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The reaction of hydrogen chloride with bis(*p*-ethoxyphenyl)telluride, a possible route to pure tellurium

Christine Elgy and William R McWhinnie
Department of Chemical Engineering and Applied Chemistry, Aston University, Aston Triangle, Birmingham B4 7ET, UK

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The reaction of hydrogen chloride with bis(*p*-ethoxyphenyl)telluride is investigated and shown to give essentially phenetole (C_6H_5COEt), tellurium, and bis(*p*-ethoxyphenyl)tellurium dichloride. Spectroscopic methods (UV–visible, ^{125}Te NMR) show that some bis(*p*-ethoxyphenyl)ditelluride is produced. This is believed to arise from a side reaction of organic telluride with an intermediate organyltellurenyl chloride which is considered to arise from initial proton attack at the Te–C bond of the telluride. The ditelluride reacts with HCl to deposit 80% of its tellurium content as the element; phenetole is the other major product. Use of a spin-trap reagent gave no evidence of radical intermediates.

An attempt to develop a reaction sequence to prepare high-purity tellurium is described. Although a purity of 99.985% could be achieved, overall yields are not economic, unless very high-purity tellurium is required. The method described is, however, very effective for the removal of traces of tin, lead, arsenic and antimony and can significantly reduce the copper, iron and selenium content; for example, one treatment of an alloy (Te, 75%; Se, 25%) gave a sample of tellurium containing 40 ppm selenium.

Keywords: Tellurium metal, preparation, alloy purification, organotellurium reaction with HCl

INTRODUCTION

Most workers who regularly deal with organyltellurium compounds have encountered reactions where elemental tellurium, apparently spontaneously, precipitates within the reaction mixture. In the relatively few cases where the cause has been investigated thermolysis,[1] photolysis,[2] or disproportionation of a tellurium(II) compound[3] provides the explanation. Such reactions, which can have a nuisance value in the laboratory, may in other contexts be useful; for example when tellurium compounds are used for imaging purposes.[4] Badesha[5] has exploited the reduction of the tellurium tetra-alkoxide formed in the reaction of tellurium dioxide and ethylene glycol to produce tellurium of high purity following separation from selenium in various alloys. We had similar objectives in the work described here.

When anhydrous hydrogen chloride reacts with bis(*p*-ethoxyphenyl)telluride, tellurium together with phenetole and bis(*p*-ethoxyphenyl)tellurium dichloride are isolated.[6] We felt that the system had potential for the upgrading of elemental tellurium and decided to investigate it in more detail. Also there are few investigations of the reaction of HCl with diorganyltellurides. Lederer reported a compound melting at 233–234°C which was formulated as $Ph_2Te \cdot HCl$;[7] however, if HCl is passed into a refluxing solution of Ph_2Te in *o*-dichlorobenzene, Ph_2TeCl_2 is prepared in 100% yield.[6] Conductivity measurements on Me_2Te in liquid HCl at $-95°C$ indicate that if $Me_2Te \cdot HCl$ is formed, the degree of ionization must be small; however, in the same report it seemed that $[Me_2TeH][BCl_4]$ was isolated as an unstable, poorly characterized intermediate.[8] In another example, Morgan and Drew[9] reported that 1-telluracyclohexane-3,5-dione decomposed in the presence of concentrated HCl, and they concluded that the stoichiometry of the reaction was:

$$2C_5H_6O_2Te + 4HCl$$

$$= 2CH_3COCH_2COCH_3 + Te + TeCl_4,$$

no discussion of mechanism was attempted.

Diphenylacyltelluride, $(PhCO)_2Te$, has been suggested to be unstable, depositing tellurium[4] but, by developing a new method of preparation, Engman[10] has now shown that the compound is not photolytically unstable. It will however decompose to $PhCOCH_3$ and elemental tellurium in the presence of mineral acid, and even wet acetone with a trace of H_2SO_4 is effective.

RESULTS AND DISCUSSION

We first investigated the stoichiometry of the reaction of HCl with bis-*p*-ethoxyphenyltelluride. Isolation and weighing of the products (Te, $(p\text{-}EtOC_6H_4)_2TeCl_2$, and PhOEt) revealed an apparent stoichiometry of:

$$2(p\text{-}EtOC_6H_4)_2Te + 2HCl$$

$$= Te + (p\text{-}C_6H_4)_2TeCl_2 + 2PhOEt$$

However, we observed that in successive experiments the amount of each component recovered fluctuated over a range of a few per cent (e.g. PhOEt, 87–96%; R_2TeCl_2, 92–94%; Te, 90–100%). Although these data are subject to experimental error, we had to allow that the fluctuations might have an alternative cause. As HCl entered the reaction mixture it was observed that an orange-red colour developed; monitoring the visible spectrum showed this to be due to the formation of bis(*p*-ethoxyphenyl)ditelluride (about 15% conversion based on intensity measurements). We next examined the reaction of the pure ditelluride with dry HCl and found that 80% of the tellurium content was deposited as the element. PhOEt was recovered but the other products were ill-defined. It seemed that the ditelluride arose from an alternative path rather than as an intermediate, thus accounting for the fluctuations in the recovery of products referred to above. Before this could be deemed to be a firm conclusion it was decided to investigate the system using other techniques, namely ESR spectroscopy and ^{125}Te NMR spectroscopy.

It has been shown[11] that the reaction of MeI with Ph_2Te involves radical intermediates and it was therefore wise to eliminate this possibility in the present case. We added the spin trap phenyl-*N*-t-butylnitrone, PhCH=N(O)(t-Bu)[12] to the HCl, $(p\text{-}EtOC_6H_4)_2Te$ reaction mixture (solvent, trichloroethane) using the conditions previously described.[11] No radicals were detectable by ESR spectroscopy; thus there is no reason to suppose the first step to be other than attack by proton at the carbon atom bonded to tellurium,[13] a position activated to electrophilic attack by the *p*-ethoxy group.

^{125}Te NMR spectra of pure R_2Te, R_2Te_2 and R_2TeCl_2 ($R = p\text{-}EtOC_6H_4$) were run in $CDCl_3$ as standards; subsequently HCl was passed into a $CDCl_3$ solution of $(p\text{-}EtOC_6H_4)_2Te$ contained in an NMR tube and the ^{125}Te NMR spectrum was recorded. Three resonances were observed attributable to the telluride, to the ditelluride (weak) and to the diorganyltellurium dichloride. The resonances were identified by comparison with spectra for the individual pure compounds. When HCl was passed until no further tellurium was deposited, only the dichloride resonance could be detected in the final solution, thus demonstrating that this compound is the only detectable organyltellurium product. When the initial experiment was repeated with careful precautions to exclude air, only the dichloride resonance was evident after the spectrum had been accumulated. It appears that air is innocent in the chemical sense and that it was merely acting as a diluent for the HCl and slowing the reaction down.

We are of the opinion that the ditelluride arises by a side reaction; from the NMR work it appears more persistent when the concentration of HCl is reduced by the presence of diluents such as air. This suggests that under those conditions some true intermediate may compete with HCl for some reactant (i.e. telluride) and produce ditelluride which, in its turn, can react independently with HCl as demonstrated above. A plausible scheme is as follows:

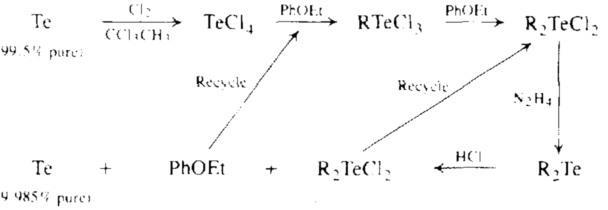
$$R_2Te + HCl = RH + RTeCl \qquad [1]$$

$$2RTeCl = Te + R_2TeCl_2 \qquad [2]$$

$$R_2Te + 2RTeCl = R_2Te_2 + R_2TeCl_2 \qquad [3]$$

The build-up of ditelluride is then likely to depend on the relative rates of [1], [2] and [3] and these will be influenced by the available concentration of HCl. Also, it seems likely that, as observed, ditelluride would be formed initially when the telluride concentration is high; furthermore the telluride reacts more quickly with HCl than does the ditelluride thus explaining the persistence of the ditelluride colour during the reaction.

We then attempted to set up a process which would enable us to convert 99.5% tellurium to high-purity tellurium; the approach is illustrated in Scheme 1. The first stage, the chlorination of tellurium in trichloroethane (TCE), works well and we have found it to be a useful reaction for the *in situ* synthesis of $TeCl_4$ in other contexts. The reactions with phenetole are well known[14] and the first stage goes well in TCE. It is interesting to note that selenium mimics tellurium in the greater part of this scheme; however, bis(*p*-ethoxyphenyl) selenide is *not* decomposed by HCl under the conditions specified.



Scheme 1 Purification process for 99.5% tellurium (R = *p*-$EtOC_6H_4$).

It was found that if the scheme were to be used to enhance the purity of tellurium, extra precautions were needed. Thus solvent purity was essential, particularly with respect to trace metals. This could be checked with a colorimetric test with dithizone. The method developed was successful in totally removing traces of tin, lead, arsenic and antimony from 99.5% tellurium; Cu (10–5 ppm), Fe (40–3 ppm), and Se (80–20 ppm) were reduced to the latter levels. Traces of other elements were introduced, namely boron, silicon, magnesium, silver and mercury. The 'glass' elements (boron, silicon) could be avoided by use of plastic ware in the final stages and ultimately drying agents were implicated as the likely source of the other contaminants.

The method, whilst under optimum conditions capable of producing tellurium of 99.985% purity (one cycle) from an input of 99.5% purity, is unlikely to be effective on a large scale. Firstly, the overall yield is disappointing (the yield on each stage is good by organometallic standards, but cumulative losses over several stages make the overall yield, 50% of the tellurium theoretically recoverable, unattractive; however, the unrecovered material would recycle in a continuous process). Secondly, the extensive prepurification of reagents makes the method potentially expensive. There is one context in which methods such as this may prove useful; thus it may be possible to upgrade alloyed tellurium prior to final purification. For example a sample of an alloy (tellurium, 75%; selenium, 25%) was treated as outlined in the scheme to give a specimen of tellurium which contained only 40 ppm selenium.

EXPERIMENTAL

All solvents were purified until they gave negative tests for heavy metals with dithizone; alternatively they were of Aristar grade. Water was deionized. Other reagents (chlorine, phenetole, hydrazine hydrate) were the best quality available. Tellurium (99.5%) was supplied by Mining Chemical Products Ltd.

Trace elements were determined mass-spectrographically by Mr A. Thompson of Mining Chemical Products Ltd. UV-visible spectra were recorded with a Pye–Unican SP8-100 instrument. ^{125}Te NMR spectra were obtained on a JEOL FX90Q instrument and ESR measurements were made with a JEOL PE-1X spectrometer.

Purification of tellurium

A brief account is presented below.

(a) Synthesis of tellurium tetrachloride

Dry TCE (CCl_3CH_3) (100 cm^3) was added to tellurium powder (7 g, 99.5%). The mixture was stirred and heated to gentle reflux, light was excluded and dry chlorine together with nitrogen was admitted at such a rate that no unreacted chlorine exited from the reaction flask. The end of the reaction was signified by the appearance (visual) of chlorine in the trap beyond the reaction flask; chlorine passage was then discontinued and the flow of nitrogen increased to remove any excess chlorine. All tellurium had reacted and a yellow solution, together with some crystals of tellurium tetrachloride, was present in the flask.

(b) Reaction of $TeCl_4$ with phenetole

The literature[14] was followed with the exception that TCE rather than chloroform was used as solvent, i.e. the above solution was used direct.

(c) Reduction of (p-$EtO \cdot C_6H_4)_2TeCl_2$

The method of Bergman[15] involving hydrazine hydrate was used. The telluride was recrystallized from methanol to m.p. 64°C (lit. 64°C).

(d) **Reaction of telluride with HCl**

Bis(*p*-ethoxyphenyl)telluride (5 g) was dissolved in TCE (50 cm^3) in a polypropylene flask. Dry HCl was passed into the solution via a PTFE tube until the reaction was complete (about 1 h). Excess HCl was removed by passage of nitrogen, after which the tellurium was recovered by centrifuging in polypropylene tubes, washed, dried and analysed for trace elements.

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