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# A thermal analysis study of some di-substituted aryltellurium (IV) trihalides

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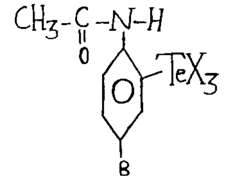
## Abstract

A thermal analysis study of some new organotellurium compounds of the type (AB–ArTe$X_3$, where A = $CH_3CONH$, B = $CH_3$, Br, $NO_2$ and X = Cl, Br) is reported. These compounds have been prepared by the mercuration route, which included the substitution of the tellurium trihalide group in the *ortho* position instead of the mercury chloride group. The new compounds have been investigated by TG and a 3-step decomposition process which, apparently, yield tellurium dihalide as an intermediate and tellurium dioxide as the final residue. © 1997 Elsevier Science B.V.

*Keywords:* Organotellurium compounds; Thermogravimetry

## 1. Introduction

There is increasing interest in the chemistry of organotellurium compounds containing nitrogen donors in the *ortho* position to the tellurium moiety of the aromatic compounds. This is owing to the formation of various complexes among certain metals, nitrogen and tellurium [1]. Organotellurium compounds are well-known [2–6], but little is known about their thermochemistry. The thermal stability of organotellurium compounds is an interesting way to find a relationship between their composition structure and material processing, having properties suitable for various technological applications, such as liquid crystal [7–9]. Recently, some new aryltelluride compounds have been studied by thermogravimetry. The 2-acetamido-5-(substituted)phenyltelluride showed different stepwise decomposition process than that of 2-acetamido-5-(substituted)phenylditelluride [10]. The general structure of the compounds that we have studied is:



where (1) B = $CH_3$, X = Cl; (2) B = Br, X = Cl; (3) B = $NO_2$, X = Cl; (4) B = $CH_3$, X = Br; (5) B = Br, X = Br; and (6) B = $NO_2$, X = Br.

## 2. Experimental

The compounds (1-6), (Table 1), were prepared and characterized by elemental analysis, IR, $^1$HNMR and mass spectra [11,12]. Elemental analysis were carried out using Herious techniques, H.p.85 IR spectra were recorded as KBR pellets in the 200–4000 cm$^{-1}$ range, using Perkin–Elmer 983 G infrared spectrometer.

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Table 1
The names of the starting material compounds

| No. | Compound | Name |
|---|---|---|
| 1. | $C_9H_{19}Cl_3NOTe$ | 2-acetamido-5-methylphenyltelluriumtrichloride |
| 2. | $C_9H_7BrCl_3NOTe$ | 2-acetamido-5-bromophenyltetturiumtrichloride |
| 3. | $C_9H_7Cl_3N_2O_2Te$ | 2-acetamido-5-nitrophenyltelluriumtrichloride |
| 4. | $C_9H_{19}Br_3NOTe$ | 2-acetamido-5-methyltelluriumtribromide |
| 5. | $C_9H_7Br_4NOTe$ | 2-acetamido-5-bromophenyltelluriumtribromide |
| 6. | $C_9H_7Br_3N_2O_2Te$ | 2-acetamido-5-nitrophenyltelluriumtribromide |

$^1$HNMR spectra were obtained using a Brucker WM-250(250 MZH) spectrometer solution in DMSO-d6 using TMS as internal standard. Mass spectra data were measured on a Finning MAT 1125 mass spectrometer at 70 eV, relative to $^{130}$Te. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected.

Thermogravimetric analysis data was obtained by using a Mettler TA 3000 thermal analysis system in a slow flow rate of nitrogen. The analysis was performed by heating at a steady rate of 10°C/min and the temperature range of 40–600°C. The platinum crucible type was used for samples.

### 2.1. 2-Acetamido 5-methylphenyl mercury chloride

4-Aminotoluene (0.31 mol), mercury dictate (0.31 mol) and methanol (400 ml) were refluxed for 12 h in a 1 l, round bottomed flask equipped with a reflux condenser, a magnetic stirrer, and heating mantle. A solution of lithium chloride (0.33 mol) in 50 ml methanol was added. The heating mantle was removed.

The mixture was stirred for 1 h and allowed to cool to room temperature. 2-Amino-5-methylphenylmercury chloride crystallized. The crystals were collected on a Buchner funnel and dried under a vacuum oil pump at 50°C. The dry 2-aminophenylmercurychloride was placed in a 500 ml beaker. Sufficient acetic anhydride was added to cover the solide completely (150 ml). The beaker was covered and set aside. After 2–3 min, the mixture warmed spontaneously. The reaction was allowed to proceed for 5 h. Then $CH_2Cl_2$ solvent (100 ml) was added. The solid product was collected by filtration, washed with $CH_2Cl_2$ solvent (100 ml) and dried under a vacuum oil pump at 50°C. Yield (94%), m.p. > 250°C.

Likewise, 4-bromoaniline and 4-nitroaniline (0.2 mol each) and mercury acetate (0.2 mol) gave 2-acetamido-5-bromophenylmercurychloride and 2-acetamido-5-nitro-phenylmercurychloride. Yields (96%) and (81%), m.p. > 250°C and > 250°C, respectively.

### 2.2. Acetamido-5-methylphenyltelluriumtrichloride

2-Acetamido-5-methylphenylmercurychloride (60 mmol), tellurium tetrachloride (60 mmol) and glacial acetic acid (350 ml) were placed into a 1 l, round bottomed flask equipped with a magnetic stirrer, a reflux condenser, and a drying tube (calcium chloride). The mixture was refluxed for 12 h. Boiling glacial acetic acid (175 ml) was then added. The hot mixture was filtered and the filtrate cooled. 2-Acetamido-5-methylphenyltelluriumtrichloride crystallized and was collected on a Buchner funnel. An analytical sample was obtained by recrystallization from acetic acid. Yield (80%); m.p. 24–244°C.

### 2.3. 2-Acetamido-5-bromophenyltelluriumtrichloride

2-Acetamido-5-bromophenylmercurychloride (40 mmol), tellurium tetrachloride (40 mmol) and glacial acetic acid were refluxed for 12 h. It gave (64%) yield product, m.p. 230–232°C.

2-Acetamido-5-nitrophenyltelluriumtrichloride was given a similar treatment. Yield (33%); m.p. 154–156°C.

## 3. Results and discussion

The thermal stability of organotellurium compounds have been studied by thermogravimetric analysis. The present work on the thermal behavior of

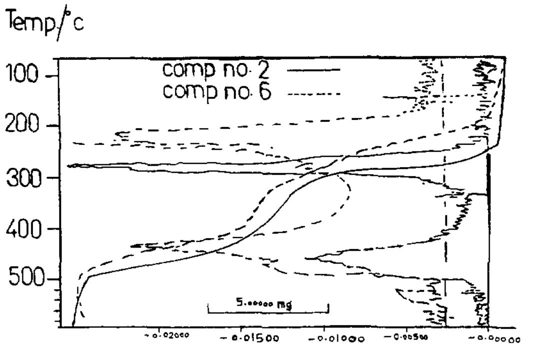

Fig. 1. TG/DTG curves for compounds 2 and 6.

some organotellurium compounds showed a 3- step decomposition process (Figs. 1 and 2).

The first step involved removal of the gases ($0.5CO + 0.5H_2$) with $CH_3COPhBTeX_3$ as the first intermediate (Table 2).

The second step corresponds to the elimination of CO gas, where $B = CH_3$, Br and $CO + NO_2$ gases together with $B = NO_2$, $CH_3PhBTeX_3$ or $CH_3PhTeX_3$ as the second intermediate, respectively.

In the third step, the mass loss of $CH_3PhBX$), where $B = CH_3Br$ or $CH_3PhX$ with $B = NO_2$ can be associated with the formation of unstable $TeX_2$ as an intermediate with the formation of $H_2TeO_3$ in the presence of three molecules of water (crystallization solvent) [13,14]. Finally, the unstable tellurous acid is readily dehydrated to $TeO_2$:

$$2TeX_2 + 3H_2O \rightarrow H_2TeO_3 + Te + 4HX$$

$$H_2TeO_3 \xrightarrow{-H_2O} TeO_2$$

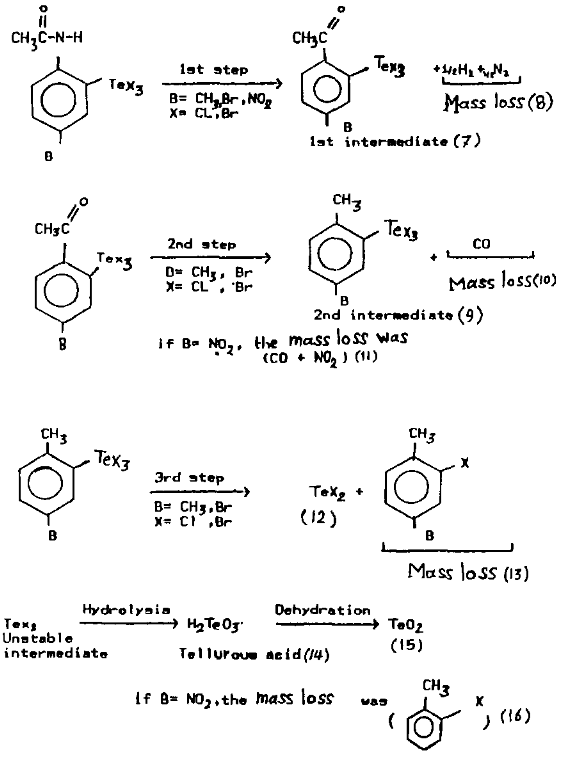

Fig. 2. The suggested mechanism of thermal decomposition process.

The melting point for Te powder is 452°C and for $TeO_2$ it is 733°C. From the data (Table 3), it can be concluded that these compounds of tellurium tribromide are of lower thermal stability than tellurium trichloride compounds because the Te–Br bond is weaker than the Te–Cl bond owing to the larger size

Table 2
The names of the intermediate and final compounds

| No. | Compound | Name |
|---|---|---|
| 7 | $C_8H_6BOTeX_3$ | 2-acetlyl-5-substituted phenyltelluriumtrihalides |
| 8 | $0.5H_2 + 0.5N_2$ | Mixture of half mole each for hydrogen and nitrogen gases |
| 9 | $C_7H_6BTeX_3$ | 2-methyl-5-substituted phenyltelluriumtrihalides; $B = CH_3$, Br and $X = CL$, Br |
| 10 | CO | carbon monoxide gas |
| 11 | $CO + NO_2$ | mixture of carbon monoxide gas and nitrous dioxide gas |
| 12 | $TeX_2$ | tellurium dihalides; $X = CL$, Br |
| 13 | $C_7H_6BX$ | 2-halo-4-substitutedtoluene, $B = CH_3$, Br and $X = Cl$, Br |
| 14 | $H_2TeO_3$ | tellurous acid |
| 15 | $TeO_2$ | tellurium dioxide |
| 16 | $C_7H_7X$ | 2-halotoluene; $X = Cl$, Br |

Table 3
Thermogravimetric results

| No. | Compounds | Temperature range (°C) | Mass loss (%) calc | Mass loss (%) exp | Notes |
|---|---|---|---|---|---|
| 1 | $C_9H_{19}C_{13}NOTe$ | 40–160 | 3.92 | 3.64 | 1st step |
| | | 160–207 | 7.92 | 7.77 | 2nd step |
| | | 207–544.6 | 36.47 | 6.78 | 3rd step |
| 2 | $C_9H_7BrC_{13}NO$ | 40–244.5 | 3.39 | 3.14 | 1st step |
| | | 244.5–331.2 | 6.26 | 6.14 | 2nd step |
| | | 311.2–505.6 | 45.97 | 45.48 | 3rd step |
| 3 | $C_9H_7CL_3N_2O_2Te$ | 40–176 | 3.62 | 3.75 | 1st step |
| | | 176–236 | 17.91 | 18.35 | 2nd step |
| | | 235–505.6 | 30.62 | 30.20 | 3rd step |
| 4 | $C_9H_{19}Br_3NOTe$ | 40–155.5 | 2.9 | 3.41 | 1st step |
| | | 155.5–191 | 5.43 | 6.54 | 2nd step |
| | | 191–535 | 5.06 | 36.37 | 3rd step |
| 5 | $C_9H_7Br_4NOTe$ | 40–227.5 | 2.48 | 3.06 | 1st step |
| | | 227.5–292.5 | 4.62 | 5.23 | 2nd step |
| | | 292.5–483 | 43.06 | 43.06 | 3rd step |
| 6 | $C_9H_7Br_3N_2O_2Te$ | 40–169.5 | 2.74 | 3.14 | 1st step |
| | | 169.5–211.2 | 13.53 | 13.83 | 2nd step |
| | | 211.2–494.5 | 31.29 | 30.81 | 3rd step |

of the bromide atom as compared with the chloride atom, hence the energy required to break Te–Br bond is less than that required to break Te–Cl bond.

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