Cyclic Voltammetry Study And Electrochemical Synthesis Of Some Organotellurium Compounds

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Abstract: The electrochemical behavior of diphenyl ditelluride, bis(2-amino-5-methyl phenyl)ditelluride and bis(2-amino-5-bromo phenyl)ditelluride have been investigated by cyclic voltammetry(CV) in methanol or THF at room temperature. The results showed two single successive electron transfer through the reduction process. This technique was used to determine the best voltage regions in order to carry out the electrochemical synthesis of unsymmetrical organic telluride, i.e.: ethyl phenyl telluride (1), propyl phenyl telluride (2), butyl phenyl telluride (3), ethyl (2-amino-5-methyl phenyl)telluride (4), propyl(2-amino-5-methylphenyl)-telluride (5), butyl (2-amino-5-methylphenyl) telluride (6), ethyl(2-amino-5-bromophenyl) telluride (7), propyl(2-amino-5-bromo phenyl) telluride (8) and butyl(2-amino-5-bromophenyl) telluride (9). All new compounds were characterized by CHN and IR spectroscopy.

1 Introduction
The electrochemistry of tellurium and its compounds has been studied since the 1920s and various mechanisms for the reduction of Te IV to Te 0 have been given[1]. Such behavior is complicated due to several oxidation states of tellurium and its electrochemical reduction is a multielectronic process[2,3]. A comprehensive review on the oxidation and reduction processes of organic tellurium compounds, including many results of electrochemical investigations, was reviewed by Detty and Logan[4]. However, electrode syntheses of organoselenium and organotellurium compounds were not discussed there. A recent review by Jaworski[5] discussed the preparation of new organic selenium or tellurium compounds by anodic functionalization of already available chalcogen compounds and the electrochemical synthesis in which organic selenium compounds play only the role of intermediates or catalysts. Furthermore, Tellurium can be cathodically reduced in acid solution to give hydrogen telluride or in alkaline solution to give Te 2- and possibly Te 2- ions. Also, it can be oxidized anodically to give (TeO2) or telluric acid (H6TeO6)[6].

Various electrochemical techniques such as linear potential scan, cyclic-voltammetry and controlled potential coulometry for diorganyl tellurides, diorganyltellurium dichlorides and diperchlorates in methylene chloride or acetonitrile containing tetrabutyl ammonium perchlorates as supporting electrolyte indicated that dichloride and diperchlorate were electrochemically reduced to the corresponding diorganyltellurides[7]. Also, it was found that diphenyl ditelluride was electro-oxidized to PhTe(ClO4)3 in the presence of ClO4- ions, while (C6H5O)2TeTe(C6H5O) can be oxidized to (C6H5O)2Te(ClO4)2 and elemental Te[8]. Many phenyl chalcogen derivatives have been synthesized electrochemically by the reduction of o- and m- chlorobenzonitrile in the...
presence of an equivalent amount of phE - prepared initially by electrochemical reduction of PhEEPh (E= Te or Se) to form phenyl chalcogen benzonitriles\cite{9}.

Symmetrical aromatic ditellurides were prepared by electrochemical reduction of unsymmetrical organic telluride. As an example, dicyanodiphenyl ditelluoride has been prepared by anodic oxidation of cyanobenzene tellurate anion \cite{10}. The direct cathodic reduction of unactivated alkyl halide in acetonitrile in the presence of an equivalent of PhE leads to ArEPH\cite{11}. Diorganyl ditellurides and diorganyl diselenides were prepared electrochemically from a reaction of alkyl halide or aryl halide with elemental Se or Te, which were used as sacrificial cathodes \cite{12}.

Anodic oxidation of various types of organic tellurium compounds was carried out in the presence of fluoride ion, which gave the corresponding diorganyl tellurium difluorides (ArRTeF2) with a high selectivity \cite{13}.

In the present work, electrochemical behavior of diphenyl ditelluride, bis(2-amino-5-methyl phenyl)ditelluride and bis(2-amino-5-bromo phenyl) ditelluride will be investigated by cyclic voltammetry in methanol or THF. Attempts will be made to prepare some new unsymmetrical tellurides electrochemically.

2 Experimental

2.1 Chemicals and reagents

Diphenyl ditelluride\cite{14} ,bis(2-amino-5-methyl phenyl)ditelluride and bis (2-amino-5-bromo phenyl)ditelluride were prepared according to the literature methods \cite{15,16}.

Electrochemical Measurements

Cyclic voltammetry (C.V) was performed by varying the voltage linearly from an initial to a final potential values as required and then directly swept back at the same scan rate to the initial one .The cyclic measurements were supported by using the controlled potential three electrode cell. The species was reduced and oxidized by a reversible reaction.

The used cell was a Pyrex glass of 30 ml capacity equipped with four openings, three of which for working Platinum, secondary platinum, and Ag/AgCl as a reference electrodes. The fourth one is for nitrogen gas inlet. A potentiostate /bipotentiostate (DY 2300 series) supplied by the American company Digi-Ivy was used. All measurements were performed at room temperature.

The negative initial potential value was set mostly equal to final positive one. The scan rate (ν) was varied from 0.05 to 0.5 vs\(^{-1}\), while the voltage was scanned between -2 to 2V. The current response is plotted as a function of voltage rather than time. Molar concentration of supporting electrolyte (Bu4NBF4 ) was 0.2 M.

2.2 Electrosynthesis cell

The electrochemical cell used was a cylindrical shape made from Pyrex glass of capacity (100ml) surrounded by an internal condenser, equipped with nickel electrode as anode (0.7×15 cm\(^2\)) and carbon cathode (0.6×15 cm\(^2\)). The cell contained two holes for both inlet and outlet of nitrogen gas, which used as inert gas throughout the electrochemical synthesis.

2.3 Electrochemical Synthesis of Unsymmetrical Tellurides

2.4 Ethyl phenyl telluride C\(_8\)H\(_{10}\)Te (1)

A mixture of 0.2g (0.48 mmol) of diphenyl ditelluride and 0.1g (0.96 mmol) of ethyl bromide was added to a solution of 0.31g (0.96 mmol) of tetrabutyl ammonium tetrafluoroborate dissolved in 60 ml of methanol in electrochemical synthesis cell under dry nitrogen gas. Constant potential of 1.4V was applied. An initial current of 13.06 mA was recorded accompanied by a change in the solution color after 4 hours. The reaction was carried out for 24 h where the current dropped to 0.63 mA. The reaction mixture was poured into 300 ml of water and extracted with chloroform (6×20 ml). The organic layer was dried over MgSO\(_4\) and then filtered.

The product was recrystallized from absolute ethanol to give an orange solid of compound 1 in 91.9% yield. The following compounds were prepared by the same method.

Propyl phenyl telluride, C\(_9\)H\(_{12}\)Te (2) in 99.1% yield, Butyl phenyl telluride, C\(_{10}\)H\(_{14}\)Te (3) in 75.8% yield, Ethyl (2-amino-5-methyl phenyl) telluride, C\(_9\)H\(_{13}\)N\(_2\)Te (4) in 88.4% yield, Propyl (2-amino-5-methylphenyl) telluride, C\(_9\)H\(_{13}\)N\(_2\)Te (5). Yield: 41.61%, Butyl (2-amino-5-methylphenyl) telluride, C\(_{11}\)H\(_{17}\)N\(_2\)Te (6) in 40.5% yield, Ethyl (2-amino-5-bromo phenyl) telluride, C\(_9\)H\(_{13}\)Br\(_2\)Te (7) in 41.4% yield, Propyl (2-amino-5-bromophenyl) telluride, C\(_9\)H\(_{13}\)Br\(_2\)Te (8) in 95.71% yield and Butyl (2-amino-5-bromophenyl) telluride, C\(_{10}\)H\(_{15}\)Br\(_2\)Te (9) in 91.9% yield.

Table 4 presented the CHN, yields and physical properties of all prepared compounds \(i.e.\ 1-9\).
3 Results and discussion

The electrochemical behavior of compounds diaryl ditellurides (diphenyl ditelluride ((C₆H₅)₂Te₂)), bis(2-amino-5-methylphenyl) ditelluride ((2-NH₂-5-CH₃C₆H₃)₂Te₂) and bis(2-amino-5-bromophenyl)ditelluride ((2-NH₂-5-BrC₆H₃)₂Te₂) was established by CV for oxidation and reduction at platinum electrode in pure THF or methanol at different scan rates, (0.05-0.5 volt.sec⁻¹) in the presence of tetrabutylammonium tetrafloroborate as supporting electrolyte and alkyl halides (ethyl bromide, propyl bromide or butyl iodide) under specific potential values, Table 1. Fig. 1 shows clearly that there is no peaks at all when both solvent and supporting electrolyte system were used. The appearance of two reduction peaks were observed for the ditellurides, which can be attributed to two successive single electron transfer sequentially, Table 2, and all compounds showed the same behavior, Fig. 2. The first may be related to the cleavage of Te—Te bond giving both anion ArTe⁻ and free radical ArTe.. The second electron transfer may takes place directly through the free radical to form another anion ArTe⁻.

In fact the electron transfer process takes place in a limited standard time depending in that on rate which indicates logically the dependence of any electrochemical reaction on scan rate. Thus at fast scan rate an electron transfer occurs only while at slow scan rate a chemical reaction may follow the electron transfer.

The same behavior of these tellurides was detected with all three alkyl halides. In general, it was observed that two reduction peaks were gained in the presence of alkyl halides at different potential values. This figure shows the deviation of cathodic reduction potential values towards larger values upon increasing the scan rates together with clear shifts in current values.

According to Sevcik-Randles equation [17] which gives the relationship between peak current Ip, and the square root of scan rate ν¹/² the first and second reduction current functions, Fpred₁ and Fpred₂ can be calculated.

Table 1: Experimental values of potentials applied and resulting currents of the reactions.

| Compound | Voltage applied V | Primery current mA | Final current mA | Time (hr.) | Color          | Voltage applied for cyclic voltammetry |
|----------|-------------------|--------------------|------------------|------------|----------------|--------------------------------------|
| 1        | 1.4               | 13.06              | 0.63             | 4          | Yellowish orange | -1.8      +1.8                       |
| 2        | 1.4               | 4.10               | 1.94             | 2.5        | Yellowish orange | -1.8      +1.8                       |
| 3        | 1.4               | 1.30               | 0.15             | 2          | Yellowish orange | -1.8      +1.8                       |
| 4        | 4.8               | 4x10⁻³             | 2x10⁻³           | 4          | Yellow         | -2        +2                        |
| 5        | 4.8               | 3x10⁻³             | 1x10⁻³           | 3          | Yellow         | -2        +2                        |
| 6        | 4.8               | 0.70               | 0.35             | 3          | Yellow         | -2        +2                        |
| 7        | 1.4               | 2.20               | 1.09             | 2          | Light Brown    | -1.2      +1.2                      |
| 8        | 1.4               | 4.50               | 2.07             | 3          | Light Brown    | -1.2      +1.2                      |
| 9        | 1.4               | 6.31               | 4.00             | 3          | Light Brown    | -1.2      +1.2                      |

Table 2: First and second reduction peaks and their currents.

| Compound               | First reduction peak potential V | Current A | second reduction peak potential V | Current A |
|------------------------|---------------------------------|-----------|-----------------------------------|-----------|
| (C₆H₅)₂Te₂             | 0.7                             | 1.16 x 10⁴| 1.58                              | 1.2 x 10⁴ |
| (2-NH₂-5-BrC₆H₃)₂Te₂   | 0.2                             | 4.0 x 10⁴ | 0.86                              | 1.0 x 10⁵ |
\[ \text{CH}_3\text{C}_6\text{H}_5\text{Te}_2 \]
\[ (2-\text{NH}_2-5-\text{BrC}_6\text{H}_5)\text{Te}_2 \]

-0.1  \[ 0.15 \times 10^{-5} \]

0.8  \[ 1.5 \times 10^{-5} \]

Figure 1: Cyclic voltammogram of solvent and supporting electrolyte only at scan rate (0.05 \( \text{v.s}^{-1} \)).

Figure 2: Cyclic voltammogram of solvent and supporting electrolyte at scan rate (0.05 \( \text{v.s}^{-1} \)) with (a) diphenyl ditelluride, (b) bis(2-amino-5-methyl phenyl) ditelluride and (c) bis(2-amino-5-bromophenyl) ditelluride.

Figure 4 show a linear relationship between \( I_\text{p} \) and \( \nu^{1/2} \) of the two reduction peaks of diaryl ditelluride in the presence of alkyl halide, indicating that the electron transfer of both reductions is process of one electron transfer under a controlled diffusion process. Figure 5 illustrated the relationships between current function and scan rate. The independence of both \( F_\text{p}^{\text{red}} \) and \( F_\text{p}^{\text{red2}} \) on \( \nu \) values represents a confirmed diagnosis of controlled
diffusion processes related to the electron transfer at the corresponding potentials [18,19], on one condition that ν should be not less than 0.15v.s-1 for all studied compounds.

Figure 3: (a) Cyclic voltammogram of diphenyl ditelluride with propyl bromide at different scan rates: A (0.05 v.s⁻¹), B (0.2 v.s⁻¹) and C (0.5 v.s⁻¹). (b) Cyclic voltammogram of bis(2-amino-5-bromophenyl) ditelluride in the presence of butyl iodide at different scan rates A (0.05 v.s⁻¹), B (0.1 v.s⁻¹), C (0.2 v.s⁻¹), and D (0.5 v.s⁻¹).

Figure 4: Relation between ν⁻¹/² and I_{pred1} and I_{pred2} of (A) diphenyl ditelluride in the presence of propyl bromide and (B) bis(2-amino-5-bromophenyl) ditelluride in the presence of butyl iodide.

Figure 5: Current function Fp_{red1}: (A) diphenyl ditelluride in the presence of propyl bromide and (B) bis(2-amino-5-bromophenyl) ditelluride in the presence of butyl iodide.
The reduction process is an irreversible process which may occur by transfer of two electrons generated through Te—Te bond leading to forming the telluride ion Te\(^{2+}\). The proposed mechanism of such related reactions is elucidated in Scheme 1, showing the electrosyntheses of the tellurides 1-9.

\[
\begin{align*}
\text{Ar}_2\text{Te}_2 & \xrightarrow{+e^-} (\text{Ar}_2\text{Te}_2)^\cdot^- \rightarrow \text{ArTe}^+ + \text{ArTe}^- \\
(\text{Te}^{1+}) & \\
(\text{Te}^{2+}) & \xrightarrow{2\text{RX}} 2\text{ArTe}^- \\
\end{align*}
\]

\(\text{RX} = \text{CH}_3\text{CH}_2\text{Br}(1), \text{CH}_3\text{C}(\text{CH}_2)\text{Br}(2), \text{CH}_3\text{C}(\text{CH}_2)\text{I}(3)\)

\(\text{Ar} = \text{Br}\text{H}_{-\text{NH}_2}, \text{H}_{-\text{C}}\text{H}_{-\text{G}}\text{H}_{-\text{NH}_2}\)

Scheme 1: proposed mechanism of two reduction process and reacting of diarylditelluride with different alkyl halides

The stability and reduction process for diaryl ditelluride occurred on tellurium atom due to the partial delocalized \(\pi\) electrons on whole molecule corresponding in that to the behavior of both selenium and sulfur metals [20,21] which may lead to the formation of Te—Ph\(^-\).

In referring to the resultant data obtained from figure2, it was found that the best potentials data to be carried out during the electrosynthesis of the organic telluride derivative, figure 6 represent the voltammogram of the unsymmetrical diorganyl telluride which is clearly in accordance with figure 2.

![Figure 6](image_url)

Figure 6: (a) Cyclic voltammogram of propyl phenyl telluride at different scan rates, A (0.05 v.s\(^{-1}\)), B (0.2 v.s\(^{-1}\)), and C (0.5 v.s\(^{-1}\)) and (b) cyclic voltammograms of butyl(2-amino-5-bromophenyl) telluride in different scan rates .A (0.05 v.s\(^{-1}\)), B (0.1 v.s\(^{-1}\)), C (0.2 v.s\(^{-1}\)),and D(0.5v.s\(^{-1}\)).

**4 Electrochemical synthesis**

During the study of cyclic voltammetry of compounds, diphenylditelluride , bis (2-amino-5-methylphenyl) ditellurid and bis (2-amino-5-bromophenyl)ditelluride , it was concluded that the best requisite values of interest for potential scanning to understand the electrochemical behavior for oscillates from one to another as follows : C.V of diphenyl ditelluride was carried out from -1.8V to +1.8V, and that range for bis(2-amino-5-
methylphenyl) ditelluride was located between -2.0V and +2.0V while the potential range of -1.2V to +1.2V was used for bis (2-amino-5-bromophenyl) ditelluride as can be seen from Table 1. These findings indicate that already the substituent on benzene ring has an effect on reduction potential. For example, the presence of bromine atom in para position leads to decrease the reduction potential, while the presence of methyl group in para position increased the potential. The same conclusion has given when electrochemical properties were studied for some diorganyl diselenides and diaryl tellurides using mercury drop electrode [21].

A reaction of each of diphenylditelluride, bis (2-amino-5-methylphenyl) ditelluride and bis (2-amino-5-bromophenyl) ditelluride with ethyl bromide, propyl bromide and butyl iodide in pure and dry methanol or THF as solvent in presence of tetrabutylammonium tetrafluoroborate as supporting electrolyte, have been carried out. In general the color of the synthesized compounds were light brown to yellowish orange. All new compounds have low melting points or appeared as oily compounds. It is well known that, the tellurium compounds containing substituents in the \textit{ortho} position, relative to the tellurium atom, have low melting points or as viscous compounds [14, 22].

Compounds 1-9 were characterized all by infrared spectra Table 3, and elemental analysis (CHN) for compounds 1, 2, 4, 6, 8 and 9. The CHN analysis indicate that the tributyl amine is coordinated to compound 1 which is possibly formed during the electrochemical synthesis. It is worth noting that same reaction was observed during the electrochemical investigation of selenide and diselenide during cyclic voltammetry processes [19]. Compounds 4, 6 and 8 showed similar behavior [14, 23, 24], Table 4.

Table 3: IR spectroscopic data of compounds 1 – 9.

| Comp. No. | C-H Aromatic Str. | C-H Aromatic Ben. | N-H Str. | N-H Ben. | C-H Aliphatic Str. | C=C Str. | C-N Aromatic Str. | C-Te Aromatic Str. |
|-----------|------------------|------------------|---------|---------|------------------|----------|------------------|------------------|
| 1         | -                | 1488.29          | -       | -       | 2962.61          | 1488.05  | -                | 521.16           |
| 2         | 3061.2           | 1468.29          | -       | -       | 2960.92          | 1600     | -                | 450              |
| 3         | 3060.24          | 1487.8           | -       | -       | 2960.68          | 1600     | -                | 451.50           |
| 4         | 3050             | 1483.61          | 3303.83 | 1689.53 | 2961.14          | 1525.59  | 1380.94          | 520.74           |
| 5         | 3050             | 1463.22          | 3286.59 | -       | 2960             | 1510     | 1375             | 510              |
| 6         | 3050             | 1475.04          | 3370.96 | 1666.2  | 2959.96          | 1515.53  | 1380.3           | 500              |
| 7         | 3100             | 1487.81          | 3294.54 | 1666.2  | 2960             | 1544     | 1392.84          | 503.33           |
| 8         | 3100             | 1483.16          | 3100    | 1685.67 | 2962.46          | 1508.23  | 1380.94          | 522.67           |
| 9         | 3100             | 1469.25          | 3250    | 1689.11 | 2961.4           | 1505     | 1381.26          | 520              |

Table 4 show some physical properties and CHN analysis for compounds 1-9.

| Compound No. | Structure | Color         | Melting point °C | Yield | CHN Found (Cal) |
|--------------|-----------|---------------|------------------|-------|-----------------|
|              |           |               |                  |       | C%    | H%   | N%   |
| 1            | ![Structure](image.png) | Yellowish orange | 146-150         | 91.9  | 57.31 (57.58) | 8.90 (8.83) | 3.34 (3.89) |
| 2            | ![Structure](image.png) | Yellowish orange | 58-60           | 99.1  | 43.62 (43.62) | 4.88 (4.81) | -                |
| 3            | ![Structure](image.png) | Yellowish orange | 56-58           | 75.8  | -                | -             | -                |
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