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Solution Characteristics of Selenium and Tellurium Tetrahalides

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Infrared spectroscopic, molecular weight and electrical conductance data are reported for selenium tetrachloride, tellurium tetrachloride and tetrabromide, and tellurium dichlorodibromide in several non-aqueous, polar solvents. These data are interpreted as indicating these substances to be present primarily as monomolecular species in these solutions, but undergoing a limited ionization. Comparison of the infrared spectrum of crystalline $TeCl_2Br_2$ *with that of the substance in benzene solution suggests a* $TeClBr_2^+Cl^-$ *formulation for the crystalline material.*

Introduction

Numerous attempts to characterize the tetrachlorides and bromides of selenium and tellurium in the crystalline state have been reported in the literature. Most of the vibrational studies of the tellurium compound[1-5] have supported an ionic formulation, $TeX_3^+X^-$, but other vibrational data,[6,7a,7b] and a nuclear quadrupole resonance report[8] have suggested a covalent arrangement. X-ray crystallographic study[9] has been unsuccessful in distinguishing between these models. The uncertainty is greater regarding the structures of the crystalline selenium tetrahalides, and vibrational data have also been interpreted as consistent with both ionic[1,5] and covalent[6,7b] structures.

Until very recently only a limited amount of information concerning the solution character of these tetrahalides was available. Thus, the observed dipole moment of $TeCl_4$ in benzene[10,11] was viewed as resulting from a monomeric, trigonal bipyramidal solute species, but infrared spectroscopic[4] and cryoscopic[4,12] results suggest some association of the solute. In concentrated benzene solutions of $TeCl_4$ trimers, and perhaps tetramers, are proposed.[13] The results of electrical conductance and molecular weight studies in polar solvents have pointed toward a strong 1:1 electrolyte behavior for $TeCl_4$ and TeBr[4,13,14] but a more limited ionization of the analogous selenium compounds. An extended examination of $SeBr_4$ in various polar solvents has demonstrated that this substance is fully dissociated to an equilibrium system of Se_2Br_2, $SeBr_2$ and Br_2.[15]

In this paper infrared spectroscopic, molecular weight and electrical conductance data for solutions of $SeCl_4$, $TeCl_4$, $TeBr_4$, and the mixed halide, $TeCl_2Br_2$, in several polar solvents are presented and the resulting implications for the nature of these substances in solution described.

Experimental Section

Commercial $TeCl_4$ (City Chemical Co.) was recrystallized from redistilled benzene prior to use. $TeBr_4$ and $SeCl_4$ were prepared following standard methods using elementary tellurium and selenium of high purity. $TeCl_2Br_2$ was prepared by the reaction of $TeCl_2$ with excess Br_2. The resulting yellow material melted at 293° (lit, 292°).[16] Solvents were purified and physical measurements carried out according to procedures previously described.[15] It should be noted that redistilled spectral grade acetonitrile (Eastman) was used in preparing MX_4—CH_3CN solutions. When the anhydrous grade was employed, although subjected to the same distillation treatment and giving equally low specific conductance values as the spectral grade material, significantly higher molar conductance values were observed for the solutions. Whether this difference had its source in greater water content, or in some other impurity not present in the spectral grade material, was not determined.

Results

The infrared absorptions of crystalline $SeCl_4$, $TeCl_4$, $TeBr_4$, and $TeCl_2Br_2$ and of the various solutions of these substances are listed in Table I. Electrical conductance findings are presented in Tables II, III, IV,

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and V. Molecular weight results are summarized in Table VI.

Table I. Infrared Absorption Frequencies (cm^{-1} for $SeCl_4$, $TeCl_4$, $TeBr_4$ and $TeCl_2Br_2$.

Crystalline $SeCl_4$: [a] 371 vs, 348 vs, 275 m, 205 w, 190 s, 165 m, 145 m, 80 m
$SeCl_4$ in benzene: 366 vs, 348 vs, 268 m-s
$SeCl_4$ in acetonitrile: 362 vs, 341 s, 288 s, 281 s
$SeCl_4$ in tetramethylenesulfone: [b] 286 s, 277 s
Crystalline $TeCl_4$: [a] 358 vs, 347 vs, 191 m, 150 s, 101 vw, 73 vw, 57 m
$TeCl_4$ in benzene: [c] 362 vs, 347 vs, 280 vs, 240 vs, 181 s
$TeCl_4$ in nitrobenzene: 371 vs, broad, 275 vs
$TeCl_4$ in acetonitrile: 367 vs, 354 vs, 279 s
$TeCl_4$ in dimethylformamide: [d] 245 s
Crystalline $TeBr_4$: [a] 240 vs, 223 vs, 125 w, 110 s, 92 w, 46 m
$TeBr_4$ in benzene: 200 w, broad
$TeBr_4$ in dimethylformamide: [d] 225 m-w, 193 vs
Crystalline $TeCl_2Br_2$: 340 vs, 247 vs, 230 vs, 146 s, 131 s
$TeCl_2Br_2$ in benzene: 279 vs, broad, 255 m, 234 m
$TeCl_2Br_2$ in dimethylformamide: [d] 246 s, broad, 195 s

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[a] Reference (5). [b] Strong solvent absorption above 320 cm^{-1}. [c] Reference(3). [d] Strong solvent absorption above 280 cm^{-1}.

Table II. Conductance Data for $SeCl_4$ in Solution.[a]

CH_3CN (25°, K = 3.5×10^{-8})

C (x 10^3)	μ
1.0	3.0
3.0	1.2
3.8	0.95
8.9	0.47
11.0	0.49

$TMSO_2$ (32°, K = 20.×10^{-8})

C (x 10^3)	μ
2.0	0.25
4.1	0.11
15.0	0.10
22.0	0.11

CH_2Cl_2 (25°, K = 7.0×10^{-9})

C (x 10^3)	μ
0.6	0.2
0.8	0.1

DMF (27°, K = 1.2×10^{-7})

C (x 10^3)	μ
2.0	42
3.9	28
4.9	20
8.1	11
15.0	6

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[a] In Tables 2, 3, 4 and 5, C represents the molar concentration, K is the solvent's specific conductance (ohm^{-1} cm^{-1}), and μ is the molar conductance (ohm^{-1} cm^2 mole^{-1}).

Table III. Conductance Data for $TeCl_4$ in Solution (25°).[a]

$C_6H_5NO_2$ (K = 5.0×10^{-9})

C (x 10^3)	μ
1.4	0.58
2.6	0.34
3.4	0.28
6.7	0.21

DMF (K = 1.2×10^{-7})

C (x 10^3)	μ
3.3	38
5.1	26
9.9	23
16.0	16
31.0	12
42.0	9
72.0	8

CH_3CN (K = 5.0×10^{-8})

C (x 10^3)	μ
1.1	18.3
2.2	12.1
6.6	4.7
16.5	3.3
31.2	2.2
77.6	1.0

CH_2Cl_2 (K = 7.0×10^{-9})

C (x 10^3)	μ
0.4	0.6
0.7	0.4
1.4	0.2

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[a] See footnote *a* in Table II.

Table IV. Conductance Data for $TeBr_4$ in Solution (25°).[a]

$C_6H_5NO_2$ (K = 4.5×10^{-8})

C (x 10^3)	μ
0.8	5.7
1.1	5.0

DMF (K = 1.2×10^{-7})

C (x 10^3)	μ
6.6	40
7.9	27
11.0	12
15.0	8
33.0	5

CH_3CN (K = 4.0×10^{-8})

C (x 10^3)	μ
0.7	27
1.4	21
1.9	16
3.2	10
4.7	7

CH_2Cl_2 (K = 7.0×10^{-9})

C (x 10^3)	μ
0.2	1.8
0.3	1.4

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[a] See footnote *a* in Table II.

Table V. Conductance Data for $TeCl_2Br_2$ in Solution (25°).[a]

$C_6H_5NO_2$ (K = 4.5×10^{-9})

C	μ
1.3	4.6
1.6	3.8
2.3	2.9
3.3	2.2

CH_3CN (K = 4.0×10^{-8})

C	μ
2.8	12.0
4.0	9.2
6.5	5.8
10.0	4.4
19.2	2.9

CH_2Cl_2 (K = 7.0×10^{-9})

C	μ
0.4	0.7
0.5	0.6

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[a] See footnote *a* in Table II.

Table VI. Molecular Weight Data for MX_4

	C (x 10^3)[a]	MW
$SeCl_4$: $TMSO_2$ (cryo.): (formula weight = 221)	0.72	262
	3.4	206
	3.8	200
CH_3CN (osmo., 25°):	3.8	210
	8.9	219
	11.0	243
$TeCl_4$: $C_6H_5NO_2$ (cryo): (formula weight = 270)	3.6	278
	4.7	274
	15.0	292
	23.0	268
CH_3CN (osmo., 25°):	8.9	279
	23.0	294
	59.0	269
	89.0	252
$TeBr_4$: CH_3CN (osmo., 25°): (formula weight = 447)	4.7	404
	4.8	413
$TeCl_2Br_2$: CH_3CN (osmo., 25°):	5.8	343
	8.8	350
	10.0	389
	19.2	336

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[a] Concentration, C, expressed as molarity.

Discussion

Selenium Tetrachloride. The molecular weight results are consistent with the presence of $SeCl_4$ in either acetonitrile or tetramethylenesulfone solution as (a) monomolecular $SeCl_4$ units, (b) simple ion-pairs, $[SeCl_3^+Cl^-]$, or (c) fully ionized complex species, *e.g.*, $SeCl_3^+$, $SeCl_5^-$ or $2SeCl_3^+$, $SeCl_6^{2-}$, for example. There is no positive indication in these data for association effects. Although the infrared spectrum of solid Rb_2SeCl_6[17] displays a strong absorption at 280 cm^{-1}, and the interpretation of the $SeCl_4$ solution spectra could accommodate the presence of the $SeCl_6^{2-}$ species, this possibility, as well as the less reasonable presence of $SeCl_5^-$ ions, seems unikely in view of the electrical conductance results which are unreasonably low for an extensively dissociated electrolyte. An unambiguous distinction between (a) and (b) is not easily made. The solution infrared spectra, complicated by the presence of solvent bands, differ distinctly from the spectrum of solid $SeCl_4$ only in the increased intensity and sharpened band character of the absorption at approximately 280 cm^{-1} in the solutions; in the solid this band is very broad and ill-defined, and of but medium intensity. The doublet character of this absorption in CH_3CN and $TMSO_2$ solutions, when combined with the two strong bands at 362 and 341 cm^{-1} for CH_3CN solutions (but not observed for $TMSO_2$ solutions due to the strong solvent absorption above 325 cm^{-1}), is in accord with the total of four infrared-active stretching frequencies expected for a $SeCl_4$ molecule of C_{2v} symmetry. Thus, the experimental findings appear to be consistent with the presence of monomolecular $SeCl_4$ in solution. The very weak electrolyte behavior of the substance in $TMSO_2$ and CH_3CN is considerably enhanced in dimethylformamide but whether this is an effect due to coordination effects of the solvent,[14] or the result of solvent impurities[15] is uncertain. Since DMF absorbs strongly above 280 cm^{-1} no useful infrared data for this solution could be obtained.

Tellurium Tetrachloride. It will be observed (Table I) that the infrared spectra of $TeCl_4$ in acetonitrile and nitrobenzene compare closely with that in benzene; the strong band appearing in the 275-280 cm^{-1} region in each case is absent in the spectrum of crystalline $TeCl_4$. The molecular weight data for $C_6H_5NO_2$ and CH_3CN solutions are in full accord with those expected for monomolecular $TeCl_4$ units. These latter data and the suggested interpretation stand in sharp contradistinction to earlier findings and conclusions, and are strongly supported by the present conductance data (Table III) which are substantially lower than those previously reported for $C_6H_5NO_2$[14] and CH_3CN[13,14] solutions. Rigorous attention to solvent purification is demanded; it was observed that the introduction of minute amounts of moisture into these solutions resulted in sharp decreases in solution resistances. The removal of the yellow-green color of the $TeCl_4$–CH_3CN systems, however, and the appearance of the white turbidity associated with hydrolytic effects required further addition of water. The present results suggest, contrary to previous reports,[13,14] that $TeCl_4$ behaves as a monomolecular species and is ionized to only a limited degree in CH_3CN and $C_6H_5NO_2$.

The strong DMF absorption above 280 cm^{-1} prevents obtaining a full spectrum but the $TeCl_4$ absorption at 245 cm^{-1} falls within the range reported for the infrared stretching mode of $TeCl_6^{-2}$ in various salts, and is close to that (226 cm^{-1}) found for *trans*-tetrachlorobis(tetramethylthiourea)tellurium(IV).[18] While the matter must remain speculative at present, a six-coordinate tellurium(I) species in the $TeCl_4$–DMF system seems not unreasonable.

Tellurium Tetrabromide. In a similar way the molecular weight results for $TeBr_4$ in CH_3CN, and the conductance data in both CH_3CN and $C_6H_5NO_2$, argue for only limited ionization of this halide in these solvents. As in earlier reports[13,14] it was observed that the conductances of the bromide exceed those of the chloride at comparable concentrations, in accord with expectations regarding the relative ease of Te–Cl and Te–Br bond scission. The low solubility of $TeBr_4$ in these solvents interfered with the recording of useful infrared spectra, but the spectrum of a saturated solution of $TeBr_4$ in benzene showed a broad, weak band centered around 200 cm^{-1}, and that of a concentrated solution in DMF displayed a strong band at 193 cm^{-1} with a weak absorption about 225 cm^{-1}. In these spectroscopic results, as in the conductance findings for DMF solution of $TeBr_4$, there is behavior parallel with that of the $TeCl_4$–DMF system.

Tellurium Dichlorodibromide. The literature is devoid of structural information concerning this mixed halide. The infrared spectrum of the substance is interesting in showing one absorption (340 cm^{-1}(in the Te–Cl stretching region and two (247 and 230 cm^{-1}) in the Te–Br range. Two other absorptions, perhaps due to bending motions, are also present. The suggested stretching frequencies are thus in agreement with those which would be predicted for a pyramidal $TeClBr_2^+$ ion of symmetry C_s. However, the breadth of the 340 cm^{-1} absorption is such that the possibility of two stretching frequencies cannot be unequivocally excluded. Nevertheless, since the 340 cm^{-1} absorption is absent from the spectrum of the mixed halide in benzene solution and a strong absorption appears at 279 cm^{-1} (Te–Cl stretch?), it appears that a structural alteration occurs when crystalline $TeCl_2Br_2$ is dissolved in benzene. The sharply lowered frequencies of the Te–Cl mode in solution compared to those in crystalline $TeCl_4$ and $TeCl_2Br_2$ may be related to the smaller positive charge of the tellurium atom and to hybridization differences for the tellurium atom in $TeClBr_2^+$ and $TeCl_2Br_2$ environments. Association effects involving chlorine bridging could also result in a pronounced reduction in the Te–Cl stretching frequency.[13] The present description of the stretching frequencies of $TeCl_2Br_2$ in benzene solution suggests a tentative assignment of the observed stretching frequencies for *monomeric* $TeCl_4$ and TeB_4 species in solutions. The axial modes of the trigonal bipyramidal molecules would be expected to appear at about 280 and 200

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(17) P. J. Hendra and Z. Jovic, *J. Chem. Soc.*, Section A, 600 (1968).

(18) N. Katsaros and J. W. George, unpublished observation.

cm^{-1}, and the equatorial stretching frequencies at approximately 350 and 225 cm^{-1} for the chloride and bromide, respectively. For DMF solutions of $TeCl_2Br_2$ the solvent absorptions restrict the observed stretching frequencies of the solute to the 246 and 195 cm^{-1} absorptions. These frequencies correspond well with those found in the spectra of DMF solutions of $TeCl_4$ and $TeBr_4$.

The molecular weight results for $TeCl_2Br_2$ in acetonitrile suggest, parallel to the conclusions advanced for $TeCl_4$ and $TeBr_4$ in this solvent, a monomolecular species, and conductance values indicate a limited ionization in CH_3CN.

As anticipated for a solvent of low dielectric constant the conductances of all tetrahalides considered in this paper were quite low in methylene dichloride.

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