Inorganica Chimica Acta, 113 (1986) 143–146

Tellurium-125 NMR and Mass Spectra of Dithiotellurides

W. MAZUREK*, A. G. MORITZ

Department of Defence, Defence Science and Technology Organization, Materials Research Laboratories, P.O. Box 50, Ascot Vale, Vic. 3032, Australia

and M. J. O'CONNOR†

Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, Vic. 3083, Australia

Received August 13, 1985

Abstract

The preparation, ^{125}Te NMR and mass spectra of some dithiotellurides, $Te(RS)_2$ (R = Ph, 2-PhCOOH, CPh_3, CH_2Ph, 3-PrCOOH, n-Bu, i-Pr, t-Bu) are discussed. The ^{125}Te chemical shifts have been found to lie within a range spanning *ca.* 690 ppm and correlate with the pK_a values of the parent thiols. The mass spectra of the alkyl derivatives (R = n-Bu, i-Pr, t-Bu) indicate an initial step-wise loss of alkenyl groups followed by the elimination of hydrogen sulfide from the resultant bis(hydrosulfido)-tellurium ion.

Introduction

^{125}Te NMR is proving to be a sensitive spectroscopic characterization technique for many organotellurides. Where previously most spectra were obtained by double resonance techniques [1, 2], more recently direct measurements have been widely used [3–15]. The ^{125}Te nucleus ($I = 1/2$, natural abundance 6.99%) is attractive because its sensitivity is comparable to that of the ^{13}C nucleus. In addition the linewidths of the ^{125}Te resonances should be narrow in the absence of quadrupolar interactions. These factors together with the large chemical shift scale ($\delta \sim 3000$) should ensure that structural and electronic effects are easily observed.

A diversity of organotellurides have been examined by ^{125}Te NMR including halides [3–5], heterocycles [6, 8, 10], esters [7], dialkyls [9, 11, 15], dialkylditellurides [15], diarylditellurides [16] and tellurium-bridged metal clusters [12, 14]. To date, however, the ^{125}Te NMR spectrum of only one dithiotelluride (bis(diethyldithiocarbamato)tellurium(II) [8]) has been reported. As part of an investigation of thiotellurides we now describe a preliminary study of the ^{125}Te NMR and mass spectra of a series of dithiotellurium(II) compounds.

Experimental

Mass spectra were measured using a VG 7035 spectrometer with an electron impact source. ^{125}Te NMR spectra were recorded on a Jeol FX200 spectrometer at *ca.* 63.01 MHz. For $CDCl_3$ solutions the spectrometer was operated in the locked mode. For DMF solutions, the unlocked mode was used after locking and shimming at the ^{2}H resonance of ^2H_2O. The spectral width was either 10 or 20 kHz with pulse repetition times of 0.5 s being used. Generally 8192 data points were employed. The pulse width was 25 μs. Satisfactory spectra were obtained after *ca.* 500–1000 transients. ^{125}Te chemical shifts were referenced to a sealed solution of 0.3 M bis(diethyldithiocarbamato)tellurium(II) [8, 17] in $CDCl_3$. Elemental analyses were performed by the Australian Mineral Development Laboratories, Port Melbourne, Vic.

Bis(3-thiopropionic acid)tellurium(II) and bis(2-thiobenzoic acid)tellurium(II) were synthesized as reported elsewhere [18].

Reagents

Tellurium hexachloride solution was prepared by dissolving tellurium dioxide (3.2 g, 0.02 mol) in concentrated hydrochloric acid (8 ml). Tellurium dioxide was obtained from BDH Chemical Ltd. while the thiols were supplied by the Aldrich Chemical Company and were used without further purification.

Bis(isopropylthio)tellurium(II)

(a) Isopropylthiol (1.9 ml, 0.02 mol) was added to a mixture of tellurium dioxide (0.8 g, 0.005 mol) in ether (5 ml). The mixture was allowed to react for 2 h after which it was filtered, and washed with

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*Author to whom correspondence should be addressed.
†Deceased, 18 March, 1985.

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methanol (20 ml). After cooling the filtrate for 2 h at −15 °C, yellow crystals formed which were filtered, washed with methanol and air dried. Yield 0.48 g (35%), melting point 32–33 °C.

(b) Tellurium hexachloride solution (2 ml, 0.005 mol) was added dropwise to a stirred solution of isopropylthiol (2.8 ml, 0.03 mol) in ethanol (20 ml). The resultant yellow solution was then cooled to −15 °C for 2 h. A yellow crystalline solid formed which was filtered, washed with methanol and air dried. Yield 0.8 g (58%), melting point 32.5–33 °C, mass spectrum, *m/z* 280, calc. for $(C_6H_{14}S_2{}^{130}Te)^{+\cdot}$, 280.

Bis(tert-butylthio)tellurium(II)

(a) tert-Butylthiol (2 ml, 0.018 mol) was added to tellurium dioxide (0.8 g, 0.005 mol) and stirred for 8 h. The resultant yellow paste was extracted with dry ether. On evaporation of the extract, yellow crystals formed. The product was filtered, washed with ethanol and air dried. Yield 0.73 g (48%), melting point 81–82 °C.

(b) Tellurium hexachloride solution (2 ml, 0.005 mol) was added dropwise to a stirred solution of tert-butylthiol (3.4 ml, 0.03 mol) in ethanol (50 ml). The yellow mixture was cooled overnight to −17 °C, filtered, washed with methanol and dried *in vacuo*. Yield 1.0 g (66%), melting point 81–82 °C, mass spectrum, *m/z* 308, calc. for $(C_8H_{18}S_2{}^{130}Te)^{+\cdot}$, 308.

Bis(n-butylthio)tellurium(II)

n-Butylthiol (21 ml) was added to a stirred suspension of tellurium dioxide (8 g, 0.05 mol) in dry ether (50 ml). When the exothermic reaction subsided an additional quantity of thiol (1.0 ml, total 0.02 mol) was added. After this reaction had subsided the mixture was warmed to 60 °C and the ether removed by distillation. The orange colored telluride was vacuum distilled (0.1 mm Hg) at 90 °C. Yield 5.9 g (39%), mass spectrum, *m/z* 308, calc. for $(C_8H_{18}S_2{}^{130}Te)^{+\cdot}$, 308.

Bis(triphenylmethanethio)tellurium(II)

Tellurium hexachloride solution (1 ml, 0.0025 mol) was added dropwise to a stirred solution of triphenylmethanethiol (4.15 g, 0.015 mol) in acetone (50 ml). A yellow precipitate formed which was removed by filtration. On standing a yellow crystalline solid formed from the filtrate. The solid was collected after 3 h, washed with acetone, dry ether and then dried *in vacuo*. Yield 0.94 g (56%), melting point *ca.* 150 °C (dec.). *Anal.* Calc. for $C_{38}H_{30}S_2Te$: C, 67.28; H, 4.46; S, 9.45. Found: C, 67.14; H, 4.92; S, 9.6%.

Bis(phenylthio)tellurium(II)

Tellurium hexachloride solution (2 ml, 0.005 mol) was added dropwise to a stirred solution of thiophenol (3.1 ml, 0.03 mol) in ethanol (80 ml) at 10 °C. An orange precipitate formed 2 min after completion of the addition. After a further 5 min of stirring the mixture was filtered, washed with ethanol and dried *in vacuo*. Yield 1.0 g (58%) melting point, 64–64.5 °C (lit. [18] 67–69 °C), mass spectrum, *m/z* 348 calc. for $(C_{12}H_{10}S_2{}^{130}Te)^{+\cdot}$, 348.

Bis(benzylthio)tellurium(II)

Tellurium hexachloride solution (2 ml, 0.005 mol) was added dropwise to a stirred solution of benzylthiol (3.5 ml, 0.03 mol) in ethanol (40 ml). On completion of the addition the mixture was stirred for 5 min. A yellow–orange liquid layer separated on the bottom. The top layer was decanted and bottom layer washed twice with methanol (~3 ml). The residual oil was cooled to 4 °C and on solidification was dispersed in methanol (5 ml), filtered, washed with methanol (2 × 2 ml) and dried *in vacuo*. Yield 1.0 g (53.6%) melting point 31–32 °C, mass spectrum, *m/z* 376, calc. for $(C_{14}H_{14}S_2{}^{130}Te)^{+\cdot}$, 376.

Results and Discussion

Preparation

The dithiotellurides were prepared by reaction of the thiols with tellurium oxide in a heterogeneous mixture and/or reaction with tellurium oxide/hydrochloric acid ($TeCl_6{}^{2-}$) [19]. During the reaction tellurium(IV) is reduced by the thiol, probably through a thermally unstable tetrathiotellurium(IV) intermediate. Such compounds have been previously isolated at low temperature [20].

$$4RSH + Te^{IV}O_2 \longrightarrow \underset{\text{(thermally unstable)}}{Te^{IV}(SR)_4} \longrightarrow Te^{II}(SR)_2 + RSSR$$

The dithiotellurium(II) compounds although apparently more stable than the tetrathio analogs are also prone to decompose to tellurium(0) and the corresponding disulfide.

$$Te^{II}(SR)_2 \longrightarrow Te^0 + RSSR$$

The stability appears to depend on the nature of the substituent group with the apparent general trend being t-Bu > i-Pr > n-Bu > Ph > CH_2Ph_2 ~ 3-Pr-COOH ~ 2-PhCOOH.

Mass Spectra

The mass spectra of the alkyl dithiotellurides show characteristic fragmentations typified by bis(tert-butylthio)tellurium(II) (Fig. 1). The mass spectrum shows the presence of a molecular ion together with ions arising from the step-wise loss of alkenyl groups and a subsequent loss of hydrogen sulfide to form the sulfidotelluride ion (Scheme 1). These steps are

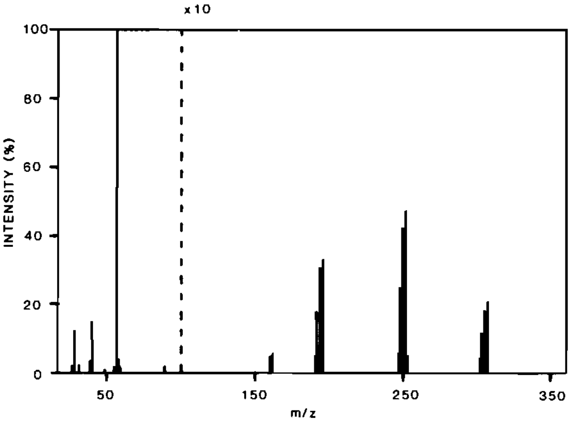
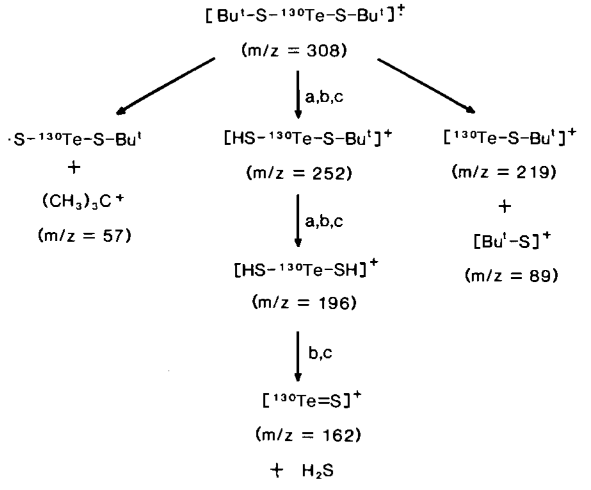


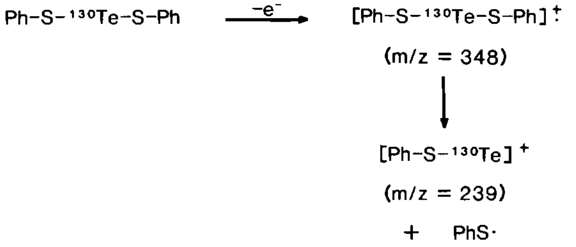
Fig. 1. Mass spectrum of $Te(t\text{-}BuS)_2$.



(a) Constant B^2/E Scan, (b) Constant B/E Scan, (c) V^{-1} Scan

Scheme 1.

supported by linked scan (constant B^2/E or B/E) as well as voltage scanning (Barber–Elliot) experiments. The observation of ions at m/z = 57, 89 and 219 suggests however that direct cleavage of the alkyl and thioalkyl group occurs.



Scheme 2.

The benzylthio analogue gives rise to a lower intensity molecular ion and no evidence of step-wise loss of C_7H_7· under the experimental conditions used. A comparison with the mass spectra of dibenzyldisulfide under similar conditions suggests that much of the mass spectrum of bis(benzylthio)tellurium(II) can be attributed to the disulfide, the product of thermal decomposition. Similarly the mass spectrum of bis(benzenethio)tellurium(II) is dominated by the presence of diphenyldisulfide but there is also evidence for the direct cleavage of the Te–S bond (Scheme 2).

Tellurium-125 NMR

^{125}Te NMR spectra of the dithiotellurium(II) compounds show relatively narrow line-widths (3–39 Hz) with no apparent evidence of long range proton coupling. However line-width variations have been found to be sensitive to minor temperature fluctuations [4, 21] which occur during long accumulations. Fluctuations of ±1 °C have been reported to contribute approximately 12 Hz to broadening.

The ^{125}Te chemical shifts are presented in Table I. The total chemical shift range is 686 ppm with all shifts being shielded relative to $Te(Et_2NCS_2)_2$. The resonance position is very sensitive to the R substituent and there is a good correlation between the chemical shifts and the pK_a of the parent thiols (Fig. 2)

TABLE I. Tellurium-125 NMR Data for Dithiotellurides

Compound	Solvent	Concentration (M)	(^{125}Te)[a] (ppm)	Linewidth[b] (Hz)
$Te(t\text{-}BuS)_2$	$CDCl_3$	0.5	62.5	3
$Te(i\text{-}PrS)_2$	$CDCl_3$	0.24	183	21
$Te(Ph_3CS)_2$	$CDCl_3$	*ca.* 0.25	342	19
$Te(n\text{-}BuS)_2$	$CDCl_3$	1.6	380	21
$Te(PhCH_2S)_2$	$CDCl_3$	0.4	383	10
$Te(3\text{-}SPrCO_2H)_2$	DMF	0.2	427	39
$Te(2\text{-}SPhCO_2H)_2$	DMF	0.15	621	17
$Te(PhS)_2$	$CDCl_3$	0.5	749	4

[a] Relative to external $Te(Et_2NCS_2)_2$, 0.3 M in $CDCl_3$. [b] Corrected for experimental line broadening.

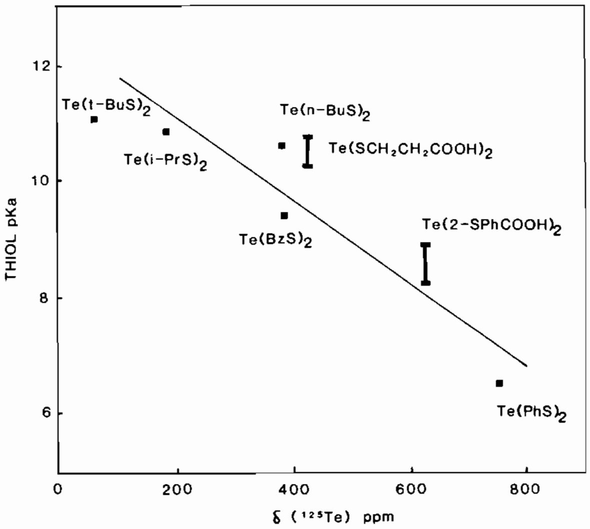


Fig. 2. Correlation between ^{125}Te chemical shifts and the pK_a (in water) of the parent thiol [22] of some dithiotellurium(11) compounds.

precluding the contribution of any unique structural variations from one compound to another.

The high sensitivity of tellurium chemical shifts render these values susceptible to secondary effects such as concentration and solvent characteristics. However, concentration effects with the concentrations indicated in Table 1 are expected to be confined to less than 10 ppm [16].

The effects of solvent characteristics can be more profound [4, 16]. Solvents such as acetonitrile and dimethylsulfoxide are capable of forming stable solvates with organotellurium trichlorides which are considered to have a dominant effect on the chemical shifts of these compounds [4]. In the case of $Te(3\text{-}SPrCO_2H)_2$ and $Te(2\text{-}SPhCO_2H)_2$, because of the low solubility in $CDCl_3$, it was necessary to resort to DMF. However, the correlation between the chemical shift and the pK_a of the parent thiol has not been significantly affected.

The variation in chemical shifts is consistent with the electron withdrawing effects of the substituent groups. Thus a decrease in chemical shifts is observed in the transition from R = Ph to t-Bu. Similar observations have been made for substituted aryltellurides [4], alkyltellurium dichlorides [5] and tellurol aryl esters [7]. The reverse effect has been noted for a series of dialkyl tellurides [15], dialkyl ditellurides [13, 15], aryl- and alkyltellurium trihalides [4, 5] where the inductive effect appears not to be dominant in influencing the shielding at the tellurium.

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