A Kinetic and Mechanistic Study of the Formation of a Diaryl Ditelluride in Solution by the Sulphite Reduction of the Aryltellurium Trichloride

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When an aqueous dioxane solution of Na_2SO_3 or of $Na_2S_2O_5$ is added to a solution of *p*-ethoxyphenyltellurium trichloride ($RTeCl_3$) in dioxane the reaction mixture remains homogeneous and the related ditelluride R_2Te_2 is formed quantitatively. This reaction has been investigated kinetically. The first step in the process is the hydrolysis of the trichloride to give the aryltellurate, $RTeO_2^-$. When the water content of the solvent is low this acid-catalysed step becomes rate determining. More usually that step is rapid and the slow step is the reduction of the $RTeO_2^-$ by HSO_3^- to give $RTeO^-$. This tellurium(II) intermediate is believed to dimerize to R(HO)TeTe(OH)R before being reduced by another mole of bisulphite to the ditelluride.

We have recently become interested in the mechanistic details of the reactions of diorgano ditellurides, RTeTeR; specifically their oxidation,[1] oxidative addition to transition metals,[2] and behaviour under irradiation.[3] The literature contains remarkably few reported mechanistic studies involving heavy typical elements, so there are likely to be unexpected differences compared with the more thoroughly examined systems. The ready homolytic cleavage of the Te–Te bond, forming radicals, is one such difference.

In this paper we turn to the preparation of the ditellurides, for reasons of synthetic convenience concentrating on *p*-ethoxyphenyl as the organic group attached to Te. Usually they are synthesised by the reduction of trihalides, $RTeCl_3$ (R = C_6H_4OEt-*p* throughout), under heterogeneous conditions. The first reported preparation made use of alkaline sodium metabisulphite,[4] while a range of other readily available reducing agents were subsequently used. We found that aqueous 1,4-dioxane, towards the organic-rich end of the range, is suitable for homogeneous studies, and so we have studied the reduction of *p*-ethoxyphenyltellurium trichloride, $RTeCl_3$, by added sulphite or metabisulphite (disulphite, $S_2O_5^{2-}$) in this medium.

Although salts of $S_2O_5^{2-}$ and SO_3^{2-} are different in the solid state, they are interrelated in aqueous solution through the equilibria (1) and (2).[5-7] Therefore one would expect to be able

$$S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^- \quad (1)$$

$$HSO_3^- \rightleftharpoons H^+ + SO_3^{2-} \quad (2)$$

to make up reagent solutions from either type of salt and obtain the same reductant species in solution. Certainly both types of salt have been used in ditelluride preparations with no obvious differences between them. Because we are using a mixed solvent we carried out separate sets of kinetic runs using the two types of salt. As we report below there are no significant differences between the kinetic results obtained, so we should be able to relate our findings to those already published for other studies of sulphite reductions. We should expect to find inner-sphere mechanisms operating while the occurrence of any one-electron processes might be indicated by the formation of dithionate, $S_2O_6^{2-}$.[8]

Experimental

Details of the preparations of all tellurium compounds used are widely documented.[1,4] We prepared fresh samples of all compounds and obtained satisfactory analytical and physical data in all cases. We found that all solutions of the ditelluride in aqueous dioxane obey the Beer–Lambert law and that the solute may be monitored at 400 nm, where it has an absorption coefficient of (1 200 ± 20) $dm^3\ mol^{-1}\ cm^{-1}$. Since no other species in our systems shows absorption at this wavelength we were able to follow reactions spectrophotometrically, using a Pye-Unicam SP8-100 spectrophotometer. AnalaR grade sodium sulphite or reagent-grade metabisulphite was used to prepare reductant solutions, which were then standardised volumetrically.

Dioxane was purified and redistilled before use.[9] (However, trial experiments showed that commercially supplied dioxane gave identical rate data to those obtained from redistilled solvent.) Pure dioxane and water form a homogeneous mixture only slowly, therefore we initiated kinetic experiments by mixing together a solution of *p*-ethoxyphenyltellurium trichloride in pure dioxane with an equal volume of a solution of the sodium salt of the reducing agent in aqueous dioxane (usually 1 : 1 by volume). Complete mixing within the response time of our pen recorder was then achieved by stirring.

The absence of dithionate from the reaction products was demonstrated for an experiment carried out with only water as solvent. A reaction between stoicheiometric quantities of $RTeCl_3$ and AnalaR sodium sulphite was performed and the ditelluride produced was removed by extraction into chloroform. A few drops of dilute NaOH solution were then added and the SO_4^{2-} and SO_3^{2-} ions were removed by careful and thorough precipitation of their barium salts. Concentrated nitric acid (15 cm^3) was then added to the filtrate (200 cm^3) and the mixture was then boiled for 1 h. Addition of more $BaCl_2$ gave no further precipitate.[10-12] We can thus set an upper limit of 4% for the $S_2O_6^{2-}$ content of the product.

Results

The preparation of diaryl ditellurides using sulphites or metabisulphites remains homogeneous in aqueous dioxane. In such solutions the ditelluride obeys Beer's law at 400 nm so that the reaction can be monitored easily. The stoicheiometric ratios required by equation (3) are $RTeCl_3 : SO_3^{2-}$ = 1 : 1.5 and

$$2RTeCl_3 + 3SO_3^{2-} + 3H_2O \longrightarrow R_2Te_2 + 3SO_4^{2-} + 6H^+ + 6Cl^- \quad (3)$$

$RTeCl_3 : S_2O_5^{2-}$ = 1 : 0.75 respectively. The good agreement between observed data and those calculated for a second-order treatment indicates that the reactions are stoicheiometric. This

Table 1. The variation of the observed rate constant for the reduction of 1.25×10^{-3} mol dm^{-3} $RTeCl_3$ in water–dioxane (1:3 v/v) at 25 °C

$10^4[Na_2SO_3]$/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}	k_2/dm^3 mol^{-1} s^{-1}
3.13	−65.8	2.11
6.25	−51.6	2.06
12.5	−27.4	2.20
25.0	+29.3	2.34
$10^4[Na_2S_2O_5]$/mol dm^{-3}		
1.25	−65.0	2.00
2.50	−58.7	2.13
3.13	−50.4	2.02
6.25	−26.8	2.14
12.0	+22.2	2.11

Table 2. The variation of rate constant with temperature for the reduction of 1.25×10^{-3} mol dm^{-3} $RTeCl_3$ in water–dioxane (1:3 v/v)

	k_2/dm^3 mol^{-1} s^{-1}	
Temp. (°C)	Na_2SO_3[a]	$Na_2S_2O_5$[b]
15.0	1.54	1.43
20.0	1.73	1.73
25.0	2.20	2.14
30.0	2.50	2.49
35.0	3.02	3.03
40.0	3.46	3.59
45.0	4.01	

[a] 1.25×10^{-3} mol dm^{-3}. [b] 6.25×10^{-4} mol dm^{-3}.

Table 3. The variation of the rate constant at 25.0 °C in water–dioxane (1:3 v/v) with added acid or base, using 1.25×10^{-3} mol dm^{-3} $RTeCl_3$ and 6.75×10^{-4} mol dm^{-3} Na_2SO_3[a]

10^3[NaOH]/ mol dm^{-3}	$10^4[H_2SO_4]$/ mol dm^{-3}	pH[b]	k_2/dm^3 mol^{-1} s^{-1}
13.5		11.1	3.65
10.4		11.0	2.89
7.30		10.9	2.77
4.17		10.6	2.46
1.04		10.0	2.29
0.10		9.02	2.31
0	0	6.84	2.26
	0.37	4.13	2.20
	1.56	3.51	2.17
	2.60	3.38	2.07
	3.65	3.14	2.01
	4.69	3.03	1.98
	5.70	2.94	1.82
	6.77	2.87	1.69
	7.80	2.81	1.55

[a] The ionic strength was maintained at 4.50×10^{-3} mol dm^{-3} by addition of Na_2SO_4. [b] Measured using a calibrated glass electrode.

Table 4. The variation of the rate constant at 25 °C in water–dioxane (1:3 v/v) with ionic strength (I) for 1.25×10^{-3} mol dm^{-3} $RTeCl_3$ and 6.25×10^{-4} mol dm^{-3} Na_2SO_3

$10^4[Na_2SO_4]$/ mol dm^{-3}	10^3I/ mol dm^{-3}	k_2/dm^3 mol^{-1} s^{-1}
2.08	2.50	2.01
4.17	3.10	2.15
6.25	3.80	2.29
8.33	4.50	2.35
9.38	4.70	2.37
10.4	5.00	2.49
11.5	5.30	2.54
12.5	5.60	2.66
14.6	6.30	2.70
15.6	6.60	3.73
16.7	6.90	4.22
18.8	7.50	6.96

was further checked under the same experimental conditions in separate experiments by adding varying amounts of reducing agent to fixed amounts of $RTeCl_3$ and measuring the amount of ditelluride produced. When freshly prepared solutions of the reducing agents are used the determined ratios are reproducible to within 5% of the expected values. The ratio of $RTeCl_3$ reagent to R_2Te_2 product when the reducing agent is in excess is $(2 \pm 0.06):1$. In a separate set of determinations we did not detect any $S_2O_6^{2-}$ amongst the reaction products.

All cited data from kinetic studies of the formation of the diaryl ditelluride were reproducible to within 5%, and refer to runs taken to at least 80% completion. At all but low water contents, the plots of absorbance *versus* time can be well fitted to the integrated forms of a second-order rate equation (4); $[S]_t$

$$d[R_2Te_2]/dt = k_2[Te]_t[S]_t \qquad (4)$$

and $[Te]_t$ are the concentrations at time t of the sulphur-containing reducing agent and $RTeCl_3$ respectively. Equation (4) applies whether solutions of Na_2SO_3 or of $Na_2S_2O_5$ are used. Equations (5)—(8) were used in the data analysis for the

$$k_{obs.}t = \ln[(A_f - XA_t)/(A_f - A_t)] \qquad (5)$$

$$k_{obs.} = k_2(n[S] - 3[Te]) \qquad (6)$$

$$k_{obs.}t = \ln[(A_f - A_t/X)/(A_f - A_t)] \qquad (7)$$

$$12\varepsilon k_2 t/n = A_t/[A_f(A_f - A_t)] \qquad (8)$$

reductions using either reagent. In these equations the subscripts 0, f, and t represent initial data, final data, and data at time t respectively. The other symbols used in the equations are A, the absorbance at 400 nm, and $X = 3[Te]/n[S]$; n takes the value of 2 for sulphite and 4 for metabisulphite. When the reducing agent was in excess, equations (5) and (6) were used; when the oxidising agent was in excess, equation (7) was used. Note that the definition of $k_{obs.}$ is kept unchanged and so its sign will change as the reaction moves from the conditions of equation (5) to those of equation (7). Under conditions where the reagents are present in stoicheiometric quantities the rate equation becomes (8), where ε is the absorption coefficient of the ditelluride.

In Tables 1—4 are presented the majority of our experimental data, those obtained in 75% (by volume) dioxane. In all cases covered by Tables 1—4 the reagent solutions were initially neutral. Table 1 lists those data that prove the applicability of equations (4)—(8), while Tables 2—4 present data obtained at differing temperatures, hydrogen ion concentrations, and ionic strengths. Table 5 contains the data obtained by varying the solvent composition from 41.7 to 83.3% (by volume) dioxane.

When the composition of the solvent is taken to higher percentages of dioxane the reaction profile ceases to fit the integrated form of the normal second-order rate equation. At 93% dioxane, the best compromise value for low-water content studies, the plot of product concentration *versus* time shows a definite sigmoidal shape as can be seen in the Figure (a). A different equation then fits the data. We found that the autocatalytic equations (9) and (10) provide a good fit, where $Z = (A_t - A_0)/(A_f - A_0)$ and $Y = 2[H^+]_0/9[Te]_0$.

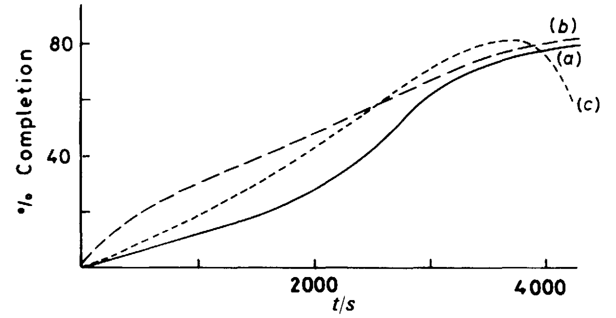

Figure. Plots of product concentration (% completion of reaction) *versus* time for the reduction of $RTeCl_3$ (1.25×10^{-3} mol dm^{-3}) to R_2Te_2 in water–dioxane, (*a*) 7:93, (*b*) as (*a*) but after pre-treatment of dioxane with water (1:47 v/v); and (*c*) with 1 mol dm^{-3} H_2SO_4 (1:47 v/v)

$$k_{obs.}t = \ln [(1 + Z/Y)/(1 - Z)] \qquad (9)$$

$$k_{obs.} = 4.5k_1[Te]_0(1 + Y) \qquad (10)$$

While such kinetic analyses can lead to false deductions, the internal consistency of our computed results suggests that the treatment is valid, and derives from reactions (11) and (12). The

$$RTeCl_3 + nH_2O + H^+ \xrightarrow[\text{slow}]{k_1} \text{first products} \qquad (11)$$

first products are $4H^+$, 3 Cl^-, and aryltellurate species such as $RTeO_2^-$. The values of k_1, $k_{obs.}$, and Y obtained are collected in

$$RTeO_2^- + SO_2OH^- \longrightarrow \{RTe(O)\text{-}O\text{-}SO_2OH^{2-}\} \longrightarrow RTeO^- + SO_4^{2-} + H^+ \qquad (12)$$

Table 6. Trial experiments showed that both reducing agents behave in the same way under these conditions also, and so sulphite was not studied in detail.

We also made the qualitative observation that the rate of the reaction appeared to be independent of the concentration of $S_2O_5^{2-}$. Because of the concentration ranges available at this low water content (7%) we could not obtain enough experimental data to provide rate constants over a range of reductant concentrations; however we note that the form of the observed rate equation is independent of the reductant concentration.

Curves (*b*) and (*c*) of the Figure show the results of extra experiments intended to check the cause of the rate change. In most of our kinetic experiments the tellurium-containing reagent first comes into contact with water when its solution in dioxane is mixed with an aqueous dioxane solution of the reducing agent at the start of the experiment. Curve (*b*) shows the effect of adding a small amount of water (1 cm^3) to the reactant solution of $RTeCl_3$ in dioxane (47 cm^3) and allowing it to stand for 30 min before mixing the reactants together. Curve (*c*) shows the results obtained using sulphuric acid (1 mol dm^{-3}, 1 cm^3) in place of water.

Discussion

Both sodium salts give essentially the same values for their second-order rate constants and activation parameters. When the data for varying temperatures are treated separately, the values of $\Delta H^‡$ are determined to be 22.4 ± 0.6 kJ mol^{-1} with Na_2SO_3 and 25.5 ± 0.8 kJ mol^{-1} for $Na_2S_2O_5$; the corresponding values of $\Delta S^‡$ are -164 ± 2 and -154 ± 2 J K^{-1} mol^{-1}. Therefore both can be regarded as equivalent even in this mixed solvent system.

Table 5. The variation of the rate of reaction at 25 °C with the solvent composition for reduction of 1.25×10^{-3} mol dm^{-3} $RTeCl_3$ with Na_2SO_3 and $Na_2S_2O_5$

Percentage dioxane[a]	D[b]	$k_2/dm^3\ mol^{-1}\ s^{-1}$	
		Na_2SO_3[c]	$Na_2S_2O_5$[c]
41.7	52.0	8.23	
50.0	49.7	7.88	7.24
58.3	47.8	5.64	5.24
66.7	45.8	3.35	3.30
75.0	43.9	2.20	2.14
83.3	41.7	1.41	1.49

[a] By volume. [b] Dielectric constant. [c] 6.25×10^{-4} mol dm^{-3}.

Table 6. The variation of the rate constant (k_1) in dioxane (93% by volume) at 25 °C using 4.5×10^{-4} mol dm^{-3} $Na_2S_2O_5$

$10^4[RTeCl_3]$/ mol dm^{-3}	$10^3 Y$*	$10^4 k_{obs.}/s^{-1}$	$k_1/dm^3\ mol^{-1}\ s^{-1}$
6.25	85	9.2	0.30
5.20	61	7.5	0.30
4.40	49	6.2	0.30
3.90	30	5.4	0.30

* $Y = 2[H^+]_0/9[Te]_0$.

In order to deduce a mechanism for the reaction we first consider the data obtained at low water content. When $RTeCl_3$ is dissolved in pure dioxane it retains its original yellow colour. This colour quickly and completely disappears when water or any aqueous solution is added to it (much more quickly than reduction can produce ditelluride). Thus the tellurium-containing reagent which is reduced is not the original trihalide but a hydrolysis product. This deduction is confirmed by the observation that the expected drop in pH occurs before ditelluride formation is apparent.

When the solvent composition is altered to give water percentages below 12% there is a clear change of shape of the reaction profile. It takes on a distinctly sigmoidal shape (Figure). The reaction is also markedly slower than in our normal 25% water mixture. A change in the slow step of the overall reaction sequence must have occurred. Probably an initial hydrolytic step is now rate determining. There are solubility problems in working at such low water contents, but we were able to follow runs at various initial tellurium concentrations but a fixed reductant concentration, and the data of Table 6 were obtained.

In studies of the methanolysis of $RTeCl_3$, which are in progress, we have observed that the replacement of Te–Cl by Te–OMe is autocatalytic due to the production of H^+. The autocatalytic rate equation observed here is probably similar, Te–OH formation having become rate determining. Equation (9) can be used to describe the slow first reaction (11), where n is a constant. This must be followed by a set of faster steps leading to the final products.

Further support for this sequence comes from the reaction profiles shown in the Figure. Curve (*a*) represents a normal reaction while curve (*b*) shows the results obtained when a small quantity of water is added to the dioxane solution of the trichloride and the mixture allowed to stand for a time before the reduction reaction is begun. The rate of formation of ditelluride is initially faster, but it is little altered in the later stages of reduction. This is consistent with the prior partial hydrolysis of the trichloride. The initial concentration of H^+ will be markedly greater, but since the water content of the reaction mixture is little changed the rate of the greater portion of the reaction will be little affected. Curve (*c*) is obtained when 1 mol dm^{-3} sulphuric acid, rather than water, is added to the stock solution of the oxidant (equivalent to making the reaction solution 1.04×10^{-2} mol dm^{-3} in the acid). A back reaction in a late stage of the reduction sequence becomes demonstrable, while before that the curve does not show a great increase in rate. We argue below that in 75% dioxane the tellurium-containing reactant is anionic. Here the protonation of that ion counteracts the effect of increasing the rate of step (11).

In summary, studies at low water contents show that the first stage of the overall reaction is the conversion of Te–Cl to Te–OH or $Te–O^-$ bonds in acid-catalysed hydrolysis reactions.

Most of our data refer to reactions in 75% dioxane, in which the only rate-determining step is first order in each of the reagents. The facts that the reduction occurs after hydrolysis has produced Te–O bonds, that the activation entropy is negative, and that there is SO_4^{2-} but no $S_2O_6^{2-}$ amongst the products, lead us to the view that the slow step is an inner-sphere reaction in which two electrons are transferred. As there is no known chemistry of Te^{III} while Te^{II} is known, the slow step is likely to involve the reduction of Te^{IV} to Te^{II}.

We have determined the rate of this step as a function of pH, see Table 3. There is no indication of any acid catalysis once hydrolysis has been effected. In fact there is a pH region (4—9) over which the rate does not vary with acidity. Outside this range the reaction shows a slight inverse dependence on $[H^+]$. This behaviour is most reasonably explained by the presence of a telluric acid and its derived ions, RTeO(OH), $RTeO_2^-$, or $RTeO_2(OH)^{2-}$. Telluric acids are known as stable compounds that can be isolated as white solids. In solution the various ions will be in rapid equilibrium with each other, and all seem able to react with the reducing agent at comparable rates. The data at differing values of pH are consistent with p*K* values of *ca.* 3 and 11 for the two protonation–deprotonation equilibria [(iii) and (iv) of the Scheme]. Thus in the pH range 4—9 almost all the tellurium reagent will be present as $RTeO_2^-$. We have found support for this deduction in the following independent measurements.

When small amounts of sodium sulphate are added to the reaction mixture the rate of reaction increases, as one would expect for a reaction between like-charged reagents. There are problems in interpreting such data for mixed solvent systems because of the preferential interaction between ions and the water component in dioxane–water mixtures,[13] because salts can alter the ionizing power of poorly ionizing solvents,[14] and because of the onset of ion pairing.[15] Nevertheless it is reasonable to deduce that the main reaction pathway at all but low pH involves like, negatively charged reagents.

An alternative source of information on the charges of the reagents is provided by data at differing solvent ratios and dielectric constants, see Table 5. The range of dielectric constants is 41.7—52.0.[16] A plot of ln k_2 *versus* $1/D$ is fitted by a straight line of gradient -410 ± 20. Therefore we again deduce that the reaction involves like-charged reagents.[17]

A two-electron, inner-sphere reduction of the tellurate ion, $RTeO_2^-$, accompanied by oxygen atom transfer, will yield $RTeO^-$ which would be rapidly protonated to RTeOH. Therefore the slow step can be written as equation (12).

Compounds of the type R′TeX, where X = Cl, Br, I, CNS, *etc.*, and R′ = aryl, have been prepared from the reduction of $R'TeCl_3$,[18,19] but not so far with X = OH. When the compound 2-naphthyltellurium iodide is hydrolysed in strongly basic medium it disproportionates yielding a mixture of R'_2Te_2 and $(R'TeO)_2O$.[20] R′TeOH might have been formed but it must be unstable under the reaction conditions employed. Therefore if our evidence favours the formation of an $RTeO^-$ intermediate, it should have only a short lifetime, as our rate data require.

$$RTeCl_3 + H^+ + 2H_2O \longrightarrow RTeO(OH) + 4H^+ + 3Cl^- \qquad \text{(i)}$$

$$RTeO_2^- + HSO_3^- \longrightarrow RTeO^- + H^+ + SO_4^{2-} \qquad \text{(ii)}$$

$$RTeO^- + H^+ \rightleftharpoons RTeOH \qquad \text{(iii)}$$

$$2RTeOH \rightleftharpoons R(HO)TeTe(OH)R \qquad \text{(iv)}$$

$$R(HO)TeTe(OH)R + HSO_3^- \longrightarrow [RTeTe(OH)R]^- + 2H^+ + SO_4^{2-} \qquad \text{(v)}$$

$$[RTeTe(OH)R]^- + H^+ \longrightarrow RTeTeR + H_2O \qquad \text{(vi)}$$

Scheme. R = C_6H_4OEt-*p*. At different pH values RTeO(OH) and $RTeO_2(OH)^{2-}$ may also be involved in stage (ii)

The overall formation of diaryl ditelluride is quantitative; no tellurium metal is precipitated nor are any other tellurium-containing side-products, or $S_2O_6^{2-}$, detected. Therefore we believe that a Te–Te dimer is formed before its two-electron reduction from Te^{II} to Te^{I} occurs. The reported[20] products of the hydrolytic disproportionation of 2-naphthyltellurium iodide are also explicable on the basis of dimerization.

One possible pair of reactions of the dimer that we eliminate from further consideration are equations (13) and (14). We find

$$R(HO)TeTe(OH)R \longrightarrow RTeTeR + H_2O_2 \qquad (13)$$

$$H_2O_2 + HSO_3^- \longrightarrow H_2O + H^+ + SO_4^{2-} \qquad (14)$$

that in solution hydrogen peroxide reacts rapidly with R_2Te_2. The reaction can yield a mixture of products including Te and probably involves radicals, *cf.* ref. 3. These findings are inconsistent with the clean quantitative reaction described here. Therefore we suggest the overall mechanism in the Scheme for the reaction. The steps up to and including the formation of $RTeO^-$ are well based in experiment; the subsequent steps are speculative.

Conclusions

When aqueous dioxane is used as the solvent medium for the homogeneous reduction of an aryltellurium trichloride by either sulphite or metabisulphite the overall reactions yield R_2Te_2 quantitatively. The reagents in the first oxidation–reduction reaction are the same in both cases. A hydrolysed tellurium species $RTeO_2^-$ is reduced by HSO_3^- to give $RTeO^-$. This tellurium(II) intermediate is believed to undergo dimerization before being reduced by another mole of bisulphite to the ditelluride.

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