A Kinetic and Mechanistic Study of the Reaction between Bis-*p*-ethoxyphenyl Ditelluride and Molecular Iodine in Solution

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The title reaction in toluene has been examined spectrophotometrically. The data are consistent with equations (1)—(3) (R = *p*-EtOC$_6$H$_4$). The rate constants k_1 and k_3 are 56 ± 2 dm^3 mol^{-1} s^{-1} at

$$R_2Te_2 + I_2 \xrightarrow{k_1} 2RTeI \qquad (1)$$

$$RTeI + I_2 \overset{K_2}{\rightleftharpoons} RTe(I_3) \qquad (2)$$

$$RTe(I_3) \xrightarrow{k_3} RTe(I)_3 \qquad (3)$$

7 °C and 6.2 × 10^{-4} s^{-1} at 25 °C, respectively. The equilibrium constant K_2 is 1 570 dm^3 mol^{-1} at 25 °C, and ΔH_2 = −22 ± 4 kJ mol^{-1}. The activation parameters for the final step are $\Delta H^\ddagger$ = 44 ± 5 kJ mol^{-1} and $\Delta S^\ddagger$ = −160 ± 15 J K^{-1} mol^{-1}.

Large bodies of information have been accumulated concerning the reactions both of transition metal complexes and of the compounds of several typical elements, especially the lighter ones. This paper reports our efforts to elucidate mechanistic features of the chemistry of one of the heavier elements, tellurium. The chemical properties and size of this element are such that predictions of reaction pathways are difficult in the almost total absence of experimental guidance.

We have chosen to investigate some of the reactions of organotellurium compounds. In this paper we deal with the reaction between iodine and a diaryl ditelluride, RTeTeR (R = *p*-EtOC$_6$H$_4$). Diaryl ditellurides are easily prepared, are orange to red in colour, and have absorption coefficients in the region of a thousand for peaks around 400 nm. Thus standard spectrophotometric techniques are applicable to kinetic studies. Aryltellurium compounds do not live up to the reputation of tellurium compounds in general as being foul-smelling.

A common preparative route to aryltellurium trihalides is that involving the oxidation of ditelluride by molecular halogen in a solvent, an example is given below. Trihalides

$$RTeTeR + 3I_2 \longrightarrow 2RTeI_3$$

are the products usually obtained from such reactions. In the case of the tri-iodides, however, a pure solid product is only obtained [1,2] when the reaction is carried out at a low temperature, typically 10—15 °C. At higher temperatures intractable mixed products are obtained. The suggestion has been made [2] that some arenetellurenyl iodide, R′TeI, comes down with the tri-iodide and that the two are inseparable by normal use of solvents. We have observed that during dissolution of pure *p*-ethoxyphenyltellurium tri-iodide in toluene the characteristic colour attributable to molecular iodine in solution initially appears. On complete dissolution of the tellurium compound the colour reverts to the yellow-brown of the product. We infer that the two compounds, RTeI and RTeI$_3$, which have different solubilities and rates of dissolution, are readily interconvertible within minutes at room temperature in toluene.

Several literature reports describe the formation of arenetellurenyl halides. The presence of an *ortho*-carbonyl substituent on the aryl group helps to stabilize these products,[3–6] making the isolation of pure products relatively easy. Without such substituents, care in the control of concentrations of reagents and the choice of solvent is needed before the monohalide product can be obtained.[7,8] Other closely related compounds can be isolated [9,10] from solutions presumably containing arenetellurenyl halide, for example [10] PhTeLX, where L represents a ligand with an S or Se donor atom. Therefore we deduce that the reaction between molecular iodine and a diaryl ditelluride in solution yields the monoiodide first, and subsequent reaction produces the tri-iodide.

Results

Equilibrium Studies.—When solutions of iodine and of bis-*p*-ethoxyphenyl ditelluride in toluene are mixed at room temperature, the appearance and visible spectrum of the mixture change relatively quickly. Over the range of concentrations studied by us (10^{-3} to 5 × 10^{-5} mol dm^{-3} I$_2$ and 5 × 10^{-4} to 2.5 × 10^{-5} mol dm^{-3} ditelluride), this initial change is complete in less than 2 min. Spectral studies show that a much slower change follows, which is sufficiently slow relative to the first to enable measurements of optical densities to be made and treated as final readings for the first stage. That is, readings taken 2 min after mixing are not significantly different from those taken 10 min later. The best wavelength for the study of this first process is 500 nm. Molecular iodine itself absorbs at this wavelength. In the Figure we show a typical plot for the variation of optical density at this wavelength with the mol ratio of reagents. The crosses indicate experimental readings while the solid line is the data fit calculated according to the following scheme. This plot represents 7 of a total of 49 observations made at 25.0 °C and 500 nm.

All sets of data show a minimum in optical density at 500 nm at a 1 : 1 mol ratio of ditelluride to iodine. Under conditions where $[R_2Te_2]_0 \geqslant [I_2]_0$, the observed optical density is well described by equation (i). In this equation ε_1 is

$$D = \varepsilon_1 l([R_2Te_2]_0 - [I_2]_0) + 2\varepsilon_3 l[I_2]_0 \qquad (i)$$

the known absorption coefficient of the ditelluride, l the path-length of the cell, and ε_3 an absorption coefficient determined

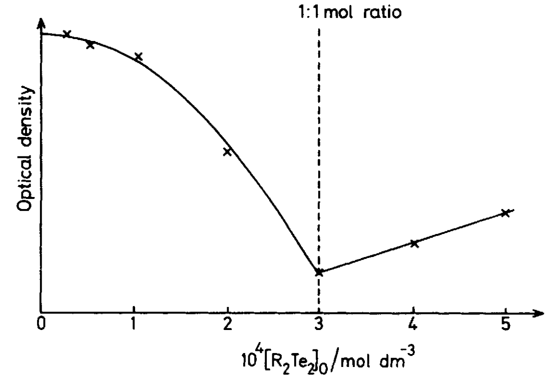

Figure. A plot of optical density at 25.0 °C and 500 nm against concentration of diaryl ditelluride initially present for solutions initially containing iodine at 3 × 10^{-4} mol dm^{-3}

here. We find that $\varepsilon_3 = 77 \pm 5$ dm^3 mol^{-1} cm^{-1}. From equivalent sets of data at other wavelengths, it would be possible to build up a complete spectrum of the species represented by the subscript 3. We have carried out such studies only at 284 and 318 nm, at which wavelengths the absorption coefficients are 6 700 and 6 600, respectively. The note reporting[8] the preparation of naphthalene-2-tellurenyl iodide shows it to be formed quickly in solution, while the illustrated spectrum agrees well with our measured absorption coefficients. Therefore we deduce that the reaction (ii) is

$$\mathrm{RTeTeR} + \mathrm{I_2} \longrightarrow 2\mathrm{RTeI} \qquad \text{(ii)}$$

complete in less than 2 min. Presumably it is an equilibrium, but, if so, it lies far over to the right. We estimate the equilibrium constant to be >100, corresponding to $\Delta G < -12$ kJ mol^{-1}, a small difference.

Solutions prepared in such a way that $[R_2Te_2]_0 < [I_2]_0$ show a different dependence of optical density on concentration. Equation (iii) now holds, where ε_2 is the known

$$D = 2\varepsilon_3 l[R_2Te_2]_0 + l([I_2]_0 - [R_2Te_2]_0)\{\varepsilon_2 + x[R_2Te_2]_0\} \qquad \text{(iii)}$$

absorption coefficient of iodine and x is a constant. If the equilibrium (iv) is set up and lies well to the left, equation (iii)

$$\mathrm{RTeI} + \mathrm{I_2} \xrightleftharpoons{K_2} \mathrm{RTeI{\cdot}I_2} \qquad \text{(iv)}$$

$$x = 2K_2(\varepsilon_4 - \varepsilon_2 - \varepsilon_3) \qquad \text{(v)}$$

will be obeyed with x given by equation (v), the absorption coefficient of RTeI·I$_2$ being ε_4.

At 10.0, 25.0, and 45.0 °C we find the values of x to be 4.8 × 10^6, 3.2 × 10^6, and 1.7 × 10^6 dm^3 mol^{-1}, respectively. This yields a value of -22 ± 4 kJ mol^{-1} for the enthalpy change. We have attempted to apply the method of least squares to our data using a more complete equation, *i.e.* the equation obtained when equilibrium (iv) is not assumed to lie far over to the left. Unfortunately, the sum of squared differences is insensitive to marked changes in K_2. The value obtained from kinetic studies (see later) lies well within the acceptable range. Therefore we conclude that K_2 is *ca.* 1 500 dm^3 mol^{-1} at 25 °C and that ε_4 is approximately 2 000 dm^3 mol^{-1} cm^{-1}.

Table 1. Second-order rate constants at 7.0 °C for the formation of RTeI from R_2Te_2 and I_2 in toluene (R = *p*-EtOC$_6$H$_4$)

$10^5[R_2Te_2]_0$/mol dm^{-3}	$10^5[I_2]_0$/mol dm^{-3}	k_1/dm^3 mol^{-1} s^{-1}
2.5	2.5	57.2
2.5	5.0	60.0
2.5	8.0	62.7
2.5	12.5	55.0
2.5	15.0	59.5
2.5	20.0	45.8
5.0	2.5	54.0
10.0	2.5	52.4

Table 2. Pesudo-first-order rate constants for the second stage of the reaction between R_2Te_2 and I_2 in toluene

$10^5[R_2Te_2]_0$/ mol dm^{-3}	$10^5[I_2]_0$/ mol dm^{-3}	T/°C	$10^6k_{obs.}$/s^{-1}
5	10	25.0	44.5
5	15	25.0	83.3
5	20	25.0	112
5	25	25.0	150
5	30	25.0	167
5	20	30.0	147
5	20	35.0	180
5	20	40.0	205
5	20	45.0	247
5	20	50.0	278
5	20	55.0	322

Kinetic Studies.—When we made these studies, we did not have available stopped-flow apparatus suitable for studying the initial rapid reaction over a range of temperatures. We were able to reduce the temperature and slow the reaction sufficiently to examine the formation of RTeI at one temperature, 7 °C. Unfortunately, we do not have data for the activation energy.

In Table 1, we quote the rate data obtained at this temperature. Observations were made at 284 nm. The rate constants are those obtained by fitting the experimental data to a rate equation first order both in iodine and in ditelluride. In the one case where the reagents were present in equal concentrations, a second-order rate equation was applied. From the data quoted, it is obvious that the rate equation (vi) holds, with $k_1 = 56 \pm 2$ dm^3 mol^{-1} s^{-1} at 7 °C.

$$d[\mathrm{RTeI}]/dt = 2k_1[R_2Te_2][I_2] \qquad \text{(vi)}$$

The optical density at 284 nm of a reaction solution increases during the formation of the arenetellurenyl iodide. It reaches a maximum as this process is completed, and subsequently a slow decrease is observed. This second stage can also be followed spectrophotometrically, but we have not followed it to completion since it is too slow, at convenient concentrations. The spectrum of the reaction solution after a long time is identical with that expected from a mixture of the aryltellurium tri-iodide and the reagent in excess. During the early part of the reaction, typically up to 50% completion, the change of optical density (D_t) with time is described well by equation (vii). Calculated values of $k_{obs.}$ are given in Table 2. From these we deduce equation (viii). At 25 °C, K_2 =

$$\ln(D_t - D_\infty) = -k_{obs.}t + \text{constant} \qquad \text{(vii)}$$

$$k_{obs.} = \frac{K_2k_3([I_2]_0 - [R_2Te_2]_0)}{1 + K_2([I_2]_0 - [R_2Te_2]_0)} \qquad \text{(viii)}$$

1 570 dm^3 mol^{-1} and $k_3 = 6.2 \times 10^{-4}$ s^{-1}. Since the formation of RTeI is completed in the initial step, the concentration of molecular iodine at the start of the slow step is ($[I_2]_0$ −

$[R_2Te_2]_0$). Therefore equation (viii) enables us to verify the equilibrium of equation (iv) and deduce that it is the adduct of that equation which subsequently reacts in a first-order step, described by k_3. Therefore the complete scheme is that shown below [(ii), (iv), (ix)].

$$R_2Te_2 + I_2 \xrightarrow{k_1} 2RTeI \qquad \text{(ii)}$$

$$RTeI + I_2 \xrightleftharpoons{K_2} RTeI{\cdot}I_2 \qquad \text{(iv)}$$

$$RTeI{\cdot}I_2 \xrightarrow{k_3} RTe(I)_3 \qquad \text{(ix)}$$

The data of Table 2 also include values of $k_{obs.}$ as a function of temperature. From these data we may deduce that the ' activation energy ' of this composite constant is 30 kJ mol^{-1}. When the contribution of K_2 is taken into account, the activation parameters for k_3 are $\Delta H^\ddagger = 44 \pm 5$ kJ mol^{-1} and $\Delta S^\ddagger = -160 \pm 15$ J K^{-1} mol^{-1}.

Discussion

Our spectral and equilibrium observations show that molecular iodine and a diaryl ditelluride react together in toluene solution to produce initially arenetellurenyl iodide. This process is quantitative, and complete in less than 2 min at room temperature. When a 1 : 1 mixture of these same reagents is made in deuteriated chloroform, proton n.m.r. evidence of this change is again obtained. The spectrum shows only one type of *p*-ethoxyphenyl group to be present, but the peaks are shifted slightly relative to the ditelluride. These shift changes are from δ 7.59 to 7.88 for protons *ortho* to Te, 6.61 to 6.80 *meta* to Te, 3.97 to 4.07 for CH_2, and 1.39 to 1.40 for CH_3.

At first sight it seems surprising to find a reaction which involves the making and breaking of covalent bonds between typical elements to be so rapid. However, tellurium and iodine are located side-by-side towards the bottom of the periodic table. Therefore, the Te–Te and I–I bonds are very similar in being long and weak. For example, diphenyl ditelluride has[11] a Te–Te bond length of 0.271 nm, compared with 0.267 nm for I_2. The dihedral angle in diaryl ditellurides is *ca.* 75°. Therefore one side of the Te–Te bond is totally open to chemical attack. Under these conditions the formation of an essentially square Te_2I_2 transition state is readily achieved. It would be of interest to compare the behaviour of the shorter and stronger F_2, Cl_2, and Br_2 with ditellurides. Dance[12] has discussed the possibility of non-radical cleavage of Te–Te bonds, in the formation of unsymmetrical ditellurides, in terms of a square Te_4 transition state, while Barton *et al.*[13] have postulated a concerted mechanism for the formation of mixed biaryls in crossover experiments in the thermal decomposition of TeR'_4 (R′ = aryl) species. Our as yet unpublished studies of the effect of light on solutions of ditellurides in the presence of alcohols and oxygen can be described by a scheme involving the step (x). These various reports point to the formation of four-centre transition states as a common mechanistic feature of ditelluride chemistry.

$$R_2Te_2^{*} + O_2 \longrightarrow R_2Te_2O_2 \qquad \text{(x)}$$

Solutions containing arenetellurenyl iodide and an excess of iodine show a further equilibrium involving a 1 : 1 adduct. This adduct is not the normal tri-iodide. The equilibrium constant describing its formation, K_2, is 1 570 dm^3 mol^{-1} at 25 °C and has $\Delta H_2 = -22 \pm 4$ kJ mol^{-1}. This adduct is probably correctly written as $RTe(I_3)$. The equilibrium constant is similar in magnitude to the constant for the equilibrium (xi) in aqueous solution between iodide and iodine, 721 dm^3 mol^{-1}.[14]

$$I^- + I_2 \rightleftharpoons I_3^- \qquad \text{(xi)}$$

This comparison should not be pushed too far, since the systems involve marked differences. Additionally, Pritzkow[15] has shown that I_2 can add to the I of a Te–I bond; he has published the structure of $(CH_3)_2TeI_4$. We are, however, proposing a considerably simpler structure than that found by Pritzkow.

A compound such as $RTe(I_3)$ with a large central atom, a bent Te–I–I angle, and fairly weak I–I bonds is ideally arranged to undergo a unimolecular rearrangement to $RTe(I)_3$. This appears to be what happens in the final step we describe, k_3. Mechanistic studies in organotellurium chemistry are adventures in uncharted territory. Therefore, the interpretation of the activation parameters for this process must be both difficult and dubious. The comparison which we would prefer to develop is that between our data and those for oxidative addition to metal centres with low co-ordination numbers and oxidation states. We feel that size and steric factors make this the most worthwhile comparison. At present we are only able to indicate possible correlations.

The oxidative addition[16] of methyl iodide to Vaska's compound exhibits activation parameters similar to those found here. Our own unpublished results for the oxidative addition of diaryl ditellurides to this same complex also show similar values. Therefore perhaps the degrees of polarity in the transition states of these different processes are similar. Tanaka[17,18] and co-workers reported the oxidative addition of molecular iodine to various transition metal complexes. In their systems a rapidly attained equilibrium yields a 1 : 1 charge-transfer complex with I_2 interacting with a ligand S atom. This charge-transfer complex then undergoes a first-order rearrangement forming two new M–I bonds. Mechanistically this is the same as we suggest for the interaction of iodine and arenetellurenyl iodide. The enthalpies of activation reported are in the same range as that found by us for k_3 but the entropies of activation vary considerably. Addition to Rh^I gives[17] $\Delta S^\ddagger = 4 \pm 6.9$ J K^{-1} mol^{-1} while addition to a dimeric Au^I complex gives[18] a value of −91.5 J K^{-1} mol^{-1}; *cf.* our value of −160 ± 15 J K^{-1} mol^{-1}. These differences may reflect a strong solvent dependence on changing from CH_2Cl_2 to toluene, or that we are attempting an inappropriate comparison.

Experimental

Bis-*p*-ethoxyphenyl ditelluride was prepared from tellurium tetrachloride (B.D.H.) and phenetole by the literature

Table 3. Characterisation data for tellurium compounds (R = *p*-$EtOC_6H_4$)

	M.p. (°C)		%C		%H		%Te		
Compound	Found	Lit.	Found	Calc.	Found	Calc.	Found	Calc.	Ref.
$RTeCl_3$	184—186	182—183	27.0	27.1	2.5	2.6			18
R_2Te_2	102—104	107—108	38.5	38.6	3.6	3.6	51.3	51.3	18
$RTeI_3$	133—134	133—134	15.5	15.3	1.4	1.5			19

method,[19] which proceeds *via* *p*-ethoxyphenyltellurium trichloride. Subsequently a comparison sample of the tri-iodide was prepared from the ditelluride. Table 3 quotes m.p. and elemental analytical data for our products. In the case of the ditelluride, tellurium was determined volumetrically by the literature methods.[20] Resublimed iodine and dried and redistilled toluene were used for all solution experiments. All optical measurements were made on a Pye Unicam SP 8–100 spectrophotometer fitted with a simple mixing system employing parallel mounted thermostatted syringes and a flow-through cell. N.m.r. spectra were recorded on a JEOL FX 900 spectrometer. Computer programs were written by us as required and processed on either an Apple II or an ICL 1905A computer

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