THE REACTION OF TELLURIUM (IV) HALIDES WITH SULFOXIDES

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Abstract – TeCl₄ and TeBr₄ have been found to react with sulfoxides in several different ways. Most alkyl sulfoxides form stable adducts of the type, TeX₄ · 3R₂SO. I.R. spectra indicate that telluriumoxygen bonding is present in the adducts. TeCl₄ reacts with $(CH_3)_2SO$ to produce H₂TeCl₆ · 4 $(CH_3)_2$ SO if a trace of water is present. Chemical, NMR, and i.r. evidence is given to support the product formula. If water is not present in the TeCl₄–(CH₃)₂SO reaction mixture, then a violent reaction may occur producing free tellurium, TeO₂, and organic sulfides. $(CH_3O)_2SO$ was found to react with the tellurium tetrahalides to produce CH₃O(SO)OCH₂TeX₃.

SEVERAL non-metal chlorides have been found to react vigorously with sulfoxides to produce chlorinated sulfides and the non-metal oxide or oxychloride[1]. For example,

 $SiCl_4 + 2(CH_3)_2SO \rightarrow 2CH_3SCH_2Cl + SiO_2 + 2HCl.$

We felt that it would be of interest to investigate the behavior of tellurium (IV) halides with sulfoxides to see if this type of reaction took place or if adduct formation occurred.

Tellurium tetrachloride and tellurium tetrabromide have recently been shown to be strongly solvated by several different types of solvents[2]. These two halides behave as 1:1 electrolytes in acetone, acetonitrile, nitromethane, pyridine, and dimethylformamide. The first three solvents are considered to be weak donors and fair to poor solvating solvents; pyridine, a good donor solvent, but a poor solvating one; and dimethylformamide, both a good donor and a good solvating solvent[3]. Pyridine (py) adducts of TeCl₄ and TeBr₄ have been prepared: TeCl₄ · py, TeCl₄ · 2py, and TeBr₄ · 2py[2]. Since dimethylsulfoxide is considered a fair donor and a good solvating solvent, the tellurium halides should be soluble in the sulfoxides and sulfoxide adducts might be formed.

There are only a small number of known oxo-adducts of the tellurium tetrahalides [4] as compared to the wide variety of adducts formed with nitrogen- and

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^{1. (}a) M. L. Lappert and J. K. Smith, *J. chem. Soc.* 3224 (1961). (b) E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw and B. C. Smith, *J. chem. Soc.* 6250 (1965).

^{2.} D. A. Couch, P. S. Elmes, J. E. Fergusson, M. L. Greenfield and C. J. Wilkins, J. chem. Soc. 1813 (1967).

^{3.} R. S. Drago and K. F. Purcell, Prog. inorg. Chem. 6, 271 (1964).

^{4.} I. Lindquist, Inorganic Adduct Molecules of Oxo-compounds. Springer, Berlin (1963).

sulfur-containing compounds[5]. Ketones do not form simple adducts with the tellurium tetrahalides; instead they usually react to produce an organotellurium compound with the elimination of the hydrogen halide[6], for example,

$$\begin{array}{c} O & O \\ \parallel \\ \mathsf{TeCl}_4 + 2\mathsf{CH}_3\mathsf{CCH}_3 \rightarrow (\mathsf{CH}_3\mathsf{CCH}_2)_2\mathsf{TeCl}_2 + \mathsf{HCl}. \end{array}$$

A variety of S=O compounds were reacted with the tellurium tetrahalides in order to see if the HX elimination reaction might occur.

EXPERIMENTAL

The tellurium tetrahalides were prepared by standard methods [7]. Their purity was checked by tellurium and halide analysis. Dimethylsulfoxide (Crown Zellerbach Chemical Co.) was purified by drying over CaO for 3 days, followed by fractional distillation under reduced pressure and collection of the fraction at 55°C. It was stored over molecular sieves. The other sulfoxides were obtained from K and K Laboratories, with the exception of tetramethylene sulfoxide (Wateree Chemical Co.). They were used without further purification. Acetonitrile was purified according to the method of Coetzee *et al.*[8]. Chloroform was purified by the method reported by Vogel[9]. Deuterium oxide, acetone- d_6 , and dimethylsulfoxide- d_6 were obtained from Diaprep, Inc.

The tellurium halide was added slowly under a blanket of nitrogen to an excess of the cold sulfoxide producing a yellow solution with the tetrachloride and an orange solution with the tetrabromide. Addition of CHCl₃ produced a precipitate after a few minutes. The precipitate was filtered and washed with cold CHCl₃ and dried in vacuo over silica gel. The products are generally soluble to slightly soluble in acetone, acetonitrile, ethanol, and ether. They were insoluble in benzene, carbon disulfide, chloroform, and carbon tetrachloride. A solid adduct was not obtained in several instances, only oils. No product, solid or oil, could be obtained with (C_6H_3)₂SO and the tellurium tetrahalides. Also TeCl₄ and SOCl₂ did not react. Analytical data on the products of the reaction are found in Table 1.

Analyses for carbon and hydrogen were performed by A. Bernhardt, Mikroanalytisches Laboratorium, Mulheim, West Germany and by Galbraith Laboratories, Knoxville, Tennessee. Tellurium was determined gravimetrically according to the method of Hillebrand *et al*[10]. Halide percentages were determined gravimetrically as the silver halides. Equivalent weight determinations were made by acid-base titration techniques employing a pH meter.

Infrared absorption spectra were obtained using a Perkin-Elmer Infracord Model 137 and a Perkin-Elmer Model 621 Spectrophotometer. The pressed KBr pellet technique and Nujol mull method were used for the solids and neat NaCl plates were used for the liquids and oils.

Nuclear magnetic resonance spectra were recorded using a Varian A-60 NMR spectrometer. The spectra were recorded at 40°C. Tetramethylsilane was used as an internal standard in every case except for those spectra in deuterium oxide.

Conductance measurements were made using an Industrial Instrument, Inc., Model RC-16B2 Conductivity Bridge and a Type L. C. conductivity cell. Measurements were made at a temperature of 25°C and at a concentration of 0.001 M. Acetonitrile having a specific conductance of 3.2×10^{-6} ohm⁻¹ was used as the solvent.

A Leeds and Northrup Electrochemograph was used to obtain the polarograms.

- 5. D. I. Ryabchikov and I. I. Nazarenko, Usp. Khim. 33, 108 (1964).
- 6. G. T. Morgan and H. D. Drew, J. chem. Soc. 121, 922 (1922); G. T. Morgan, J. chem. Soc. 127, 2611 (1925); G. T. Morgan and O. C. Elvins, J. chem. Soc. 127, 2625 (1925).
- 7. J. F. Suttle and C. R. F. Smith, Inorg. Synth. 3, 140 (1950); B. Brauner, J. chem. Soc. 55, 382 (1889).
- 8. J. F. Coetzee, G. P. Cunningham, D. K. McGuire and G. R. Padmanabhan, Analyt. Chem. 34, 1139 (1962).
- 9. A. I. Vogel, Textbook of Practical Organic Chemistry, Longmans Green, London (1951).
- W. F. Hillebrand, G. E. Lundell, M. S. Bright and J. I. Hoffman, *Applied Inorganic Analysis*, p. 3318. Wiley, New York (1962).

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		Melting										
		point		%Те		Х%		X/Te	%C		₩%	
Reactants	Products	(°C)	Formula	expt.	calc.	expt.	calc.	expt.	expt.	calc.	expt.	calc.
TeCl ₄ (CH ₃) ₂ SO	yellow	115	H ₂ TeCl ₆ · 4(CH ₃) ₂ SO	19-45	19-48	32·48	32.50	6-011	14-73	14-67	3-99	3-99
TeBr ₄ (CH ₃) ₂ SO	orange	68	TeBr ₄ · 3(CH ₃) ₂ SO	18-24	18-71	47·68	47-00	4-174	9-95	10-36	2·64	2.66
TeCl4(CH2)4SO	yellow green	116	TeCl ₄ · 3(CH ₂) ₄ SO	21.75	21-91	24.72	24-36	4·091	24-00	24-75	4·30	4.15
TeBr4 (CH2)4SO	yellow	85	TeBr ₄ · 3(CH ₂) ₄ SO	16.32	16.79	41.82	42-06	4·092	19-23	18.66	3-46	3.19
TeCl4 (C2H3)2SO	yellow	oil	$TeCl_4 \cdot 3(C_2H_5)_2SO$	21-52	21·69	24-45	24-14	4·089				
TeBr ₄ (C ₂ H ₅) ₂ SO	orange	95	$TeBr_4 \cdot 3(C_2H_5)_2SO$	19-02	19-34	48·16	48-46	4-043				
TeCl ₄ (n-C ₄ H ₉) ₂ SO	yellow	oil	$TeCl_4 \cdot 3(C_4H_9)_2SO$	17-84	16.85	19-07	19-45	3-847				
TeBr ₄ (n-C ₄ H ₉) ₂ SO	red orange	oil	TeBr ₄ ·3(C ₄ H ₉) ₂ SO	11-63	13-61	33.17	34-22	4-554				
TeCl4 (CH3O)2SO	white	oil	TeCl ₃ CH ₂ O(SO)OCH ₃	35-45	37.19	28-50	30-99	2.894				
TeBr ₄ (CH ₃ O) ₂ SO	brown	> 360	TeBr ₃ CH ₂ O(SO)OCH ₃	27-38	26.78	50-60	50-31	2-951				
$TeX_4 (C_6H_5)_2 SO$	 No reaction 											
TeCI ₄ SOCI ₆	No reaction											

RESULTS AND DISCUSSION

Adduct formation

For most of the alkyl sulfoxides the addition of tellurium tetrahalides leads to adducts having the general formula, $TeX_4 \cdot 3R_2SO$ (Table 1). This composition suggests that the adducts might be formulated as $[TeX_3(R_2SO)_3]^+X^-$. The TeX_3^+ cation has been found by infrared data to be present in solid $TeCl_4$ and $TeBr_4$ [11]. Conductivity measurements of $TeCl_4$ and $TeBr_4$ in several solvents have shown them to behave as 1:1 electrolytes, presumably yielding TeX_3^+ and $X^$ ions in solution[2]. Therefore, the TeX_3^+ ion is a species which might serve to bind three other ligands, such as sulfoxide molecules, forming an octahedral complex. Six-fold coordination is known for the tellurium (IV) state, e.g. $TeCl_6^{-2}$. In the solid adducts the tellurium atom may be exhibiting six-fold coordination; however, in solution this probably is not the case.

Acetonitrile solutions of $TeBr_4 \cdot 3(CH_3)_2SO$, $TeCl_4 \cdot 3(CH_2)_4SO$, and TeBr₄ · 3(CH₂)₄SO have molar conductivities (Λ_m) in the range of 180-220 ohm⁻¹ cm² (Λ_m 1:1 electrolyte = 90–130[2]). TeBr₄ · 3(CH₂)₄SO has a Λ_m (222) greater than those of $\text{TeCl}_4 \cdot 3(\text{CH}_2)_4 \text{SO}(178)$ and $\text{TeBr}_4 \cdot 3(\text{CH}_3)_2 \text{SO}$ (205). In acetonitrile these adducts ionize to a great degree, more than expected for a 1:1 electrolyte. The average mole ratio of bound halide: tellurium is less than three, producing a large Λ_M . This indicates that there is a large interaction between the sulfoxide and the tellurium, producing displacement of halide ions from the coordination sphere of the tellurium. Thus, considering only the sulfoxide and the halide ions, the average coordination number of the tellurium in solution is less than six. NMR measurements on a saturated solution (ca. 0.001 M) of TeBr₄. $3(CH_3)_2$ SO in acetone- d_6 showed that the sulfoxide interacts in solution with the tellurium. The spectrum showed a signal at -178.5 Hz. downfield from tetramethylsilane used as an internal standard. This methyl proton peak shifted upfield toward that of the free sulfoxide peak (-154.4) when dimethylsulfoxide was added to the solution. Unfortunately no quantitative measurements on the relation between the amount of the shift and the amount of sulfoxide added were possible since the solution was so dilute. However, the measurements did show that in the acetone solution at least a portion of the sulfoxide is bound and the rate of exchange between the bound and free sulfoxide is rapid.

The sulfoxide oxygen atom no doubt serves as the donor atom for adduct formation. The i.r. spectra of the free sulfoxides have a very intense absorption band in the region of $1020-1060 \text{ cm}^{-1}$ which has been assigned to the SO stretching frequency[12]. This band for the adducts is reduced in intensity and a new band appears at a lower wavenumber of approximately 1000 cm^{-1} (Table 2). This shift indicates that the oxygen atom of the sulfoxide is acting as a donor atom toward the tellurium tetrahalide[13].

Reaction of TeCl₄ with (CH₃)₂SO

The reaction of $TeCl_4$ with dimethylsulfoxide is more exothermic than its reaction with other sulfoxides. A violent reaction may result unless the sulfoxide

^{11.} J. W. George, N. Katsaros and K. J. Wynne, Inorg. Chem. 6, 903 (1967).

^{12.} D. Barnard, J. M. Fabian and H. P. Koch, J. chem. Soc. 2442 (1949).

^{13.} F. A. Cotton and R. Francis, J. Am. chem. Soc. 82, 2986 (1960).

(CH ₃) ₂ SO	$H_2TeCl_6 \cdot 4(CH_3)_2SO$	TeBr ₄ · 3(CH ₃) ₂ SO
1065-1045	1027,997	1035,1003
(CH ₂) ₄ SO	TeCl ₄ · 3(CH ₂) ₄ SO	$TeBr_4 \cdot 3(CH_2)_4SO$
1030-1018	935	935
$(C_2H_5)_2SO$	$TeCl_4 \cdot 3(C_2H_5)_2SO$	$TeBr_4 \cdot 3(C_2H_5)_2SO$
1052	1027	1020
(<i>n</i> -C ₄ H ₉) ₂ SO	$TeCl_4 \cdot 3(n-C_4H_9)_2SO$	$TeBr_4 \cdot 3(n-C_4H_9)_2SO$
1025-1015	948	970-950

Table 2. Sulfur-oxygen stretching frequencies (cm⁻¹)

is cold and the $TeCl_4$ added very slowly to the liquid. The presence of a small amount of water in the sulfoxide may prevent the violent reaction (vide infra). Addition of either chloroform or benzene produces a yellow solid. Better crystallization of the product is obtained if chloroform is used. This solid reacts with water to produce an acidic solution and TeO_2 . The acid equivalent weight of the compound in water is 110.8. Using the elemental analysis the formula weight is 652.8 per mole of tellurium. Therefore, the number of equivalents per mole is 5.91 (TeBr₄ · 3(CH₃)₂SO also reacted with water producing TeO₂ and an acidic solution. It has an equivalent weight of 178.2; molecular weight, 681.6; number of equivalents per mole, 3.82.) Since the chlorine: tellurium ratio of the yellow compound is 6.01 (Table 1) then all of the chloride ions are apparently hydrolyzed when the solid is placed into water. Analysis indicates that four moles of (CH₃)₂ SO or some related compound per mole of Te are present in the solid. Since all of the chlorides are rapidly hydrolyzed it is doubtful that chlorinated sulfoxides are present in the compound, but this possibility was not overlooked.

The tellurium is probably not in the +6 oxidation state in the yellow solid. The +6 state is only known in TeF₆, TeO₃, and H₆TeO₆[14]. The reaction of the yellow solid with water produces TeO₂ and no oxygen or strong oxidizing species. TeCl₄ and the yellow solid were each dissolved in 0.1 F KCl, saturated citric acid, 0.1 F ammonium citrate, and 2 F acetic acid (1% gelatin) and the polarogram obtained for each solution. The polarograms were identical for each pair using a specific solvent. This indicated that the tellurium species in both solutions were the same and that no unusually strong oxidizing species were present in the yellow solid solution.

A 0.001 M acetonitrile solution of the compound has a molar conductivity of $178 \text{ ohm}^{-1} \text{ cm}^2$. Apparently the compound ionizes to a greater extent than 1:1.

The formula that might be proposed for the yellow compound is $H_2TeCl_6 \cdot 4(CH_3)_2SO$ or $[(CH_3)_2SOH]_2TeCl_6 \cdot 2(CH_3)_2SO$. A compound of such composition should exhibit large conductivity in acetonitrile and should hydrolyze readily in water solution to produce six equivalents of protons per mole:

 $H_2TeCl_6 \cdot 4(CH_3)_2SO(s) + 2H_2O \rightarrow TeO_2(s) + 6HCl(aq) + 4(CH_3)_2SO.$

14. K. W. Bagnall, The Chemistry of Selenium, Tellurium, and Polonium. Elsevier, New York (1966).

The hexachlorotellurate (IV) anion is a well-characterized tellurium species [16] and dimethylsulfoxide is able to act as a proton acceptor. For example, the nitrate salt of dimethylsulfoxide has been prepared [15]. Compounds containing the TeCl₆⁻² anion have an i.r. absorption band in the region of 240 cm⁻¹[16]. The yellow solid has a broad absorption band at 250 cm⁻¹. The SO stretching frequency of the yellow solid (Table 2) is less than that of the free sulfoxide because of the interaction of the oxygen atom with the acid protons. This represents possibly the first isolation of hexachlorotelluric acid. There have been reports in the literature of its isolation as H₂TeCl₆ · 2H₂O[14] but so far none of these reports have been substantiated [5].

In order to show that no chlorinated sulfoxides or sulfides were in the yellow solid, NMR spectra were obtained in $(CD_3)_2SO$ and D_2O . Two peaks were found in the $(CD_3)_2SO$ solution (0.1 M) spectrum: -153.7 and -701.0 Hz. The first peak is due to the methyl protons of the $(CH_3)_2SO$ in the compound and the second to the acid protons. Two peaks were also found in the $(CD_3)_2SO$ solution (0.1 M) spectrum of TeBr₄ · $3(CH_3)_2SO$: -153.5 and -516.6 Hz. The second peak was much less intense than that seen in the chloro compound spectrum. The pure solvent showed weak absorption at -198 Hz which indicates that the $(CD_3)_2SO$ does contain a trace of water. This water may hydrolyze the tellurium compounds to a slight extent and interact by fast exchange with the acid protons producing an average proton signal. An equilibrium of the following type would be established in the tellurium solutions:

$$H_3O^+ + (CD_3)_2SO = (CD_3)_2SOH^+ + H_2O.$$

Since rapid proton exchange occurs, the wide variation of the second peak of the three spectra is due to concentration effects on the equilibrium. Both $H_2TeCl_6 \cdot 4(CH_3)_2SO$ and $TeBr_4 \cdot 3(CH_3)_2SO$ hydrolyzed in D_2O to produce TeO_2 and solutions whose NMR spectra were identical. Old samples of both compounds were foul-smelling and when dissolved in appropriate solvents showed weak signals in the region assigned to organic sulfides [17].

In order to account for the production of $H_2TeCl_6 \cdot 4(CH_3)_2SO$ in $(CH_3)_2SO$, water must be present to supply acid protons. One-half of the TeCl₄ partially ionizes or hydrolyzes to produce the additional chlorides required by the product. The yield of the product based on the initial amount of TeCl₄ was always between 40 to 50 per cent. No TeO₂ was observed in the reaction. The NMR spectrum of the $(CH_3)_2SO$ —CHCl₃ solution mixture from which the yellow solid had been removed was obtained. No unusual signals were found. A weak signal at -508 Hz was observed which probably arises from the presence of water. The solution is still yellow after removing the chloro compound. The exact nature of the tellurium remaining in the solution is unknown.

The $(CH_3)_2SO-CHCl_3$ solution was also passed through a gas chromatograph and no evidence of dimethyl sulfide or dimethyl sulfone was found. This is further evidence that no oxidation or reduction of tellurium took place in the reaction.

^{15.} A. Sabyzeff, Ann. Chem. 144, 148 (1867); P. Nylen, Z. anorg. allg. Chem. 246, 227 (1941).

^{16.} N. N. Greenwood and B. P. Straughan, J. chem. Soc. 962 (1966).

^{17.} G. R. Pettit, I. B. Douglass and R. A. Hill, Can. J. Chem. 42, 2357 (1964).

TeX₄ and sulfoxides

A violent reaction definitely producing elemental tellurium, TeO_2 , and sulfides (detected by odor), usually occurred when freshly distilled $(CH_3)_2SO$ was used. Dimethyl sulfoxide which had been stored over molecular sieves for a period of time did not seem to produce the violent reaction. Even with molecular sieves present $(CH_3)_2SO$ retains water (seen by NMR) and the presence of this water may prevent the highly exothermic reaction.

The reaction producing $H_2TeCl_6 \cdot 4(CH_3)_2SO$ was unexpected – a violent reaction or adduct formation being the expected reaction. A mechanism has been proposed for the reaction of non-metal chlorides with $(CH_3)_2SO[1b]$. It involves the formation of an oxo-adduct, loss of HCl from the adduct, the breaking of the sulfur-oxygen bond, and finally addition of the halide ion to the methylene group forming a chlorinated sulfide. Tellurium tetrachloride should be able to react in this manner and probably does so in the violent reaction. Dimethyl sulfoxide might also act as a reducing agent forming sulfones and free tellurium. Apparently a trace of water is enough to produce $(CH_3)_2SOH^+$ and $TeCl_6^{-2}$ ions which can then form a stable, crystalline solid with additional $(CH_3)_2SO$.

Reaction of $(CH_3)_2SO_3$ with tellurium tetrahalides

Dimethyl sulfite reacts readily with the tellurium tetrahalides to produce products that have a halogen:tellurium ratio of approximately three to one (Table 1). This indicates that a tellurium-carbon bond is formed with the loss of hydrogen halide. The compounds are very hygroscopic and are not soluble in most common solvents. Dimethyl sulfite appears to be one SO type compound which behaves with tellurium (IV) halides in the same manner as the carbonyl compounds—loss of hydrogen halide and formation of a tellurium-carbon bond. One of the methyl protons of $(CH_3O)_2SO$ is sufficiently acidic to be displaced by a TeX₃ group. This is evidently due to the large electronegativity effect of the SO₃ group.