The presence of three electron-withdrawing halogen atoms bonded to the chalcogen atom in each instance should reduce the possibility of the removal of a halogen as an ion. This electron-withdrawing effect is amply evident in the large downfield shift of the proton resonance of CH_3TeBr_3 in CCl_4 as compared to $(CH_3)_2TeBr_2$. In addition, the pronounced intermolecular association observed for solutions of CH_3TeBr_3 and of CH_3SeCl_3 may also be significant in preventing interaction with BX_3.

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A Scale of Relative Lewis Acidities from Proton Magnetic Resonance Data[1]

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Abstract: A scale of relative Lewis acidities has been set up for a number of inorganic halides and substituted inorganic halides based on the ratios of changes in the pmr chemical shifts of the α protons of ethers on complex formation. The sterically most favorable ether, tetrahydrofuran, was chosen as the reference base. Rapid exchange of Lewis acids among excess Lewis base sites occurs with all but the strongest acid–strongest base system studied. The pmr data on the complexes of boron fluoride and boron chloride indicate that back bonding persists in the complexes and that the bonding is dominantly electrostatic in character. When steric factors are not differentiating in either acid or base, relative Lewis acidities are unaffected by changes in the reference ether base. Steric inaccessibility in either acid or base causes pronounced changes in relative Lewis acidities toward ethers. For the chlorides of group IIIB elements, acidities increase with the electronegativity of the element. For the halides of group IVB elements steric rather than electronic factors appear to be controlling.

The relative strengths of Lewis acids have been compared using a variety of methods, and the results have been reviewed in the literature.[3,4] Although it has been reported by Diehl[5] that the interaction of a typical Lewis acid, boron fluoride, with ethers causes a marked downfield shift of the α-proton magnetic resonance, presumably due to electron withdrawal by the Lewis acid, this type of measurement has not been systematically used for the measurement of relative Lewis acidities. In the present paper are presented the results of some such measurements on a variety of inorganic halide- and substituted inorganic halide–ether systems.

To minimize steric effects, tetrahydrofuran was selected as a standard reference base for a scale of relative Lewis acidities. A value of 100 has been assigned to boron chloride, the strongest Lewis acid studied. The relative acidities of other Lewis acids are expressed as a percentage of the effect observed for boron chloride. Additional reference bases have been used to evaluate steric factors in Lewis acid–Lewis base interactions.

Experimental Section

The ethers used in this work were commercial products and were purified by fractional distillation. The inorganic halides were reagent grade chemicals and except for titanium tetrachloride were used as received. The titanium tetrachloride was fractionally distilled before use. The alkyl-substituted boron halides were products previously prepared in this laboratory.[6]

The boron fluoride complexes were prepared by direct synthesis and purified by vacuum distillation. The remaining Lewis acid–Lewis base systems were prepared by direct weighing of the components. No solvents were used other than excess of Lewis acid or base and approximately 5% tetramethylsilane. Samples for measurements were prepared and handled in an atmosphere of dry nitrogen.

Proton magnetic resonance spectra were obtained using a Varian Associates Model HR-60 high-resolution nmr spectrometer. Chemical shifts were obtained using the side-band technique with tetramethylsilane as internal standard. A Hewlett-Packard Model-521C electronic counter was used to measure side bands to 0.1 cps. The chemical shifts so obtained showed an average deviation of less than 0.4 cps. Measurements were made at ambient temperature (28 ± 1°). Liquids for measurement were kept at Dry Ice temperature until the spectra were run. None of the pmr spectra gave evidence of the presence of cleavage products.

Results and Discussion

The downfield shifts of the α-proton resonances of ethers on complexing with Lewis acids were determined, when solubility and melting point factors permitted, both for the pure complex and for solutions con-

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