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A Kinetic and Mechanistic Study of the Reduction of an Aryltellurium Trichloride by Chromium(II) and Vanadium(II) Ions

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Abstract

The reduction of an aryltellurium trichloride by Cr^{2+} and V^{2+} in aqueous dioxane solutions has been investigated. The reactions are quantitative forming the ditelluride and M^{III} products. The reaction sequence begins with hydrolysis which leads to rapidly maintained equilibria between RTeO(OH), RTeOCl and $RTeO_2^-$. The first reductive step is rate determining, and is believed to be a one-electron, inner-sphere process. Reactions involving the use of the Te–OH group to form the bridge are slower than those using Te–Cl or Te–O^-. Rate data were measured over a range of experimental conditions; rate and activation parameters are quoted. A few experiments using the outer-sphere reductant $[Ru(NH_3)_6]^{2+}$ are also reported. Reduction still occurs, but at a slower rate than with the Cr^{2+} and V^{2+} ions.

Introduction

There are few reports of detailed mechanistic studies of compounds containing the heavier p-block elements. Although most of the reactions are likely to be similar to those of the lighter elements, the larger sizes of the atoms and the weaker bonds formed may allow some reactions to proceed by routes not previously found. We are investigating this area using compounds containing the aryltellurium moiety. The diarylditellurides, RTeTeR, are especially useful in this context as they exhibit strong absorptions in the visible region. In this paper we describe the reduction of an aryltellurium trichloride to the ditelluride, $RTeCl_3$ to RTeTeR, by one-electron reductants.

It is usually necessary, as here, to work in mixed aqueous solvents to obtain homogeneous conditions for such reduction. Under these conditions the rapid hydrolysis of the trihalide precedes its reduction, as we found for reduction by sulphite in aqueous dioxane [1]. The hydrolysis products of $RTeCl_3$ in moist air, and in various aqueous media have been identified already by other workers [2–5]. Usually RTeOCl is the product isolated, although a halide free species could have been present in solution. In this paper we report the equilibrium constant for the loss of that chloride. Methanolysis follows a similar route and its mechanism has been more thoroughly investigated. The substitution of coordinated halide was found to be acid catalysed [6]. Therefore, when reductions are carried out in acidic media hydrolysis is expected to be rapid. Subsequent inner-sphere reactions could use either Te–O or Te–Cl for bridging. The reaction with the two-electron reductant sulphite follows an inner-sphere mechanism involving the formation of a Te–O–S bridge, and the first reductive step from the stable Te^{IV} oxidation state is rate determining [1]. The studies described here use one-electron reductants to assess the likelihood of an outer-sphere reduction taking place. The tellurium containing reagent used is $RTeCl_3$, where R represents the *para*-ethoxyphenyl group. This group yields compounds that are easily prepared in a pure state.

Results and Discussion

A few experiments on the reduction of $RTeCl_3$ by the substitution inert $[Ru(NH_3)_6]^{2+}$, which is known as an outer-sphere, one-electron reductant [7], were carried out under a nitrogen atmosphere. The reaction is very slow. It is difficult to follow accurately as the visible absorptions of the ruthenium(II) reagent, at 410 nm, and the ditelluride product, at 400 nm, are close together. Also precipitation occurs when $[Ru(NH_3)_6]Cl_2$ in water is added to $RTeCl_3$ in dioxane, if the solutions are too concentrated. For a solution containing 9.3×10^{-4} mol dm^{-3} $RTeCl_3$ and 5.1×10^{-3} mol dm^{-3} $[Ru(NH_3)_6]Cl_2$ in aqueous dioxane (1:1 vol./vol.) at 25 °C, the initial rate constant describing the increase of absorbance at 400 nm is approximately 10^{-4} s^{-1}. This indicates a second order rate constant of approximately 0.04 dm^3 mol^{-1} s^{-1}. We did not proceed further with these studies because of the experimental problems involved.

Reduction to ditelluride by either Cr(II) or V(II) is markedly faster than by $[Ru(NH_3)_6]Cl_2$ and there is no difficulty in following spectral changes at the

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absorption maximum of the ditelluride. Therefore we investigated these reactions in more detail. In all instances the reductants were used within one day of their preparation, a time over which we detected no change in their concentrations. The results of potentiometric and spectrophotometric titrations show that $RTeCl_3$ is quantitatively reduced to Te_2R_2 by both Cr(II) and V(II) in aqueous dioxane solutions, and that the stoichiometric ratio $RTeCl_3$: M(II) is 3:1 in both cases. We have investigated the metal-containing products, but obtained from experiments at higher concentrations than those used for kinetic studies. They show an oxidation state increased by one unit. The vanadium product was shown to be solvated V(III) by comparing the visible spectrum of a completed reaction solution with the spectra of known vanadium compounds dissolved in the same medium (1:3 vol./vol. aqueous dioxane). A more thorough characterisation of the chromium product was made. Thin layer chromatographic studies on silica gel of product solutions showed only one chromium containing species. In one experiment we isolated $[CrCl(H_2O)_5](SO_4)$ as a single product, in good yield. It was characterised by its visible spectrum and by elemental analysis. Comparison of its spectrum, superimposed on that of the diarylditelluride, with the solution spectrum before product isolation showed no detectable differences. Therefore, at initial Cr(II) concentrations of 0.05 and 0.15 M $RTeCl_3$, the main or sole product containing Cr(III) is the mono-chloro complex.

In preliminary experiments we noted that the formation of a homogeneous mixture when water and dioxane are brought together can take several seconds. Therefore experimental conditions for kinetic studies were chosen to give slow reactions and so eliminate problems due to the slow mixing. One consequence is that we rarely worked with one reagent in a large excess. This is reflected in the rate equation fitted to the data, eqn. (1), and in the tabulated information.

Kinetic results for reduction by Cr(II) are considered first. When an aqueous solution containing Cr(II) is added to a dioxane solution of the aryltellurium trichloride the rate of reduction to ditelluride depends on the acidity of the mixture. A convenient acid concentration was selected and experiments to determine the order of reaction are summarised in Table 1. A reaction producing a dimeric product from reagents in a 3:1 stoichiometric ratio, whose rate determining step is first order in each reagent, can be described by eqn. (1). This has the same form as the commonly met equation for reactions with 1:1 stoichiometry and monomeric products. It differs only in the presence of the proportionality constants of 2 and 3. We found that this equation fits our observed data to at least 90% completion. Therefore one step in the overall reaction sequence proposed later in this paper is much slower than the rest and is rate determining.

TABLE 1. Effect of the concentration of the reductant on the calculated second order rate constant for reactions in aqueous dioxane (1:3 vol./vol.) at 25 °C with an initial $RTeCl_3$ concentration of 5×10^{-4} mol dm^{-3}

Reductant	Concentration ($10^{-3} \times$ M)	k (dm^3 mol^{-1} s^{-1})
Cr(II)[a]	1.93	15.2
	2.06	15.0
	2.50	15.0
	3.18	15.2
	4.00	15.1
V(II)[b]	1.72	6.93
	2.00	6.99
	2.30	6.95
	2.60	6.96

[a] 0.235 M H_2SO_4. [b] 0.250 M H_2SO_4.

$$\ln\{[A](2[M] - 3[D])/([M](2[A] - 3[D]))\} = k([M] - 3[A])t \quad (1)$$

Here $[A]$ and $[M]$ represent the initial concentrations of $RTeCl_3$ and the reductant M^{2+} ion respectively, and $[D]$ is the concentration of RTeTeR at time t. The rate constants quoted in the Tables were determined by fitting experimental data to this equation, using the method of least-squares, and were found to be reproducible.

The effect of the sulphuric acid concentration on the reduction is seen in the data of Table 2. In our studies of the reduction of $RTeCl_3$ by SO_3^{2-} we worked over a pH range from 3 to 11. The rate constants were almost independent of pH except near the ends of the range. We attributed that to the protonation equilibrium (2) with a $pK_a < 3$, and to a

TABLE 2. The effect of acid concentration on the rate of reduction of 5×10^{-4} M $RTeCl_3$ by 2.00×10^{-3} M Cr^{2+} in aqueous dioxane (1:1 vol./vol.) at 25.0 °C

$[H^+]$ (M)	k (dm^3 mol^{-1} s^{-1})	
	observed	calculated[a]
0.042	32.4	31.3
0.052	30.2	29.6
0.073	24.0	26.8
0.157	22.7	20.9
0.209	19.1	19.0
0.260	17.0	17.8
0.469	15.2	15.1
0.521	14.9	14.8
0.625	13.4	14.2

[a] $k = (11\,[H^+] + 44K)/([H^+] + K)$, $K = 0.067$ (i.e. $pK_a = 1.2$).

further equilibrium between $RTeO_2^-$ and $RTeO_2(OH)^{2-}$ with a pK_a value >11 [1]. The data of Table 2 also show the effect of such a protonation.

$$\underset{(a)}{RTeO(OH)} \rightleftharpoons \underset{(b)}{RTeO_2^-} + H^+ \qquad (2)$$

A least-squares treatment can be used to separate out from the overall rate constant the values of the rate constants for the reduction of (a) and (b), and the appropriate ionisation constant. In the final column of Table 2 we list calculated second order rate constants obtained using 1.2 for the pK_a value, and rate constants of 11 and 44 for the reduction of (a) and (b) respectively. The relative magnitudes of k_a and k_b are consistent with reactions with a cationic reagent. At the acidities used in all the remaining experiments, the effect of $RTeO_2^-$ on the overall reaction being observed is small.

Added chloride ions, on their own, have an effect on the tellurium-containing reagent. In the absence of Cr(II) the ultra-violet absorption spectra of solutions formed from $RTeCl_3$ change with the concentration of added chloride (see Table 4). The changes in absorbance at the 278 nm peak can be explained using equilibrium (3)

$$RTeO(OH) + H^+ + Cl^- \rightleftharpoons RTeOCl + H_2O \qquad (3)$$

A least-squares treatment of the observed data yields a value of 82 for the ratio $[RTeOCl]/\{[RTeO(OH)][Cl^-]\}$ under the specified conditions, while the extinction coefficients of RTeO(OH) and RTeOCl are determined to be 2500 and 18 000 $mol^{-1}\ dm^3\ cm^{-1}$ respectively. The final column of Table 4 contains expected absorption data calculated from these values.

TABLE 3. The effect of added KCl on the rate of reduction of 5×10^{-4} M $RTeCl_3$ in aqueous dioxane (1:3 vol./vol.) at 25.0 °C using 2.00×10^{-3} M Cr^{2+} and 0.235 M H_2SO_4

$[KCl] \times 10^{-3}$ (M)	k ($dm^3\ mol^{-1}\ s^{-1}$)	
	Observed	Calculated[a]
0	15.1	15.1
1.56	17.5	17.8
3.65	20.1	20.5
5.73	22.7	22.7
7.81	24.7	24.5
9.38	25.9	25.6

[a] $k = (12 + 41\,K'\,[Cl^-]_{total})/(1 + K'\,[Cl^-]_{total})$, $K' = 82$.

When the rate constants of Table 3 are plotted against the absorbances at 278 nm for the reaction solutions, at time $t = 0$, as calculated from the data of Table 4, a very good straight line graph is obtained. Obviously both values are controlled by the same equilibrium (3). Therefore the rate determining step in the overall reaction sequence must be the first reductive step: of RTeO(OH) or RTeOCl to a more reactive species such as RTeO(solv). Using the spectrophotometrically determined equilibrium constant, the rate constants for the reduction of RTeO(OH) and RTeOCl can be calculated to be 11 and 42 $dm^3\ mol^{-1}\ s^{-1}$ respectively. The calculated rates given in Table 3 were determined from these values and the equilibrium constant. The order of reactivity of the aryltellurium(IV) species is

TABLE 4. The effect of added KCl on the absorbance at 278 nm of a solution of 1.5×10^{-4} M $RTeCl_3$ in aqueous dioxane (1:3 vol./vol.) at 25.0 °C containing 0.235 M H_2SO_4

$[KCl] \times 10^{-3}$ (M)	Absorbance	
	Observed	Calculated[a]
0	0.467	0.463
1.02	0.653	0.630
2.03	0.773	0.772
6.09	1.16	1.19
10.2	1.51	1.46
14.2	1.61	1.65
18.3	1.75	1.79

[a] Absorbance = $(0.38 + 2.7\,K'\,[Cl^-]_{total})/(1 + K'\,[Cl^-]_{total})$, $K' = 82$.

$$R(O)Te{-}OH < R(O)Te{-}Cl \doteqdot R(O)Te{-}O^-$$

Under the conditions of most of our experiments, the major reaction pathway for the reduction of Te(IV) must be via RTeO(OH). That is the case for the data of Table 5, for experiments carried out at different temperatures. The activation enthalpy and entropy for the reduction are calculated to be (24 ± 0.4) kJ mol^{-1} and (−140 ± 2) J $mol^{-1}\ K^{-1}$ respectively.

TABLE 5. Variation of rate constants with temperature for reactions in aqueous dioxane (1:3 vol./vol.) using 5.00×10^{-4} M $RTeCl_3$

Temperature (°C)	Rate constants ($dm^3\ mol^{-1}\ s^{-1}$)	
	Cr(II)[a]	V(II)[b]
15	12.4	4.9
20	14.7	6.1
25	17.9	6.8
30	21.2	7.9
35	25.3	8.7
40		10.5
45		11.6

[a] 2.00×10^{-3} M Cr^{2+} and 0.125 M H_2SO_4. [b] 2.30×10^{-3} M V^{2+} and 0.250 M H_2SO_4.

TABLE 6. The effect of the solvent composition on the rate of reaction between 5×10^{-4} M $RTeCl_3$ and 2.00×10^{-3} M Cr(II) at 25 °C and at 0.235 M H_2SO_4

Dioxane by volume (%)	Dielectric constant (Debyes)	k (dm^3 mol^{-1} s^{-1})
50.0	49.7	29.4
55.2	48.1	29.1
59.4	47.1	22.6
63.4	46.1	20.5
67.7	45.0	18.8
71.9	44.0	15.9
75.0	43.7	15.4
76.0	43.1	14.2
80.2	42.1	13.9

The last set of rate data for reduction by the chromous ion are those of Table 6, which show the effect of varying the water:dioxane ratio in the solvent. As the water content drops, so too do the dielectric constant of the medium and the observed rate constant. Such variations are sometimes used as guides to reaction mechanism, see for example ref. 8. That is consistent with the mechanistic scheme given below, but we do not press the argument here.

When the reductant used is V^{2+}, rather than Cr^{2+}, the metal containing product is V^{3+}solv. Therefore we again deduce that the reaction involves a sequence of one-electron steps. Again the rate increases with added chloride. The fit of observed to calculated rate constants assuming that equilibrium (2) applies is shown in Table 7. The data of Table 5 give values of $\Delta H^{\ddagger} = (18.6 \pm 0.8)$ kJ mol^{-1} and $\Delta S^{\ddagger} = (-166 \pm 3)$ J mol^{-1} K^{-1}. Rate constants and activation parameters are very similar for both M^{2+} reductions.

In our view the results we have obtained can be used to argue that the mechanisms for the reductions by Cr^{2+} and V^{2+} follow inner-sphere pathways. For example Toppen and Linck [9] have shown that for outer-sphere reactions in aqueous solution the ratio $k_{Cr(II)}/k_{V(II)}$ is approximately 0.02. Here the ratio is 3.4 at the same acid concentration. Although we are working in a different medium, a mixed aqueous solvent, that ratio suggests an inner-sphere mechanism. A comparison of the rates of reduction by Cr^{2+} and V^{2+} with that seen using the outer-sphere reagent $[Ru(NH_3)_6]^{2+}$ also favours the assignment of an inner-sphere mechanism for the first row ions. When those ions behave as outer-sphere reductants they do so more slowly than does the ruthenium reagent [7], e.g. a ratio of $k_{V(II)}/k_{Ru(II)}$ of 0.2 has been found [7]. Using our estimated rate constant for the reduction of $RTeCl_3$ by $[Ru(NH_3)_6]^{2+}$, a value of 0.008 dm^3 mol^{-1} s^{-1} can then be deduced for the expected rate for its outer-sphere reduction by V^{2+}. The rate constant observed by us is almost 10^3X greater than that, and is therefore attributable to a different mechanism; inner-sphere.

TABLE 7. The effect of added KCl on the rate of reduction of 5×10^{-4} M $RTeCl_3$ in aqueous dioxane (1:3 vol./vol.) at 25.0 °C using 2.30×10^{-3} M V^{2+} and 0.25 M H_2SO_4

[KCl] $\times 10^{-3}$ (M)	k (dm^3 mol^{-1} s^{-1})	
	Observed	Calculated [a]
0	6.95	7.8
0.31	8.10	8.2
0.73	8.85	8.7
1.04	9.47	9.1
3.13	12.1	11.3
5.21	13.2	13.1
7.29	14.3	14.4
9.38	15.1	15.6

[a] $k = (5.4 + 27 K' [Cl^-]_{total})/(1 + K' [Cl^-]_{total})$, $K' = 82$.

The activation parameters for the M^{2+} ion reductions also indicate an inner-sphere process. The large negative entropy changes are typical of associative processes, while the value are comparable with results obtained by other workers for various inner-sphere Cr^{2+} and V^{2+} reductions [7, 10]. The RTeO(OH)/RTeOCl equilibrium constant can be used to show that >95% of the tellerium-containing reagent is present as RTeOCl at the concentrations needed for product isolation; while only 10% is in this form in the kinetic experiments. Therefore product isolation is only a guide to the mechanism operating for a minor reagent. The identification of $[CrCl(H_2O)_5]SO_4$ indicates that RTeOCl also follows an inner-sphere route via Te–Cl–Cr.

Conclusions

Since it is possible to reduce in solution aryltellurium(IV) species to ditelluride using $[Ru(NH_3)_6]^{2+}$ as the reductant, albeit slowly, outer-sphere one-electron mechanisms must be feasible for these heavy typical element reagents. Inner-sphere reductions by Cr^{2+} and V^{2+} are much faster, but still proceed one-electron at a time. The first step in the overall reaction sequence, reduction from Te(IV) to Te(III), is rate determining and proceeds via a Te–O–M^{II} or a Te–Cl–M^{II} bridge. Therefore we suggest Scheme 1 for the major route for reduction by Cr^{2+} in acid.

Experimental

The preparation of *p*-ethoxyphenyltelluriumtrichloride has already been reported [1]. All other reagents used were of AnalaR grade and, if liquid, were dried and redistilled prior to their use. Stock solutions of chromium(III) sulphate were prepared

$$RTeCl_3 + 2H_2O \longrightarrow RTeO(OH) + 3Cl^- + 3H^+$$

$$RTeO(OH) \rightleftharpoons RTeO_2^- + H^+$$

$$RTeO(OH) + H^+ + Cl^- \rightleftharpoons RTeOCl + H_2O$$

$$RTeO(OH) + Cr^{2+}(aq) \longrightarrow RTeO + [Cr(OH)(H_2O)_5]^{2+} \text{ r.d.}$$

$$RTeOCl + Cr^{2+}(aq) \longrightarrow RTeO + [CrCl(H_2O)_5]^{2+} \text{ r.d.}$$

$$2RTeO + 4Cr^{2+}(aq) \longrightarrow RTeTeR + 4Cr^{III}$$

Scheme 1.

from the trioxide and sulphuric acid. Vanadyl sulphate was used to make up the vanadium stock solution. These solutions were reduced using zinc amalgam under an atmosphere of nitrogen [11]. The resulting solutions, containing M(II) ions, were stored under nitrogen, analysed by potentiometric titration, and prepared freshly each day. We found no difference between titration data for these solutions obtained at the start and at the end of the working day. The nitrogen gas was passed through a solution containing chromous ions before being admitted to the working solutions.

The following procedure was carried out under a nitrogen atmosphere with deoxygenated solutions, to prepare an isolable quantity of the chromium-containing product, free of zinc contamination. Solid chromous sulphate was prepared from a 0.1 M stock solution (75 cm^3) by first adding a sodium acetate solution to precipitate the brick red-coloured chromous acetate. This was then re-converted to the pale blue sulphate by stirring it thoroughly with sulphuric acid. The solid was filtered off, and washed with a small quantity of cold methanol, before being dissolved in distilled water (10 cm^3). This solution was added at room temperature to a slight excess of a 0.1 M solution of $RTeCl_3$ in dioxane (25 cm^3). After half an hour the organotellurium species were completely removed by solvent extraction into diethyl ether, while the green-coloured aqueous layer was washed several times with ether. It was then concentrated under reduced pressure at 30 °C until precipitation occurred. The solid product (yield 60% based on Cr) was filtered off, washed with water, and dried over P_2O_5 *in vacuo*. Physical and analytical data are all consistent with $[CrCl(H_2O)_5]SO_4$. *Anal.* Found: H, 3.75; Cl, 12.3; Cr, 18.9; S, 12.7. Calc.: H, 3.66; Cl, 12.8; Cr, 19.0; S, 11.7%.

All reactions were investigated kinetically using a Pye Unicam SP8-100 spectrophotometer fitted with a rapid mixing device, and under an atmosphere of nitrogen. Reactions were initiated by mixing together a solution of the aryltellurium trichloride in pure dioxane with the appropriate solution of reducing agent in aqueous dioxane. They were then followed for several half lives. Data were then manipulated using least-squares computer programs written for an Apple IIe microcomputer.

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