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THE DECOMPOSITION OF DIMETHYLTELLURIUM DIIODIDE IN POLAR SOLVENTS

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SUMMARY

Dimethyltellurium diiodide decomposes readily at room temperature in acetone and similar solvents, especially if water or an inorganic salt be present. Products include a tellurium–oxygen polymer containing some iodine and methyl groups, along with CH_3I and various inorganic species. This decomposition is discussed in relation to other organometallid reactions.

INTRODUCTION

Vernon reported[1] that dimethyltellurium dihalides existed in two forms (α and β series) and postulated them as *cis,trans* isomers. Drew[2] confirmed the existence of two series, but claimed that the α-series consisted of covalent momoners while the members of the β-series were ionic dimers, $(CH_3)_3Te^+CH_3TeX_4^-$. This has been confirmed recently by crystallographic studies on α-$(CH_3)_2TeCl_2$[3] and β-$(CH_3)_2TeI_2$[4].

The chemical conversion of α-dihalides to β-dihalides[2] implies a methyl migration, which in turn suggests lability of the Te–C bond. As part of an extended investigation into Te–C bond properties of higher-valent organotellurium compounds, we studied the decomposition of α-$(CH_3)_2TeI_2$ (I) in solution.

RESULTS

(I) dissolves readily in most organic solvents. No appreciable decomposition occurs in solvents of low polarity (CCl_4, C_6H_6, ether). In acetone, a pale yellow color appears, and addition of aqueous Ag^+ precipitates AgI immediately. Acetonic (I) has been converted to $(CH_3)_2TeF_2$ by reaction with AgF[5].

Upon standing at room temperature, the yellow solution turns fiery red and a white solid (II) precipitates. Addition of ionic salts or water markedly accelerates this

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precipitation. Dilution with ether, even to a 10/1 ratio, slows but does not stop the reaction. Similar reactions occur in acetonitrile, 2-butanone, hexamethylphosphoric triamide, pyridine, acetophenone, cyclohexanone and tetrahydrofuran. Sometimes particles of elemental tellurium will also form in the initial stages. Precipitation will continue for extended periods, even if the solid is removed.

(II) is an amorphous powdery material that is uniform in nature, showing no indications of being a mixture. It shows some variation in elemental composition depending on reaction conditions, but always contains about 90% tellurium and oxygen. When KSCN was used, thiocyanate anion was not incorporated into the precipitate. The insolubility of (II) in almost every solvent prevented any determination of its molecular weight. A mass spectral study showed that the highest peaks corresponded to $Te_2O_2^+$ and $ITeO_2^+$. Other fragments observed were Te_2O^+, TeI^+, Te_2^+, I_2^+, TeO_2^+, TeO^+, I^+, O_2^+, OH^+, and CH_3^+. (II) dissolves in aqueous acids or bases, but is insoluble in common solvents. AgI is precipitated from these solutions upon addition of Ag^+. Boiling (II) in concentrated HNO_3 gives TeO_2.

The color of the supernatant liquid varies from yellow to deep red-violet, depending on solvent and concentration. A small peak, probably a charge-transfer band, appears at 500 nm in the visible spectrum of acetone solutions. Fractional distillation gave CH_3I and acetone as the only volatile components, leaving a black residue of Te, I_2, TeI_4 and whatever salt was used as catalyst.

The decomposition of (I) in acetone was monitored by NMR. (I) initially gives a single peak at δ 3.26 with satellite bands at 3.08 and 3.48. These latter are probably due to $^1H-^{125}Te$ coupling, with a J value of approximately 24 Hz. The corresponding value for J(Te–H) in $(CH_3)_2Te$ is 20.7 Hz[6]. Almost immediately a peak appears at δ 2.22; this is due to CH_3I. Other weak peaks also appear as reaction proceeds. One at δ 3.75 is due to absorbed water. A second, at δ 3.53, which overlaps with the satellite band, may be due to CH_3TeI_3[7].

If 50 mole % or more of CH_3I or C_2H_5I is added to the reaction solution, no decomposition occurs. Lesser amounts slow down but do not prevent reaction. C_6H_5I had no effect at any concentration. NMR spectra show no evidence for the incorporation of ethyl or phenyl groups onto tellurium.

DISCUSSION

Wynne and co-workers[8,9] have studied the nature and behavior of organoselenium and organotellurium halides in solution. They find that the rate of decomposition depends on the solvent system used (being much faster in $C_6H_5NO_2$ than in CH_2Cl_2). CH_3TeCl_3 gives CH_3Cl as the primary organic decomposition product[7]. (I) gives CH_3I and, in addition, always displays the faint odor of $(CH_3)_2Te$.

While the complete mechanism remains to be determined, the first step is almost certainly

$$(CH_3)_2TeI_2 \rightarrow CH_3TeI + CH_3I \tag{1}$$

plus, to a slight extent,

$$(CH_3)_2TeI_2 \rightarrow (CH_3)_2Te + I_2 \tag{2}$$

Methyltellurium(II) iodide is unknown. Based on the reported properties of CH_3SeI[10]

and aryltellurium halides[11], CH_3TeI would be expected to decompose rapidly under these conditions, giving, among other products, CH_3TeI_3, which decomposes in turn. The reaction proceeds when water is rigidly excluded, but is accelerated by traces of moisture or ionic salts. No CH_3SCN or CH_3NCS could be detected when KSCN was present.

Even if water is present in great excess however, the reaction is not a simple hydrolysis. The product expected [by analogy to hydrolysis of $(CH_3)_2SiI_2$ or $(CH_3)_3PI_2$] would be Drew's β-base[2], $[(CH_3)_2TeO]X$. No such species were found, although they were specifically sought. Nor does the composition of (II) differ very significantly according to the amount of water present. On the basis of available evidence, (II) appears to be a polymeric solid of high molecular weight. Microscopic and X-ray powder diffraction studies indicate the absence of any crystalline structure.

Apparently the important reaction, then, is loss of CH_3I. Hydrolysis, when it occurs, affects only the tellurium iodide intermediates (CH_3TeI_3, TeI_4, possibly TeI_2). This indicates that the Te–CH_3 bond is quite labile, which is consistent with the earlier work already cited[1,2], and that this lability varies in the order $CH_3TeI_3 > (CH_3)_2TeI_2 \gg (CH_3)_3TeI$. In this respect (I) differs very strongly from analogous metals of Groups IV or V, and tends to resemble its sulfur and selenium analogs.

EXPERIMENTAL

Reagents and purification

$(CH_3)_2TeI_2$ was purchased from Strem Chemicals Inc. and used without further purification. Salts used included KI, NaI, KSCN, KSeCN, NaBr and NaCl; they were recrystallized and dried before use. Most solvents were reagent grade and used directly from previously unopened bottles. Acetone and acetonitrile were distilled from P_4O_{10} and used immediately. Acetone-d_6 (99.5%) was purchased from Volk Radiochemical Co. and used immediately from unopened vials.

Decomposition of $(CH_3)_2TeI_2$

In a typical experiment 1.00 g (2.43 mmole) dimethyltellurium diiodide was dissolved in 100 ml dry acetone and 0.010 g (0.067 mmole) NaI added. The solution, initially pale yellow, rapidly turned fiery red and soon showed turbidity. A very finely divided white solid slowly settled out. After 24 h the solid was filtered off. More solid began to settle out. Repeated filtrations were made for a period of one week. These were combined and dried in an oven to give 0.28 g white solid. Based on the elemental analysis, this contained 62.2% of the tellurium present in the starting material. The white solid decomposes when heated at 250°.

Workup of the supernatant liquid

After the white solid had been removed, the solution was distilled. A small quantity of liquid boiling at 40–48° came over first, followed by the bulk of the solvent at 55–56°. The first fraction was shown to be CH_3I by its infrared spectrum and chemical reaction. A black residue remained behind. This was extracted ether, leaving behind NaI, TeI_4, Te and a trace of the white solid. The ether-soluble fraction consisted exclusively of elemental iodine.

Analyses

These were performed by Galbraith Laboratories, Knoxville, Tennessee. The molecular weight of $(CH_3)_2TeI_2$ in acetone was found to be 435 ± 12 (Calcd. for monomer: 411.48). Elemental analyses are shown in Table 1.

TABLE 1

ELEMENTAL ANALYSES OF THE WHITE SOLID

Solvent/Catalyst	C(%)	H (%)	I (%)	Te + O (%)[a]
Acetone/NaI	0.73	0.42	11.80	87.05[b]
Acetone/H_2O	2.64	1.02	7.45	88.89
Acetone/C_6H_5I	0.97	0.55	4.39	94.09
Acetonitrile/NaI	1.40	0.32		[c]
Acetophenone/NaI	1.44	0.50	7.57	90.49
2-Butanone/NaI	2.58	0.69	8.49	88.24

[a] By difference. [b] Tellurium alone was 68.80%. [c] Iodine content not determined. Tellurium was 74.02%.

Spectroscopic studies

Infrared spectra were run on a Perkin–Elmer Model 337 grating spectrometer linear in wavenumber over the range 400–4000 cm^{-1}. Polystyrene was used for calibration. The NMR studies were done on a Varian T-60 recording spectrometer, using internal benzene as standard. Peak positions were then corrected to TMS as standard. CH_3I and H_2O were identified by addition of small quantities to the sample vessel. Mass spectra were run on a Hitachi–Perkin–Elmer RMU-73 mass spectrometer. The ionizing voltage was 70 electron-volts, and the pressure of the system 2×10^{-6} mm.

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