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Tellurium-125 Nuclear Magnetic Resonance and Electrochemical Investigation of Exchange and Redox Reactions of Organotellurium(IV) Dithiolate and Organotellurium(II) Complexes Occurring in Solution and at Electrode Surfaces

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Tellurium-125 NMR studies on a series of xanthate (xan), dithiophosphate (dtp), and dithiocarbamate(dithiolate) (dtc) organotellurium(IV) complexes $Ph_2Te(S\text{–}S)_2$ [where $[S\text{–}S]^-$ = $[S_2COEt]^-$, $[Etxan]^-$; $[S_2P(OEt)_2]^-$, $[Et_2dtp]^-$; $[S_2CNEt_2]^-$, $[Et_2dtc]^-$] formed in situ by reaction of Ph_2TeCl_2 and dithiolate ligand show their instability in solution with respect to metal reduction to give Ph_2Te and ligand oxidation to give $(S\text{–}S)_2$. The rate of this internal redox decomposition reaction increases in the order Etxan > Et_2dtp > Et_2dtc and is dependent on temperature and solvent. In contrast, mixed-ligand compounds $Ph_2Te(Cl)(S\text{–}S)$ formed by exchange reactions between Ph_2TeCl_2 and $[S\text{–}S]^-$ and the series of $C_8H_8Te(S\text{–}S)_2$ compounds (C_8H_8 = *o*-xylene-α,α-diyl) appear to be relatively stable in solution. Exchange reactions between different $Ph_2Te(S\text{–}S)_2$ complexes also are observed on the synthetic time scale, but in this case the reverse order of reactivity is found with Et_2dtc complexes reacting to a significant extent and Etxan only to a minor extent. Electrochemical investigation on the $C_8H_8Te(S\text{–}S)_2$ and $Ph_2Te(S\text{–}S)_2$ complexes in dichloromethane confirms the importance of exchange reactions between tellurium(IV), tellurium(II), and ligand species as well as with mercury electrodes. For example, reduction of $C_8H_8Te(S\text{–}S)_2$ at platinum electrodes follows the pathway

$$C_8H_8Te(S\text{–}S)_2 + 2e^- \rightarrow C_8H_8Te + 2(S\text{–}S)^-$$

and occurs at very negative potentials. At mercury electrodes, the rapid intermolecular exchange process

$$C_8H_8Te(S\text{–}S)_2 + Hg \rightleftharpoons C_8H_8Te + Hg(S\text{–}S)_2$$

occurs at the electrode surface and is followed by reduction of the mercury complex. The same overall products are produced as is the case with reduction at platinum electrodes. However, at mercury electrodes, substantial catalysis of the reduction process is achieved in the sense that the potential for reduction is more than a volt less negative than at platinum electrodes. Exchange reactions at mercury electrodes also influence oxidation processes. One of the processes observed at mercury electrodes in the presence of C_8H_8Te is

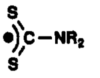
$$3C_8H_8Te + Hg \rightleftharpoons [(C_8H_8Te)_3Hg]^{2+} + 2e^-$$

which involves oxidation of electrode mercury. Unfortunately, the electrochemical processes observed at chemically inert platinum electrodes are all completely irreversible, so that no information could be obtained on the thermodynamic relationships existing in the Te(IV)/Te(II) dithiolate chemistry.

Introduction

It has been established by NMR measurements that a solvent-dependent equilibrium exists between tellurium(IV) dithiocarbamate (structure 1a), thiuram disulfide (structure **1b**), and tellurium(II) dithiocarbamate complexes,[3,4] e.g. eq 1. The predicted inorganic Te(IV) dithiophosphate and Te(IV) xanthate complexes containing dithiolate ligands (structures **2a** and **3a**) related to dithiocarbamate have not yet been prepared, presumably because such complexes are unstable with respect to reduction to tellurium(II) complexes and formation of the disulfide (structures **2b** and **3b**) from oxidized dithiolate. However, introduction of alkyl or aryl substituents seems to stabilize tellurium(IV) complexes to the extent that complexes of the type $C_8H_8Te(S\text{–}S)_2$ (where C_8H_8 = *o*-xylene-α,α-diyl) and $Ph_2Te(S\text{–}S)_2$ (where $[S\text{–}S]^-$ = $[S_2CNEt_2]^-$, $[S_2P(OEt)_2]^-$, $[S_2COEt]^-$, also abbreviated to $[Et_2dtc]^-$, $[Et_2dtp]^-$, and $[Etxan]^-$ for dithiocarbamate, dithiophosphate, and xanthate, respectively) containing two tellurium–carbon bonds (structures 4 and 5) have been synthesized and characterized both in the solid state and in solution.[5,6] Additionally, $Te(Et_2dtc)_2$ may take part in

$$Te(Et_2dtc)_4 \rightleftharpoons Te(Et_2dtc)_2 + (Etdtc)_2 \qquad (1)$$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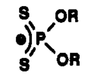
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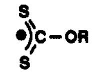
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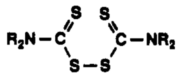
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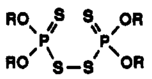
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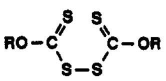
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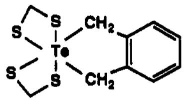
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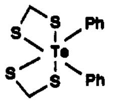
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oxidative addition reactions with MeI to form the tellurium(IV) compound $MeTe(Et_2dtc)_2$ (I).[7] A range of relatively stable organometallic complexes are therefore available for studies of exchange and redox reactions in tellurium solution chemistry.

NMR techniques are suitable for studying chemical aspects of redox processes involving Te(IV)/Te(II) dithiolate redox chemistry because all species involved in the reaction are diamagnetic. Electrochemical techniques are well-suited to study the electron-transfer component of redox processes. Consequently with tellurium dithiolate redox chemistry, NMR and electrochemical methods may provide complementary information. While no reports on the electrochemical behavior of the aryl compounds $Ar_2Te(S{-}S)_2$ ($Ar_2 = C_8H_8$, Ph_2) have appeared to date, the extensive work of Liftman and Albeck on a range of organotellurium(IV) halides[8-11] is available. In the electrochemical studies of aryltellurium chlorides[8-10] and diaryl tellurides[11] in dichloromethane at platinum electrodes it has been shown that stepwise replacement of chloride in tellurium(IV) tetrachloride with a phenyl group results in a progressively more negative reduction potential to the tellurium(II) oxidation state. Phenyltellurium trichloride and diphenyltellurium dichloride reduction yielded diphenyltellurium(II) (Ph_2Te) as the major product. This species can be oxidized in a two-electron step to $Ph_2Te(IV)(ClO_4)_2$.[11] The electrochemistry of tellurium complexes containing easily oxidized dithiolate ligands is likely to be much more complex because the ligands themselves are also electroactive. In this paper, the results of both NMR and electrochemical investigations of redox and exchange reactions involving dithiocarbamate, dithiophosphate, and xanthate ligands and organotellurium(IV) dithiolate and organotellurium(II) complexes are presented to further characterize the importance of these reactions in tellurium solution chemistry.

Experimental Section

Syntheses. All compounds studied in this paper were prepared by using literature methods.[5-7,12-14]

Instrumentation. NMR spectra were recorded by using a JEOL FX 100 spectrometer with broad-band decoupling. A JEOL NM 5471 controller was used for temperature control, and the temperatures in the probe were measured with a calibrated platinum resistance thermometer. ^{125}Te spectra were recorded at 31.4 MHz (20 kHz spectral window) with an external ^7Li lock. The pulse width was 22 ms and the pulse delay 50 ms. Spectra were recorded in the presence of $Cr(acac)_3$ (Hacac = acetylacetone) to reduce relaxation times. ^{125}Te chemical shifts were references against 0.7 M K_2TeO_3 in water. ^{13}C spectra were recorded at 25.0 MHz and referenced against tetramethylsilane.

Voltammetric measurements were made by using a Princeton Applied Research Corp., PAR (Princeton, NJ), Model 174A polarographic analyzer with a dropping mercury or a polished platinum disk working electrode. For experiments with a rotating platinum disk electrode a Metrohm Model 628-50 electrode assembly and Model 628-10 drive unit were used. A platinum wire served as the auxiliary electrode while the reference electrode Ag/AgCl (saturated LiCl in ethanol) was separated from the test solution by a salt bridge containing the solvent. The $[(C_5H_5)_2Fe]^+/(C_5H_5)_2Fe$ redox couple was measured frequently to provide an internal check on the stability of the reference electrode. The reversible half-wave potential of the ferrocene oxidation process was 0.48 V vs Ag/AgCl. All electrochemical measurements were made at 20 °C in dichloromethane (0.1 M Bu_4NClO_4).

Controlled-potential electrolysis experiments were performed in dichloromethane (0.1 M Bu_4NClO_4) at either mercury pool or platinum gauze working electrodes with a PAR Model 173 potentiostat/galvanostat used in conjunction with a Model 179 digital coulometer. The platinum gauze auxiliary electrode was isolated from the test solution via a salt bridge and the reference electrode was the same as that used for the voltammetry.

Results and Discussion

(A) NMR Investigations. ^{125}Te NMR measurements provide ready identification of the different tellurium species which can be formed in both oxidation state II and IV. Chemical shift and other NMR data for the various species of interest in this work are contained in Table I. Because of the specificity of the NMR method for detecting species formed during the course of reactions, data obtained from this technique are presented prior to the results of the electrochemical studies.

NMR Study of $Ph_2Te(Et_2dtc)_2$, $Ph_2Te(Et_2dtp)_2$, and $Ph_2Te(Etxan)_2$. NMR studies of the synthesized dithiolate compounds, $Ph_2Te(S{-}S)_2$, in a range of solvents demonstrate that they are all unstable with respect to formation of Ph_2Te and oxidized dithiolate ligand. However, while data suggested that the rate of decomposition was greatest for $Ph_2Te(Etxan)_2$ and least for $Ph_2Te(Et_2dtc)_2$ the reactions were too fast in a number of instances to be studied coveniently by NMR spectroscopy. Consequently, the reactivity was studied in detail after in situ preparation via the exchange reaction of Ph_2TeCl_2 with the dithiolate ligands. Results of this study are presented in the next section and provide information on both exchange reactions between chloride and dithiolate ligands and the redox-based decomposition reaction of $Ph_2Te(S{-}S)_2$. Conclusions reached from this study with respect to the decomposition reaction are consistent with those implied by direct measurement of the NMR spectra of the organometallic dithiolate compounds.

NMR Study of Reactions of $NaEt_2dtc$, KEt_2dtp, and KEtxan with Ph_2TeCl_2. Reaction of equimolar amounts of Ph_2TeCl_2 and $NaEt_2dtc$ in dichloromethane at room temperature results in the observation of three species, Ph_2TeCl_2, $Ph_2Te(Cl)(Et_2dtc)$, and Ph_2Te as deduced from the $^{125}Te\{^1H\}$ spectrum. That is, both exchange and redox reactions must have occurred to produce $Ph_2Te(Cl)(Et_2dtc)$ and Ph_2Te, respectively. The same species are detected when equimolar amounts of Ph_2TeCl_2 and $Ph_2Te(Et_2dtc)_2$ are dissolved in dichloromethane at 25 °C. The resonances assigned to Ph_2TeCl_2 and Ph_2Te were confirmed by comparison with the ^{125}Te spectrum of pure samples of each of these compounds.

In contrast, the $^{125}Te\{^1H\}$ spectrum of a dichloromethane solution recorded 1 h after mixing equimolar amounts of Ph_2TeCl_2 and $NaEt_2dtc$ at −35 °C indicates that only very small amounts of Ph_2TeCl_2 and $Ph_2Te(Et_2dtc)_2$ are present with the major species in solution being $Ph_2Te(Cl)(Et_2dtc)$. The $^{125}Te\{^1H\}$ spectrum is virtually identical 2 h after initial mixing. Similar results are obtained when the experiment is repeated in dimethylformamide solvent at −35 °C. That is, the exchange process remains important under these conditions but the rate of the redox process has been slowed down significantly. Importantly, no Ph_2Te, which is the expected product of the redox-based process, is

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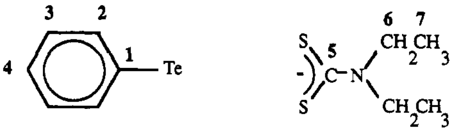
Table I. NMR Data for Compounds Studied in This Paper $Ph_2Te(Cl)_n(S\text{-}S)_{2-n}$ [(S-S) = Et_2dtc, Et_2dtp, Etxan; n = 0, 1, 2]



compound	$\delta(^{125}Te)$	$\delta(^{13}C)^e$						
		1	2	3	4	5	6	7
$Ph_2TeCl_2{}^a$	-826	136.3	134.3	130.6	132.4			
$Ph_2Te(Cl)(Et_2dtc)^b$	-943							
$Ph_2Te(Et_2dtc)_2{}^d$	-1056							
$Ph_2Te(Et_2dtc)_2{}^b$	-1046							
$Ph_2Te(Et_2dtc)_2{}^c$	-1037							
$Ph_2Te(Et_2dtc)_2{}^a$	-1040	135.3	135.7	130.1	130.7	199.2	49.2	12.7
$Ph_2Te(Cl)(Et_2dtp)^b$	-926							
$Ph_2Te(Cl)(Et_2dtp)^{a,h,i}$	-901							
$Ph_2Te(Et_2dtp)_2{}^{c,j}$	-951							
$Ph_2Te(Et_2dtp)_2{}^b$	-925	133.6	136.1	130.4	131.5		62.7^f	29.0
$Ph_2Te(Cl)(Etxan)^b$	-900							
$Ph_2Te(Cl)(Etxan)^c$	-899							
$Ph_2Te(Etxan)_2{}^c$	-967	133.0	136.1	130.4	131.8	221.0	71.4	14.4
$Ph_2Te(Etxan)_2{}^b$	-962							
$Ph_2Te(Et_2dtc)(Etxan)^c$	-1003							
$Ph_2Te(Et_2dtc)(Et_2dtp)^b$	-996							
$Ph_2Te(Et_2dtc)(Et_2dtp)^{c,k}$	-1006^h							
Ph_2Te^a	-1048							

[a] In dichloromethane at 25 °C. [b] In dimethylformamide at -40 °C. [c] In tetrahydrofuran at -40 °C. [d] In toluene at -40 °C. [e] Assignment of ^{13}C shifts is presented according to the scheme below for Et_2dtc and according to analogous schemes for other ligands. [f] $^2J_{C-P}$ = 5 Hz. [g] $^3J_{C-P}$ = 10 Hz. [h] $^2J_{Te-P}$ = 30 Hz. [i] $\delta(^{31}P)$ 90.5 ppm. [j] $\delta(^{31}P)$ 92.8 ppm. [k] $\delta(^{31}P)$ 96.8 ppm.

observed in either solvent at low temperature. Reaction of Ph_2TeCl_2 with excess $NaEt_2dtc$ at room temperature in dichloromethane (or toluene) initially only gives $Ph_2Te(Et_2dtc)_2$. After 24 h, the $^{125}Te\{^1H\}$ spectra indicate the presence of both $Ph_2Te(Et_2dtc)_2$ and Ph_2Te, the latter being 40% of the integrated signal intensity. These results suggest that exchange reactions occur prior to the redox reaction which only appears to occur to a significant extent after formation of $Ph_2Te(Et_2dtc)$ or $Ph_2Te(Cl)(Et_2dtc)$. Equations 2 and 3 summarize the reaction pathway.

$$Ph_2TeCl_2 + NaEt_2dtc \rightarrow Ph_2Te(Cl)(Et_2dtc) + NaCl \quad (2a)$$

$$Ph_2Te(Cl)(Et_2dtc) + NaEt_2dtc \rightarrow Ph_2Te(Et_2dtc)_2 + NaCl \quad (2b)$$

$$Ph_2Te(Et_2dtc)_2 \rightarrow Ph_2Te + (Et_2dtc)_2 \quad (3)$$

The $^{125}Te\{^1H\}$ NMR spectrum at room temperature of a dichloromethane solution containing equimolar quantities of Ph_2TeCl_2 and KEt_2dtp indicates the presence of Ph_2TeCl_2, $Ph_2Te(Cl)(Et_2dtp)$, $Ph_2Te(Et_2dtp)_2$, and Ph_2Te in solution. The major species, present as approximately 40% of the total tellurium is the exchange product $Ph_2Te(Cl)(Et_2dtp)$ and approximately 20% is present as the reduction product Ph_2Te. The $^{125}Te\{^1H\}$ spectrum of a similar solution prepared at −35 °C indicates that the tellurium-containing species in solution are Ph_2TeCl_2 (60%), $Ph_2Te(Cl)(Et_2dtp)$ (15%), and $Ph_2Te(Et_2dtp)_2$ (25%), and there is no evidence for formation of Ph_2Te. Raising the temperature to −20 °C results in the appearance of Ph_2Te (6%) and at 0 °C, approximately 20% of the total tellurium is present in the form of Ph_2Te. Reaction of Ph_2TeCl_2 with 2 mol equiv of KEt_2dtp in dichloromethane results in the observation of two $^{125}Te\{^1H\}$ resonances corresponding to the species $Ph_2Te(Et_2dtp)_2$ and Ph_2Te with approximate relative intensities of 1:3.

Changing the solvent to tetrahydrofuran, did not prevent Ph_2Te formation at room temperature with $Ph_2Te(Et_2dtp)_2$ and Ph_2Te being observed, the latter accounting for 70% of the total tellurium. Formation of Ph_2Te, in benzene solution, at room temperature, occurs to a lesser degree than in tetrahydrofuran. The major species in benzene solution is $Ph_2Te(Et_2dtp)_2$, with only a trace of $Ph_2Te(Cl)(Et_2dtp)$ being present. Similar results occur in toluene at room temperature, with approximately 80% of the total tellurium being present as $Ph_2Te(Et_2dtp)_2$.

The equations describing the reactions are therefore again considered to be a combination of exchange and redox process (eqs 4, 5) with $Ph_2Te(Cl)(Et_2dtp)$ being more stable than $Ph_2Te(Et_2dtp)_2$ and the redox reaction (eq 5) being faster than for the Et_2dtc situation (eq 3).

$$Ph_2TeCl_2 + KEt_2dtp \rightarrow Ph_2Te(Cl)(Et_2dtp) + KCl \quad (4a)$$

$$Ph_2Te(Cl)(Et_2dtp) + KEt_2dtp \rightarrow Ph_2Te(Et_2dtp)_2 + KCl \quad (4b)$$

$$Ph_2Te(Et_2dtp)_2 \rightarrow Ph_2Te + (Et_2dtp)_2 \quad (5)$$

$^{125}Te\{^1H\}$ and $^{13}C\{^1H\}$ NMR spectra at room temperature of a dichloromethane solution initially containing an equimolar ratio of Ph_2TeCl_2 and KEtxan show the presence of $Ph_2Te(Cl)(Etxan)$, Ph_2Te, $(Etxan)_2$, and unreacted Ph_2TeCl_2. The proportion of each compound varies slowly with time. After several hours, $^{13}C\{H\}$ data indicate that all the xanthate ion has been converted to dixanthogen, $(Etxan)_2$. A $^{125}Te\{^1H\}$ spectrum after several hours shows the mixture to consist of Ph_2TeCl_2 and Ph_2Te in about equal proportions. These observations are explained by the existence of three reactions (eqs 6–8) where eq 6 is an exchange reaction and eq 7 and 8 involve the reduction of tellurium(IV) to tellurium(II) and oxidation of the ligand to dixanthogen $(Etxan)_2$. However, the redox reaction associated with $Ph_2Te(Cl)(Etxan)$ is much slower than that for $Ph_2Te(Exan)_2$, indicating that $Ph_2Te(Cl)(Etxan)$ is the

$$Ph_2TeCl_2 + KEtxan \rightarrow Ph_2Te(Cl)(Etxan) + KCl \quad (6a)$$

$$Ph_2Te(Cl)(Etxan) + KEtxan \rightarrow Ph_2Te(Etxan)_2 + KCl \quad (6b)$$

$$Ph_2Te(Etxan)_2 \rightarrow Ph_2Te + (Etxan)_2 \quad (7)$$

$$2Ph_2Te(Cl)Etxan \rightarrow Ph_2TeCl_2 + Ph_2Te + (Etxan)_2 \quad (8)$$

more stable species. The analogue of eq 8 could also apply to the Et_2dtp and Et_2dtp systems but was not specifically identified. The rate of decomposition with Etxan as the ligand is much faster than for the other dithiolate complexes examined.

The same experiment carried out in dimethylformamide solution at room-temperature indicates that Ph_2Te is the only tellurium species in solution, which implies that tellurium reduction reactions are faster in this solvent at room temperature. However, when the experiment was repeated with the reactants added to a solution of dimethylformamide maintained at −40 °C, the $^{125}Te\{^1H\}$ spectrum shows resonances arising from Ph_2TeCl_2, $Ph_2Te(Cl)(Etxan)$, $Ph_2Te(Etxan)_2$, and Ph_2Te. The latter species is present only in a small amount while the resonances of the other three species have an intensity ratio which approximates 1:2:1. In contrast, the same experiment in tetrahydrofuran solution at −40 °C shows only three species, $Ph_2Te(Etxan)_2$, Ph_2TeCl_2, and $Ph_2Te(Cl)(Etxan)$, and the reduced species Ph_2Te is not observed.

When Ph_2TeCl_2 is reacted with 2 mol equiv of KEtxan in dichloromethane at room temperature, the only species observed in the $^{125}Te\{^1H\}$ spectrum is Ph_2Te. The same reaction at −40 °C gives predominantly $Ph_2Te(Etxan)_2$, with only a small amount of $Ph_2Te(Cl)(Etxan)$ being present, indicating that the reaction had not gone to completion at this lower temperature at the time when the NMR spectrum was measured. Replacing dichloromethane by toluene as solvent, results in the formation of only $Ph_2Te(Etxan)_2$ whereas in dimethylformamide solvent at −40 °C the product is mostly $Ph_2Te(Etxan)_2$ with some Ph_2Te also being evident. The dimethylformamide solution, reexamined after several days, shows Ph_2Te as the only tellurium-containing species in solution.

In summary, the complexes $Ph_2Te(S{-}S)_2$ appear unstable in solution with respect to spontaneous formation of reduced Ph_2Te and oxidized $(S{-}S)_2$ as in eq 9. The rate

$$Ph_2Te(S{-}S)_2 \rightarrow Ph_2Te + (S{-}S)_2 \qquad (9)$$

of formation of Ph_2Te is dependent on the solvent in a complex manner and on temperature with $Ph_2Te(S{-}S)_2$ being moderately stable at low temperatures. The rates of this redox reactions also are dependent on the nature of the dithiolate ligand, with the rate increasing in the order Etxan > Et_2dtp > Et_2dtc. Interestingly, for all dithiolate ligands the mixed-ligand species $Ph_2Te(Cl)(S{-}S)$ appears to be much more stable with respect to the redox decomposition pathway than $Ph_2Te(S{-}S)_2$.

NMR Study of Mixtures of $Ph_2Te(S{-}S)_2$ Complexes. Experiments with mixtures of the dithiolate complexes were carried out in tetrahydrofuran solution.

The $^{125}Te\{^1H\}$ spectrum (Figure 1) of an equimolar mixture of $Ph_2Te(Et_2dtc)_2$ and $Ph_2Te(Et_2dtp)_2$, in tetrahydrofuran at −40 °C consists of three resonances of approximate relative intensity 1.2:1.9:1.0 [$\delta(^{125}Te) = -951$, -1006 (d), $^2J_{Te-P} = 29$ Hz, -1037 ppm] which are assigned as due to $Ph_2Te(Et_2dtp)_2$, $Ph_2Te(Et_2dtc)(Et_2dtp)$, and $Ph_2Te(Et_2dtc)_2$, respectively. The assignment is confirmed by the $^{31}P\{^1H\}$ spectrum in which two resonances are observed, one at 92.83 ppm due to $Ph_2Te(Et_2dtp)_2$ and the other at 96.76 ppm, attributed to $Ph_2Te(Et_2dtc)(Et_2dtp)$. This result shows that intermolecular exchange of dithiolate ligands is rapid on the preparative time scale but slow on the NMR time scale at −40 °C.

The $^{125}Te\{^1H\}$ spectrum at −40 °C of a tetrahydrofuran solution containing an equimolar ratio of $Ph_2Te(Etxan)_2$ and $Ph_2Te(Et_2dtc)_2$ indicates the presence of the starting materials and only a small amount of the mixed-ligand complex $Ph_2Te(Et_2dtc)(Etxan)$. Raising the temperature leads to formation of substantial quantities of Ph_2Te and the disappearance of $Ph_2Te(Et_2dtc)(Etxan)$.

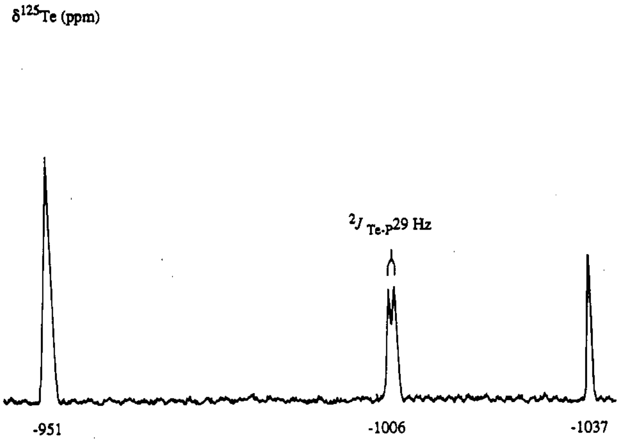


Figure 1. $^{125}Te\{^1H\}$ spectrum for an equimolar mixture of $Ph_2Te(Et_2dtc)_2$ and $Ph_2Te(Et_2dtp)_2$ in tetrahydrofuran solution.

Finally, the $^{125}Te\{^1H\}$ spectrum of an equimolar solution of $Ph_2Te(Etxan)_2$ and $Ph_2Te(Et_2dtp)_2$ in tetrahydrofuran solution shows only the unreacted starting materials at −40 °C. Raising the temperature leads to formation of substantial quantities of Ph_2Te without any evidence for the formation of the mixed ligand species $Ph_2Te(Etxan)(Et_2dtp)$. These results suggest that while the order of reactivity for the redox-based decomposition reaction is Etxan > Et_2dtp > Et_2dtc, the reverse order applies for the exchange reactions.

NMR Study of the Reaction of C_8H_8Te with $(Et_2dtc)_2$, $(Et_2dtp)_2$, and $(Etxan)_2$. In contrast to the $Ph_2Te(S{-}S)_2$ series, the series $C_8H_8Te(S{-}S)_2$ appears to be stable in solution. In fact, the compound C_8H_8Te reacts with each of the oxidized forms of the ligand, $(Et_2dtc)_2$, $(Et_2dtp)_2$, and $(Etxan)_2$ (generally referred to as $(S{-}S)_2$) in dichloromethane solution to give the corresponding Te(IV) complex $C_8H_8Te(S{-}S)_2$ as in eq 10. For $(Et_2dtc)_2$

$$C_8H_8Te + (S{-}S)_2 \rightarrow C_8H_8Te(S{-}S)_2 \qquad (10)$$

and $(Et_2dtp)_2$, the reaction is rapid and essentially quantitative in favor of formation of the Te(IV) complex. However for $(Etxan)_2$, the ^{125}Te spectrum shows only formation of approximately 15% of the Te(IV) complex 1 h after mixing the components. No change in product ratio was observed when the spectrum was recorded 7 days later. This result again shows that the Te(II) oxidation state is more favored when xanthate is the ligand than is the case with the other dithiolate ligands examined.

The solid-state structures of $C_8H_8Te(S{-}S)_2$, $Ph_2Te(Et_2dtp)_2$, and $Ph_2Te(Et_2dtc)_2$ have been determined[5,6] and while they show differing degrees of secondary bonding (i.e. bonds which are longer than the sum of the covalent radii but shorter than the sum of the van der Waals radii of the appropriate atoms) involving the tellurium atom, there appears to be no structural feature which accounts for the redox-based instability of $Ph_2Te(S{-}S)_2$ compounds relative to the compounds $C_8H_8Te(S{-}S)_2$.

(B) Electrochemical Investigations. Electrochemical Studies on C_8H_8Te at Platinum and Mercury Electrodes. The NMR studies described above demonstrate that redox reactions between organometallic tellurium compounds in oxidation states II and IV and dithiolate ligands in reduced and oxidized forms are interrelated. Additionally, the complexes are able to participate in ligand exchange reactions indicating that they are labile on the synthetic time scale. Electrochemical studies at platinum and mercury electrodes were undertaken to ascertain what information relevant to the redox processes and exchange reactions could be obtained by this technique. Unfortunately, the complete irreversibility of all processes at a chemically inert platinum electrode meant that no thermodynamic information could be gained on the redox reactions associated with Te(IV)/Te(II) chemistry. However, confirmation of the importance of exchange reactions associated with the lability of the complexes, as deduced from the NMR measurements, was confirmed by electrochemistry at mercury electrodes, where electrode mercury facilitates exchange processes and on some occasions permits the formation of new classes of mercury–tellurium complexes. Thus while the electrochemical studies are not inherently informative in the thermodynamic sense, they have provided a considerable contribution to the chemistry of the systems and results therefore are presented with particular emphasis on the comparison of data obtained at platinum and mercury electrodes which emphasize the importance of the exchange processes.

An examination of the electrochemistry of C_8H_8Te was undertaken to complement the data available on Ph_2Te[8-11] and in an endeavor to ascertain whether oxidation state IV is more readily achieved with C_8H_8Te as might be implied by the NMR data. Studies on dichloromethane solutions of C_8H_8Te at both platinum and mercury electrodes show that the compound is not reducible in the available potential range (approximately −2 V vs Ag/AgCl). This is consistent with data available for Ph_2Te at platinum electrodes in the same solvent.[11] This class of compound therefore appears to be very difficult to reduce.

At positive potentials, with a platinum electrode, an irreversible oxidation response for C_8H_8Te was recorded in dichloromethane (0.1 M Bu_4NClO_4) which had an oxidation peak potential, E_p^{ox}, of 1.02 V vs Ag/AgCl at a scan rate of 200 mV s^{-1}. A peak for reduction of a product resulting from the oxidation process was observed on the reverse scan (E_p^{red} = 0.34 V vs Ag/AgCl) under conditions of cyclic voltammetry. Oxidative controlled potential electrolysis was carried out at 1.1 V vs Ag/AgCl with a platinum gauze electrode and the charge transferred was 2.0 ± 0.2 faraday mol^{-1}, the solution becoming cloudy due to the formation of a white precipitate. These results are similar to those reported for Ph_2Te under the same conditions[9] where $Ph_2Te(ClO_4)_2$ is postulated to have been formed and the white product is therefore formulated by analogy to be $C_8H_8Te(ClO_4)_2$. However, this product has not been characterized in any definitive manner. The oxidation process at platinum electrodes can therefore be written as

$$C_8H_8Te + 2ClO_4^- \rightarrow C_8H_8Te(ClO_4)_2 + 2e^- \qquad (11)$$

where the perchlorate anion is provided by the electrolyte. Unfortunately, the irreversibility of the oxidation processes at platinum electrodes precludes thermodynamic data from being obtained which may have explained the greater stability in oxidation state IV of $C_8H_8Te(S\text{–}S)_2$ complexes relative to $Ph_2Te(S\text{–}S)_2$ complexes.

At mercury electrodes, entirely different behavior for C_8H_8Te was observed relative to the case at a platinum electrode. The dc polarogram (Figure 2a) shows two well-defined oxidation processes characterized by half-wave potentials $E_{1/2}(1)$ = 0.26 V vs Ag/AgCl and $E_{1/2}(2)$ = 0.61 V vs Ag/AgCl. The ratio of the limiting currents for the two processes is 2:1. Each process exhibits a high degree of chemical reversibility, as evidenced by the nature of the cyclic voltammogram recorded in the same potential region as the DC polarogram (Figure 2b). Oxidative controlled potential electrolysis using a mercury pool working electrode, with the potential set between the two processes at 0.4 V vs Ag/AgCl resulted in the transfer of 0.65 ± 0.05 faraday mol^{-1} (two electrons per three molecules) and voltammetric responses for the resulting oxidized solution are shown in Figure 3. The dc polarogram in Figure 3a shows that both waves are still present after oxidative electrolysis and the limiting currents (apart from a change in sign) are similar to those recorded before electrolysis. The response for the supporting electrolyte in the solvent alone is also shown and now passes midway between the two waves confirming that the current for the first process is now reductive rather than oxidative as was the case prior to electrolysis. Thus, as suggested by the chemical reversibility of the cyclic voltammetry (Figure 2b), the product of the first oxidation process at mercury electrodes is a stable species.

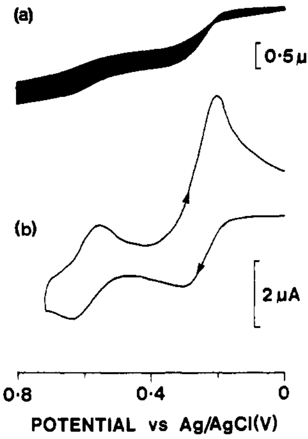


Figure 2. Oxidation responses observed at 20 °C in dichloromethane (0.1 M Bu_4NClO_4) at the dropping mercury electrode in the presence of 5 × 10^{-4} M C_8H_8Te: (a) dc polarogram, drop time = 0.5 s; (b) cyclic voltammogram, scan rate = 500 mV s^{-1}.

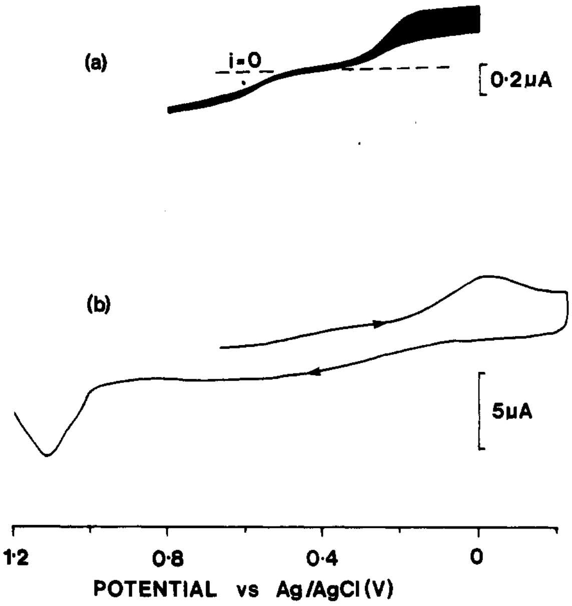


Figure 3. Voltammetry of 5 × 10^{-4} M C_8H_8Te at 20 °C after oxidative electrolysis (0.67 e, mercury electrode) in dichloromethane (0.1 M Bu_4NClO_4): (a) dc polarogram, drop time = 0.5 s; (b) cyclic voltammogram, platinum electrode, scan rate = 500 mV s^{-1}.

More information on the product of the oxidative process was obtained by examining the voltammetric behavior at a platinum electrode on the solution previously electrolyzed at the mercury pool electrode. A cyclic voltammogram is shown in Figure 3b and single reduction peak is noted at 0.02 V vs Ag/AgCl, with a sharp oxidation or stripping peak on the reverse scan at 1.1 V vs Ag/AgCl. The latter process is due to the oxidation of elemental mercury deposited on the platinum electrode[12] and demonstrates that mercury has been incorporated into the tellurium complex during the oxidation of the mercury pool electrode.

Quantification of the mercury present in the newly formed product was possible by carrying out quantitative reductive controlled potential electrolysis (platinum gauze working electrode, −0.2 V vs Ag/AgCl) on a solution of the product from oxidative electrolysis at a mercury pool electrode. The mercury that was plated onto the platinum working electrode was analyzed gravimetrically with the weight corresponding to formation of 1 mol of mercury per mole of starting material. The charge transferred was close to 0.67 faraday mol^{-1}, and the resulting solution contained only C_8H_8Te at the original concentration present prior to electrolysis, as verified by polarographic analysis. The results were consistent with the initial oxidation step at mercury electrodes corresponding to eq 12. That is, unlike

$$3C_8H_8Te + Hg \rightleftharpoons [(C_8H_8Te)_3Hg]^{2+} + 2e^- \quad (12)$$

the situation at a platinum electrode where Te(II) → Te(IV), it is electrode mercury and not the compound which has been oxidized and the product (formulated empirically as $[(C_8H_8Te)_3Hg]^{2+}$) is stable. The reverse reaction to that in eq 12 may be accomplished readily at either a mercury or a platinum electrode. The same species (electrochemical evidence) can be produced by reaction of C_8H_8Te with mercury(I) perchlorate, $Hg_2(ClO_4)_2$, in dichloromethane according to the reaction given in eq 13.

$$Hg_2^{2+} + 3C_8H_8Te \rightarrow [(C_8H_8Te)_3Hg]^{2+} + Hg \quad (13)$$

The second oxidation process observed at mercury electrodes ($E_{1/2}$ = 0.61 V vs Ag/AgCl) in the presence of C_8H_8Te also was investigated by oxidative controlled potential electrolysis at a mercury pool electrode. The transfer of 1.1 ± 0.1 faraday mol^{-1} of C_8H_8Te was noted. The product was not sufficiently soluble in dichloromethane for characterization by voltammetric techniques although it is almost certainly a mercury-rich cationic complex formed according to an equation of the kind

$$2C_8H_8Te + 2Hg \rightleftharpoons [(C_8H_8Te)_2Hg_2]^{2+} + 2e^- \quad (14)$$

That is, the summation of the two oxidation processes for C_8H_8Te in the presence of mercury leads to the overall transfer of one electron per molecule via formation of a stable intermediate species which also contains both mercury and tellurium. The data at mercury electrodes do not provide any relevant thermodynamic information concerning the Te(II)/Te(IV) oxidation states, but demonstrate the lability with respect to exchange reactions.

Reduction Processes for $Ar_2Te(S-S)_2$. (a) Platinum Electrodes. Figure 4 shows the cyclic voltammetric responses at a platinum electrode for reduction of $C_8H_8Te(Et_2dtc)_2$ (Figure 4a) and $C_8H_8Te(Et_2dtp)_2$ (Figure 4b) in dichloromethane. For the dithiocarbamate compound, an irreversible and complex process is observed at around −1.8 V vs Ag/AgCl which is just prior to the solvent reduction. On the reverse (oxidative) scan, an oxidation peak is observed at 0.08 V vs Ag/AgCl which corresponds to the oxidation of free diethyldithiocarbamate released during the course of the reduction process. Similarly, after reduction of $C_8H_8Te(Et_2dtp)_2$ at −1.5 V vs Ag/AgCl (Figure 4b) an oxidation peak at 0.42 V vs Ag/AgCl (inset) due to free ligand is also observed on the reverse scan. However, in this case, the reduction peak is well-resolved from the solvent reduction region, allowing controlled potential electrolysis experiments to be carried out with some precision. With the potential set at −1.6 V vs Ag/AgCl the charge passed was close to 2 faraday mol^{-1} and the resulting solution contained C_8H_8Te and diethyl dithiophosphate. Both were identified electrochemically at the concentrations corresponding to complete reduction of the starting material.

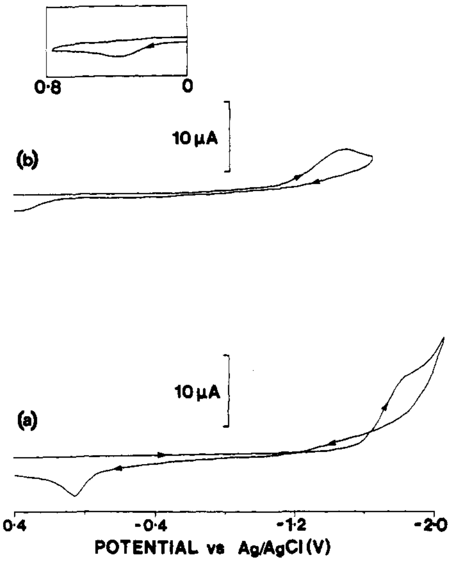


Figure 4. Reductive cyclic voltammograms at a platinum electrode for 5 × 10^{-4} M solutions of (a) $C_8H_8Te(Et_2dtc)_2$ and (b) $C_8H_8Te(Et_2dtp)_2$ in dichloromethane (0.1 M Bu_4NClO_4), scan rate = 500 mV s^{-1}, T = 20 °C. Inset shows the continuation of the scan for b, under the same conditions.

For $C_8H_8Te(Etxan)_2$ no clearly defined reduction peak was seen on scanning the platinum electrode in the negative direction up to potentials corresponding to the solvent reduction. Rather a broad ill-defined process is observed. However, again an oxidation peak for free xanthate ligand was observed on the reverse positive direction scan indicating an analogous mechanism also applies for this complex. Thus the reduction process for all complexes can be written as in eq 15. Analogous results were obtained

$$C_8H_8Te(S-S)_2 + 2e^- \rightarrow C_8H_8Te + 2(S-S)^- \quad (15)$$

for $Ph_2Te(Et_2dtc)_2$. The other $Ph_2Te(S-S)_2$ complexes were too unstable to study since decomposition to Ph_2Te and $(S-S)_2$ occurs prior to commencement of voltammetric studies. Thus at an inert electrode material such as platinum, the reduction of $Ar_2Te(S-S)_2$ (Ar_2 = diaryl, Ph_2, C_8H_8) to the diaryl telluride is an unfavorable process as indicated by the very negative potentials required to achieve reduction. Again, unfortunately, the completely irreversible nature of the processes does not permit thermodynamic understanding of the Te(IV)/Te(II) redox reactions to be achieved.

(b) Mercury Electrodes. Figure 5 shows dc polarograms for reduction of each of the $C_8H_8Te(S-S)_2$ complexes in dichloromethane solutions alongside dc polarograms for the reduction of the corresponding mercury(II) complexes, $Hg(S-S)_2$. The reduction potential for $C_8H_8Te(S-S)_2$ at a mercury electrode is vastly less negative than at a platinum electrode and is similar to that for $Hg(S-S)_2$. The similarity between the $C_8H_8Te(S-S)_2$ and $Hg(S-S)_2$ responses are evidenced by a comparison of the reduction potentials obtained from the differential pulse polarographic technique (Table II). In each case, the dc limiting currents per unit concentration also were similar for the mercury and tellurium complexes. However, for the di-

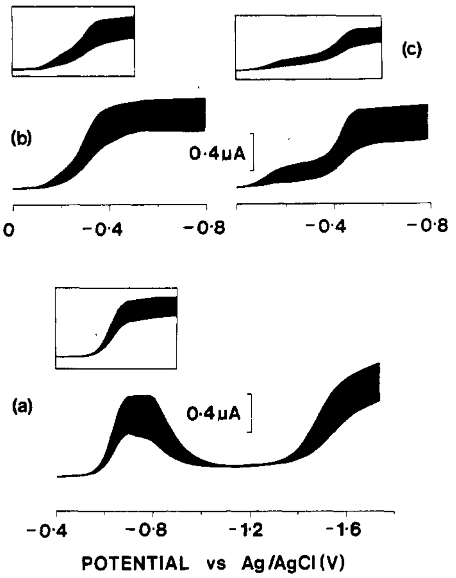


Figure 5. Reductive dc polarograms, drop time 0.5 s, T = 20 °C for 5 × 10^{-4} M $C_8H_8Te(S\text{–}S)_2$ in dichloromethane (0.1 M Bu_4NClO_4), (S–S) = (a) Et_2dtc, (b) Et_2dtp, and (c) Etxan. Insets are for the respective $Hg(S\text{–}S)_2$ complexes.

thiocarbamate compounds (Figure 5a) an obvious difference exists since the response for $C_8H_8Te(Et_2dtc)_2$ features a pronounced current minimum in the limiting current region which is absent with $Hg(Et_2dtc)_2$. This current minimum disappears prior to the onset of the solvent reduction process and is very similar to that reported for reduction of $Te(Et_2dtc)_4$ under the same conditions.[3] The reduction processes for both the tellurium and mercury complexes was shown to be chemically reversible by cyclic voltammetry at a mercury electrode.

The dc polarographic responses for $Hg(Et_2dtp)_2$ (Figure 5b) and $Hg(Etxan)_2$ (Figure 5c) both consist of two waves, the ratio of currents being approximately 1:2. These results are similar to those for the free ligands, Et_2dtp[13] and Etxan[14] reported in acetone (0.1 M Et_4NClO_4). Thus the polarographic behavior of $Hg(Et_2dtp)_2$ and $Hg(Etxan)_2$ complexes is apparently unaffected by changing the solvent from acetone to dichloromethane and the mechanism for reduction that was elucidated earlier[13,14] is applicable.

$$3Hg(S\text{–}S)_2 + 2e^- \rightleftharpoons Hg + 2[Hg(S\text{–}S)_3]^- \quad (16a)$$

$$2[Hg(S\text{–}S)_3]^- + 4e^- \rightleftharpoons 2Hg + 6(S\text{–}S)^- \quad (16b)$$

$$[(S\text{–}S)]^- = [Et_2dtp]^-, [Etxan]^-$$

with the overall response being

$$Hg(S\text{–}S)_2 + 2e^- \rightleftharpoons Hg + 2(S\text{–}S)^- \quad (16c)$$

which is also the case with the single step response for reduction of $Hg(Et_2dtc)_2$.

All results on the tellurium complexes suggest that exchange reactions with electrode mercury determine the course of the polarographic reduction, although the overall reduction process is apparently still the same as at a platinum electrode. Equation 17 summarizes the reduction processes.

$$C_8H_8tTe(S\text{–}S)_2 + Hg \rightleftharpoons C_8H_8Te + Hg(S\text{–}S)_2 \quad (17a)$$

$$Hg(S\text{–}S)_2 + 2e^- \rightleftharpoons Hg + 2(S\text{–}S)^- \quad (17b)$$

overall

$$C_8H_8Te(S\text{–}S)_2 + 2e^- \rightleftharpoons C_8H_8Te + 2(S\text{–}S)^- \quad (17c)$$

$$S\text{–}S = Et_2dtc, Et_2dtp, Etxan$$

Table II. Differential Pulse Polarographic Data[a] for $Ar_2Te(S\text{–}S)_2$, $Hg(S\text{–}S)_2$, and C_8H_8Te in Dichloromethane (0.1 M Bu_4NClO_4) at 20 °C

compound $Ar_2Te(S\text{–}S)_2$		peak potential			
Ar	(S–S)	E_p^{ox}, V[b]		E_p^{red}, V[b]	
C_8H_8	Et_2dtc	*c*	0.64	-0.63	
C_8H_8	Etxan	0.25	0.68	-0.12	-0.43
C_8H_8	Et_2dtp	0.23	0.67	-0.05	-0.21
Ph_2	Et_2dtc	0.44	0.65	-0.63	
Ph_2	Etxan	0.57	*d*		-0.47
Ph_2	Et_2dtp	0.59	0.74		-0.23
$[Hg(S\text{–}S)_2]$	Et_2dtc	0.45	0.63	-0.63	
	Etxan	0.65	0.72	-0.13	-0.42
	Et_2dtp		0.66	-0.07	-0.20
C_8H_8Te		0.26	0.62	*e*	*e*

[a] Dropping mercury electrode, drop time = 0.5 s, pulse amplitude = ±50 mV. [b] Potential vs Ag/AgCl (saturated LiCl in ethanol). [c] Very broad process over the range 0.2 to 0.5 V. [d] Small peak is also present which is unresolved from the major process. [e] Not reduced up to solvent limit of approximately -2.0 V vs Ag/AgCl.

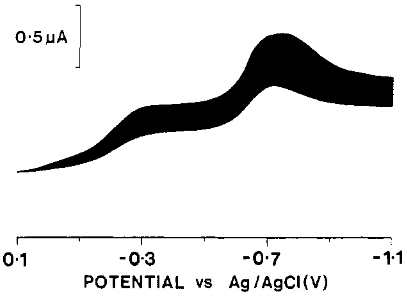


Figure 6. Reductive dc polarogram, drop time = 0.5 s, T = 20 °C for a mixture of 5 × 10^{-4} M $C_8H_8Te(Et_2dtp)_2$ and 5 × 10^{-4} M $Hg(Et_2dtc)_2$ in dichloromethane (0.1 M Bu_4NClO_4).

Consequently, exchange reactions can be said to catalyze the reduction process at mercury electrodes.

Evidence for eq 17a was obtained by storing $C_8H_8Te(Et_2dtc)_2$ over a mercury pool at open circuit for several days. ^{125}Te and ^{199}Hg spectra of this solution indicate that complete conversion took place to form C_8H_8Te and $Hg(Et_2dtc)_2$. The latter was also distinguished electrochemically from the other possible product, $(Et_2dtc)_2$, by its characteristic voltammetric behavior at platinum electrodes.[12]

The overall process in eq 17c was confirmed by carrying out reductive controlled potential electrolysis in the limiting current region for $C_8H_8Te(S\text{–}S)_2$ ($[S\text{–}S]^- = [Et_2dtp]^-$ and $[Et_2dtc]^-$) at a mercury pool electrode. This meant that for $C_8H_8Te(Et_2dtc)_2$, the potential was set at −0.7 V vs Ag/AgCl, i.e. prior to the current suppression region. In both cases the passage of 2.0 ± 0.1 faraday mol^{-1} of complex was noted. The reduced solutions contained the free ligand, which in the case of dithiophosphate was stable in dichloromethane, allowing comparison with a standard solution of an authentic sample. This experiment showed that all the ligand had been released from the complex. The presence of C_8H_8Te was detected electrochemically according to the behavior already described.

The observation of rapid exchange between these aryltellurium compounds and electrode mercury suggested further investigation of exchange processes should be undertaken by voltammetric monitoring. Figure 6 shows the dc polarogram for an equimolar mixture of $C_8H_8Te(Et_2dtp)_2$ and $Hg(Et_2dtc)_2$. The responses for the individual compounds are shown in Figure 5. In Figure 6, three waves are observed with the first two (at less negative potentials) due to a compound of dithiophosphate. The

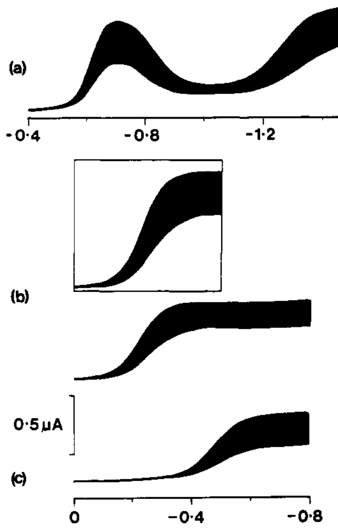


Figure 7. Reductive dc polarograms, drop time = 0.5 s, T = 20 °C for 5 × 10^{-4} M $Ph_2Te(S\text{-}S)_2$ in dichloromethane (0.1 M Bu_4NClO_4), S–S = (a) Et_2dtc, (b) Et_2dtp (inset shows response for $(Et_2dtp)_2$) and (c) Etxan, 20 °C. Upper voltage scale applies to Figure 7a. Lower voltage scale applies to Figure 7, parts b and c.

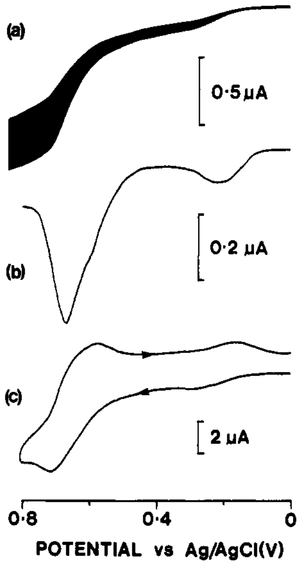


Figure 8. Oxidation responses observed at 20 °C in dichloromethane (0.1 M Bu_4NClO_4) at the dropping mercury electrode in the presence of 5 × 10^{-4} M $C_8H_8Te(Et_2dtp)_2$: (a) dc polarogram, drop time = 0.5 s, (b) differential pulse polarogram, pulse amplitude = 50 mV, and (c) cyclic voltammogram, scan rate = 500 mV s^{-1}.

third wave, at −0.62 V vs Ag/AgCl, corresponds to a dithiocarbamate species and features a minimum in the limiting current region similar to that in Figure 5a for $C_8H_8Te(Et_2dtc)_2$. This observation is taken to be evidence for the presence of the latter in the bulk solution since this electrochemical phenomenon appears to be characteristic of tellurium(IV) dithiocarbamate species. Intermolecular dithiolate ligand exchange reactions between two different $C_8H_8Te(R_2dtc)_2$ compounds have been demonstrated to occur in dichloromethane solution by NMR techniques.[5] Thus exchange processes are also indicated to occur between these compounds and mercury complexes. It was found that any combination of aryltellurium compound and mercury complex, with different sulfur ligands, provided electrochemical evidence of exchange reactions which are represented as in eq 18.

$$C_8H_8Te(S\text{-}S)_2 + Hg(S'\text{-}S')_2 \rightleftharpoons C_8H_8Te(S'\text{-}S')_2 + Hg(S\text{-}S)_2 \quad (18)$$

Figure 7 shows a reductive dc polarogram for each of the three $Ph_2Te(S\text{-}S)_2$ species. The response for reduction of the dithiocarbamate complex (Figure 7a) bears a close resemblance to that for $C_8H_8Te(Et_2dtc)_2$ (Figure 5a) and the $E_{1/2}$ value coincides with that for reduction of $Hg(Et_2dtc)_2$. In contrast $Ph_2Te(Etxan)_2$ and $Ph_2Te(Et_2dtp)_2$ do not follow parallel pathways to that for $Ph_2Te(Et_2dtc)_2$. This observation is consistent with the fact that both $Ph_2Te(Etxan)_2$ and $Ph_2Te(Et_2dtp)_2$ are less stable and undergo the redox reaction described in the NMR section to form Ph_2Te and the disulfides, the dixanthogen $(Etxan)_2$, and the bis(phosphorodithioate) $(Et_2dtp)_2$, respectively, prior to obtaining electrochemical data. A reductive dc polarogram for the latter species is shown in the inset of Figure 6b and the response consists of a single wave at $E_{1/2}$ = −0.23 V vs Ag/AgCl. The limiting current per unit concentration is the same as that observed for solutions of $Ph_2Te(Et_2dtp)_2$, indicating that the internal redox reaction has occurred. Thus, the reduction responses for solutions of $Ph_2Te(Etxan)_2$ and $Ph_2Te(Et_2dtp)_2$ are due to reduction of the respective disulfides which, in both cases, occur in the same potential region as the reductive processes for the corresponding mercury(II) complex.

Since $Ph_2Te(Et_2dtc)_2$ remains intact in solution (according to the known time scale for the internal redox reaction in dichloromethane, see above) the reduction process parallels eq 17. However, for the xanthate and dithiophosphate analogues, the internal redox reactions are extensive and eq 19 best describes the observed behavior. Due to their instability in solution, the electrochemistry of the xanthate and dithiophosphate complexes was not studied further. The peak potentials obtained under conditions of differential pulse polarography for all the polarographic reduction processes are given in Table II.

$$Ph_2Te(S\text{-}S)_2 \rightarrow Ph_2Te + (S\text{-}S)_2 \quad (19a)$$

$$(S\text{-}S)_2 + 2e^- \rightarrow 2(S\text{-}S)^- \quad (19b)$$

Oxidation Processes Associated with $Ar_2Te(S\text{-}S)_2$. (a) Platinum Electrodes. Oxidation responses for $Ar_2Te(S\text{-}S)_2$ complexes at platinum electrodes were observed at very positive potentials but are ill-defined. The responses are believed to be ligand based, but products have not been identified. No further studies were undertaken on the oxidation processes at platinum electrodes.

(b) Mercury Electrodes. In contrast to data obtained at platinum electrodes, the electrochemical oxidation responses observed in the presence of $C_8H_8Te(Et_2dtp)_2$ at a dropping mercury electrode are extremely well defined as shown in Figure 8. The DC polarogram (Figure 8a) and differential pulse polarogram (Figure 8b) show two major processes with $E_{1/2}$ values of 0.23 and 0.67 V vs Ag/AgCl with the latter process having the larger limiting current. Figure 8c shows the cyclic voltammogram and chemical reversibility is noted for each process. Comparison with polarograms in Figure 2 for C_8H_8Te under the same conditions, shows that the first oxidation process occurs at a similar potential in both cases.

Oxidative controlled potential electrolysis at a mercury pool electrode with the potential set at 0.4 V vs Ag/AgCl resulted in the transfer of 0.66 ± 0.05 faraday mol^{-1}. The dc polarogram for the resulting solution is shown in Figure 9a and the response for the solvent-supporing electrolyte (current zero) passes midway between the two processes.

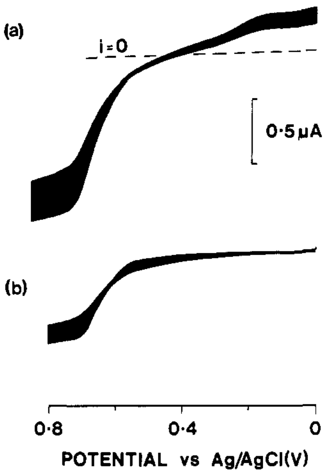


Figure 9. Dc polarograms, drop time = 0.5 s: (a) after electrolysis of a mercury electrode in the presence of 5 × 10^{-4} M $C_8H_8Te(Et_2dtp)_2$ (0.67e, mercury electrode) and (b) 2.5 × 10^{-4} M $Hg(Et_2dtp)_2$ in dichloromethane (0.1 M Bu_4NClO_4), 20 °C.

Further voltammetric studies at a platinum electrode demonstrate the presence of $[(C_8H_8Te)_3Hg]^{2+}$, which is also the product of oxidative electrolysis at mercury electrodes in the presence of C_8H_8Te (see above). The other species present in solution is $Hg(Et_2dtp)_2$ as shown by comparison with Figure 9b which is the oxidative dc polarogram for a dichloromethane solution in the presence of an authentic sample of this compound. The slight difference in the oxidation waves of the two compounds at around 0.67 V vs Ag/AgCl is attributable to the presence of the overlapping additional response for $[(C_8H_8Te)_3Hg]^{2+}$ (Figure 9a). The presence of the mercury complex in the solution after bulk electrolysis was established unambiguously by cyclic voltammetry at a platinum electrode. As is the case with $Hg(Et_2dtc)_2$ complexes, $Hg(Et_2dtp)_2$ is reducible at the platinum electrode giving rise to the characteristic oxidation peak for stripping of elemental mercury on the reverse or oxidative scan of cyclic voltammograms.

The data for the oxidation processes have some parallels with those from the reduction study. That is, the $C_8H_8Te(S\text{-}S)_2$ complexes readily exchange the dithiolate ligand with the mercury electrode to form two very stable species (eq 20). If the potential chosen for bulk oxidative electrolysis at a mercury pool electrode is between the two oxidation processes, then the C_8H_8Te available at the electrode surface immediately undergoes an oxidation process according to eq 12.

$$C_8H_8Te(S\text{-}S)_2 + Hg \rightleftharpoons C_8H_8Te + Hg(S\text{-}S)_2 \quad (20)$$

Oxidative controlled potential electrolysis in the presence of $C_8H_8Te(Et_2dtp)_2$ was also carried out with the applied potential set at 0.8 V (limiting current region of the second process) at a mercury pool electrode. The quantity of charge passed was 2.35 ± 0.1 faraday mol^{-1} and a white precipitate was produced. The resulting solution displayed voltammetric behavior that is identical with a solution of $Hg(Et_2dtp)_2$ subjected to the same procedure. Thus, all the tellurium is removed from solution as a white precipitate previously postulated to be $C_8H_8Te(ClO_4)_2$ in accordance with the results obtained for C_8H_8Te under the same conditions (see above). The only species remaining in solution is the same as the product of the two-electron oxidation of the mercury electrode in the presence of $Hg(Et_2dtp)_2$ solution.

The dc polarograms for $C_8H_8Te(Etxan)_2$ and $C_8H_8Te(Et_2dtc)_2$ are shown in Figure 10 and the responses are similar to that for the dithiophosphate complex although they are not as well defined. Nevertheless, again the oxidation processes for the xanthate and dithiocarbamate complexes commence near to the potential for the mercury electrode oxidation process in the presence of C_8H_8Te. Conclusive evidence for the exchange process is supplied in Figure 10c which shows the oxidative dc polarogram for a solution containing an equimolar mixture of C_8H_8Te and $Hg(Et_2dtc)_2$. Comparison with Figure 10b shows both responses to be identical with respect to shape and potential confirming that eq 14 is generally applicable at positive as well as negative potentials at the electrode surface.

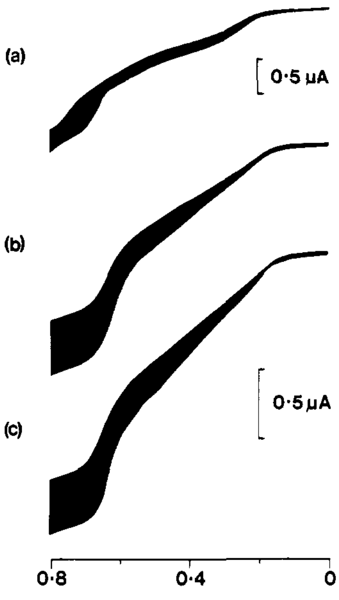


Figure 10. Oxidative dc polarograms, drop time = 0.5 s, T = 20 °C, in dichloromethane (0.1 M Bu_4NClO_4) in the presence of (a) 5 × 10^{-4} M $C_8H_8Te(Etxan)_2$, (b) 5 × 10^{-4} M $C_8H_8Te(Et_2dtc)_2$, and (c) a mixture of 5 × 10^{-4} M C_8H_8Te and 5 × 10^{-4} M $Hg(Et_2dtc)_2$.

Differential pulse polarographic data for the oxidation processes are collected in Table II.

Conclusions

NMR data show that in solution, $Ph_2Te(IV)(S\text{-}S)_2$ systems are far less stable with respect to formation of reduced $Ph_2Te(II)$ and oxidized ligand $(S\text{-}S)_2$ than are $C_8H_8Te(IV)(S\text{-}S)_2$ systems. Formation of Ph_2Te is dependent on both solvent and temperature. Low temperatures stabilize the tellurium(IV) complexes. The rate and possibly the equilibrium position of the redox reactions are solvent-dependent. However, the precise role of the solvent in mediating these internal redox-based processes remains unclear.

Perhaps the most interesting feature of the electrochemistry of these systems is the ease with which the dithiolate ligands are removed from the tellurium center in the presence of mercury. This reflects both the affinity of mercury for sulfur ligands and the stability of mercury–tellurium species and Ar_2Te complexes formed as a result of exchange and redox processes. The reactions at mercury electrodes are all rapid and give rise to well-defined, diffusion-controlled polarographic responses that are readily linked to corresponding processes observed for the mercury(II) chelates. The organotellurium moiety, C_8H_8Te, also shows characteristic polarographic behavior at mercury electrodes and a polarographic process involving oxidation of the mercury electrode leads to the formation of compounds containing both tellurium and mercury. The electrochemical behavior at platinum electrodes, in comparison to that at mercury electrodes, is not well-defined. In most cases, oxidation and reduction processes take place very irreversibly at platinum electrodes only under extreme conditions (potentials). The contrast in behavior at mercury and platinum electrodes is particularly obvious for reduction of $C_8H_8Te(S–S)_2$ complexes. The same products are formed at both electrode materials yet reduction occurs at much less negative potentials at the mercury electrode surface relative to a platinum electrode by approximately 1 V by virtue of catalytic pathways provided by the formation of easily reduced $Hg(S–S)_2$ complexes at the mercury electrode surface. Unfortunately, because of the complete irreversibility of the electrochemical processes at platinum electrodes, no data has been obtained to define the thermodynamics of the Te(IV)/Te(II) redox chemistry.

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Registry No. Ph_2TeCl_2, 1206-36-6; $Ph_2Te(Cl)(Et_2dtc)$, 72484-14-1; $Ph_2Te(Et_2dtc)_2$, 72546-43-1; $Ph_2Te(Cl)(Et_2dtp)$, 135074-29-2; $Ph_2Te(Et_2dtp)_2$, 106820-93-3; $Ph_2Te(Cl)(Etxan)$, 135074-30-5; $Ph_2Te(Etxan)_2$, 118108-53-5; $Ph_2Te(Et_2dtc)(Etxan)$, 135074-31-6; $Ph_2Te(Et_2dtc)(Et_2dtp)$, 135074-32-7; Ph_2Te, 1202-36-4; $C_8H_8Te(Et_2dtc)_2$, 135074-33-8; $C_8H_8Te(Etxan)_2$, 135074-34-9; $C_8H_8Te(Et_2dtp)_2$, 115481-98-6; $Hg(Et_2dtc)_2$, 14239-51-1; $Hg(Etxan)_2$, 29649-60-3; $Hg(Et_2dtp)_2$, 1446-05-5; C_8H_8Te, 56568-60-6; $NaEt_2dtc$, 148-18-5; KEt_2dtp, 3454-66-8; KEtxan, 140-89-6; ^{125}Te, 14390-73-9.