A Kinetic and Mechanistic Study of the Solvolysis of Aryltellurium Trihalides in Organic Solvents

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When an aryltellurium trichloride reacts with methanol in a mixed solvent also containing benzene or dioxane the reaction can be followed by monitoring the generation of acid. The first Te–Cl bond cleavage is acid catalysed and is rate determining. It exhibits a small activation enthalpy, but a large and negative activation entropy. The other trihalides have similar activation parameters. The mechanism is believed to involve protonation of a co-ordinated Cl, with dissociative loss of HCl being rate determining. The compounds RTe(O)Cl and $RTe(OMe)_2Cl$ have been isolated as solid products but, since the reactions occurring in solution are reversible, the products in dilute solution may be different from these. Kinetic experiments to study the variation of rate with the solvent composition and the nature of the alcohol are also reported, as are results of reactions in aqueous dioxane.

A common first step during the reduction of aryltellurium trihalides, $RTeX_3$, in mixed aqueous solvents is the hydrolysis of at least one Te–X bond.[1] As we are studying oxidation–reduction reactions involving organotellurium compounds we need more information on their solvolysis reactions, hence the work described here. The hydrolysis products of $RTeX_3$ in moist air, and in various aqueous media, have been identified already by other workers,[2–4] and a mechanism for the hydrolysis in solution has been proposed, but it was based only on product isolation.[5] In this paper we describe the results of kinetic studies of the alcoholysis of $RTeX_3$ in mixed solvents, where R represents the *p*-ethoxyphenyl group and X = Cl, Br, or I. We used mainly methanol rather than water as the reagent since this gives slower reactions during which both reagents and products remain in solution, while the *p*-ethoxyphenyl group yields compounds that are easily prepared in a pure state.

Results and Discussion

We have studied the reactions between the $RTeX_3$ compounds and methanol in mixed benzene–methanol and dioxane–methanol media. The reactions were initiated by rapidly mixing together the trihalide, dissolved in the pure inert component, with the appropriate methanol-containing mixture. As the reaction proceeds the yellow/orange colour of the trihalide fades and the acidity of the solution increases, typically taking several minutes to reach completion. We found it easiest to follow the reaction by monitoring the change in pH-meter readings.

We have isolated and characterised the reaction products, but they are probably different from those present in the colourless, dilute solutions which occur at the end of kinetic experiments. Some HCl can be removed under reduced pressure from such solutions and trapped in silver nitrate solution, but the yield of silver chloride is low and not reproducible.

Upon concentration, the colour of these solutions always reverts to that of the trichlorides, and a precipitate forms if the concentrations are high enough. Using repeated precipitation and dissolution cycles, white RTe(O)Cl can eventually be obtained. A similar product has been reported when $R'TeCl_3$ is hydrolysed under acidic conditions.[5] The isolated product is free from halide only when that hydrolysis is carried out under alkaline conditions. We have obtained a different white solid, $RTe(OMe)_2Cl$, after treating methanolic solutions of $RTeCl_3$ with NaOMe (mol ratio of 1:3.1).

We therefore reason that the R–Te bonds are not affected in the reaction between $RTeCl_3$ and methanol in organic solvents, which involves only the substitution of Te–OMe bonds for TeCl, and that the reaction is reversible. When the concentration of tellurium-containing species is low and the mole fraction of methanol present is not small, at least two and perhaps all three of the Te–Cl bonds are replaced to produce either $RTe(OMe)_2Cl$ or $RTe(OMe)_3$.

Table 1. Variation in observed rate constant with the initial concentration of $RTeCl_3$ at 25 °C in benzene–methanol (5:1, v/v)

10^5 Initial $[RTeCl_3]$/ mol dm^{-3}	$k_{obs.}$/ s^{-1}	$k_{obs.}(3[RTeCl_3])^{-1}$/ dm^3 mol^{-1} s^{-1}	Final meter reading
9.34	0.613	2 190	0.45
6.96	0.461	2 210	0.60
4.91	0.311	2 110	0.63
3.03	0.194	2 130	0.82
1.33	0.148	3 710	1.15

Although the response of a glass electrode in alcohol–water mixtures is virtually unimpaired at compositions below 90% (w/w) alcohol,[6] that is not the case in our solvent systems. The electrode responses observed by us are not pH readings but rather measurements of acidity functions (*Q*). These have been defined and discussed for non-aqueous organic solvents.[7] They are equivalent to pH and can be written as in equation (1) where

$$Q = z - y \log_{10}[H^+] \qquad (1)$$

z and *y* are constants whose values depend on the solvent used. We find that the readings from a pH-meter, equipped with glass and calomel electrodes immersed in benzene–methanol or dioxane–methanol mixtures, can be described by equation (1). Data illustrating equation (1) can be found in Table 1. We have used readings of *Q* as a means of monitoring our reactions.

After a solution of an aryltellurium trihalide in the pure non-reacting solvent is added to a solvent mixture containing methanol, typically giving approximately 10^{-4} mol dm^{-3} Te, *Q* changes markedly. We used measurements in methanol-rich mixtures to calibrate the scale, and concluded that the overall change in *Q* corresponds to the release of 3 mol of H^+ per mol of $RTeCl_3$ in such dilute solutions. Therefore, we have employed a value of $n = 3$ when using equation (4) to calculate all rate constants. Notice however that the first substitution is rate determining and that we are following the conversion of $RTeCl_3$ into $RTe(OMe)Cl_2$ kinetically.

Table 2. Variation of rate constant with temperature for $RTeCl_3$ in benzene–methanol (5:1, v/v). Initial reagent concentration = 6.65×10^{-5} mol dm^{-3}

Temperature/°C	k/dm^3 mol^{-1} s^{-1}
5.0	1 410
10.0	1 560
15.0	1 820
20.0	1 930
25.0	2 200
30.0	2 380

Table 3. Activation parameters under various conditions

Solvent ratio (v/v)	Reagent	k_{25}/ dm^3 mol^{-1} s^{-1}	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
5:1	$RTeCl_3$	2 200	12.3 ± 1	-220 ± 11
2:1	$RTeCl_3$	2 260	5.1 ± 0.4	-203 ± 6
2:1	$RTeBr_3$	2 130	5.8 ± 2.2	-200 ± 34
2:1	$RTeI_3$	1 660	8.2 ± 0.8	-181 ± 8

Table 4. Variation of rate constant with composition of benzene–methanol mixture at 25 °C. Initial reagent concentration = 2.87×10^{-5} mol dm^{-3}

Methanol (%, v/v)	Mol fraction MeOH	k/dm^3 mol^{-1} s^{-1}
98.4	0.993	4 900
95.1	0.977	3 880
90.2	0.953	3 170
83.3	0.917	3 080
73.8	0.861	2 430
66.7	0.808	2 320
57.4	0.748	2 250
49.0	0.679	2 470
33.0	0.520	2 430
25.0	0.423	2 650
16.7	0.306	2 440
8.2	0.164	2 470

Table 5. Variation of rate constant with added LiCl at 25 °C in benzene–methanol (5:1, v/v). Initial reagent concentration = 2.57×10^{-5} mol dm^{-3}

10^5 [LiCl]/mol dm^{-3}	k/dm^3 mol^{-1} s^{-1}
514	2 590
236	2 720
111	3 320
77.3	2 850
28.7	2 780

Table 6. Variation of rate constant with added glacial acetic acid at 25 °C in benzene–methanol (5:1, v/v). Initial reagent concentration = 3.90×10^{-5} mol dm^{-3}

10^5 [$MeCO_2H$]/mol dm^{-3}	k/dm^3 mol^{-1} s^{-1}
1 140	2 140
570	2 000
114	2 110
85.5	2 280
57.0	2 260

Table 7. Variation of rate constant with added sodium acetate at 25 °C in benzene–methanol (5:1, v/v). Initial reagent concentration = 8.83×10^{-5} mol dm^{-3}

10^5 [NaO_2CMe]/ mol dm^{-3}	k/dm^3 mol^{-1} s^{-1}	Overall change in meter reading
61.4	302	1.45
50.3	332	1.55
44.4	362	1.73
29.6	400	2.11
20.7	453	2.42
14.8	914	4.04
0	2 150	6.01

We carried out kinetic experiments by following Q, and hence H^+, to at least 75% completion. All sets of data could be fitted well by equation (2) where the subscripts i, f, and t refer to initial

$$k_{obs.}t = \ln\{[H^+]_t([H^+]_f - [H^+]_i)/[H^+]_i([H^+]_f - [H^+]_t)\} \quad (2)$$

and final readings and the reading at time t. The observed rate constant was computed by minimising the sum of squared differences between observed and calculated values of Q, and not of $[H^+]$. That is necessary because of the relative magnitudes of the changes in Q and $[H^+]$; *e.g.* for a reaction mixture initially containing 8.3×10^{-5} mol dm^{-3} $RTeCl_3$, $[H^+]$ will increase from an extremely small value to 2.5×10^{-4} mol dm^{-3}. So the influence of the earlier data points on the sum of squared differences for $[H^+]$ would be negligible. By contrast the early values are important using Q. Rate constants so calculated are reproducible within experimental error. The results of kinetic experiments are collected together in the various tables.

Equation (2) is the rate equation appropriate to an autocatalytic reaction such as (3). Thus it seems that the meth-

$$\text{Reagent} + H^+ \longrightarrow \text{Products} + (n + 1)H^+ \quad (3)$$

anolysis of Te–X bonds is catalysed by one of the reaction products. In this equation we show the active species as H^+ but Cl^-, which is formed with H^+, must also be considered. Notice that n appears in the rate equation (2) only *via* the final hydrogen-ion concentration which is part of the observed rate constant [equation (4)]. None of the experiments that we

$$k_{obs.} = k[H^+]_f \quad (4)$$

undertook gave any indication of more than one slow step, nor of any rapid initial spectral changes or generation of acid. Because we were measuring Q, the rapid generation of even 1% of the total acid would have been apparent. Therefore we reason that the solvolysis of the first Te–X bond is rate determining.

Table 1 contains data obtained at 25 °C in benzene–methanol (5:1, v/v) which show the applicability of equations (1) and (4). In Tables 2—4 the effect of varying the temperature and solvent composition can be seen. Qualitative observations showed that much faster reactions occur after HCl gas has been passed through either of the reagent solutions prior to mixing, but we could not carry out those experiments with sufficient control of the HCl concentration to provide data for tabulation. The identification of H^+ as the active product is made through the data of Tables 5—7. These show the results obtained when various concentrations of lithium chloride, glacial acetic acid, and sodium acetate respectively are added to reaction mixtures. In Table 8 we summarise the results of using a range of different alcohols in place of methanol during solvolysis. Lastly, Tables 9 and 10 contain data obtained when dioxane–methanol and dioxane–water are used for the solvolysis of the trichloride.

While we could not carry out experiments of sufficient accuracy to determine k in the presence of known concentrations of added hydrogen chloride, we did observe that the

Table 8. Variation of rate constant with alcohol at 25 °C in benzene–alcohol (5:1, v/v) mixtures. Initial reagent concentration = 6.70×10^{-5} mol dm^{-3}

Alcohol	k/dm^3 mol^{-1} s^{-1}	pK_a
MeOH	2 220	15.1
EtOH	1 660	15.9
Pr^{n}OH	652	16.1
Pr^{i}OH	642	17.1
Bu^{n}OH	303	16.1
Bu^{t}OH	348	19.2

Table 9. Variation of rate constant with solvent composition in dioxane–methanol at 25 °C. Initial reagent concentration = 8.3×10^{-5} mol dm^{-3}

Methanol (%, v/v)	Mol fraction MeOH	k/dm^3 mol^{-1} s^{-1}
16.7	0.297	462
25.0	0.413	434
33.3	0.512	442
41.7	0.602	502
50.0	0.678	679
58.3	0.747	1 140
66.7	0.808	1 250
75.0	0.864	1 580
83.3	0.913	2 040

Table 10. Variation of rate constant with composition of aqueous dioxane at 25 °C. Initial reagent concentration = 1.0×10^{-4} mol dm^{-3}

Water (%, v/v)	Mol fraction H_2O	k/dm^3 mol^{-1} s^{-1}
8	0.294	330
12	0.395	430
16	0.477	500

rate of reaction increased with the addition of HCl. Therefore either H^+ or Cl^- is responsible for the autocatalysis. Known concentrations of added Cl^- can be obtained using LiCl. Even at a 200:1 ratio of Cl^-:Te the observed rate constant is unchanged within experimental error (Table 5). Thus we can eliminate chloride ion as the active product. The data of Tables 6 and 7 confirm that we are dealing with acid catalysis. The addition of acetic acid has little or no effect on the rate of reaction even at a 400:1 ratio (Table 6). By contrast, the addition of sodium acetate causes a marked reduction in rate (Table 7). The final acidity of the reaction solution also decreases with increasing [NaO_2CMe] because H^+ is being removed as undissociated acetic acid. If equations (3) and (4) are combined we can deduce that $\log_{10}k_{\text{obs.}}$ should vary linearly with the overall change in meter reading from start to finish of the reaction. The data of Table 7 show that dependence. The idea of an acid-catalysed reaction is well founded.

When other alcohols are used in place of methanol in the solvent mixture the rate constant varies from one to another, see Table 8. These variations correlate quite well with the various parameters that have been used to measure solvent properties:[8] *i.e.* the pK_a, dielectric constants of the solvents, or the terms of Reichardt, Kosourer, Grunwald and Winstein, or Brownstein. Since we already know that H^+ is involved in the reaction we list pK_a in the Table. The solvolysis of *N*-(trialkylsilyl)amines has been reported to be both associative and acid catalysed.[9] The rates for that reaction vary in the order H_2O > MeOH > EtOH > Pr^{i}OH, an order which is reproduced in the data of Table 8. Unfortunately that work did not include the determination of activation parameters.

We have other data which help in identifying the reaction mechanism. Over a very wide range of benzene–methanol compositions the rate of reaction is independent of the solvent composition (Table 4). The rate of reaction increases only when the mol fraction of methanol in the reaction medium reaches 0.9. Unless the reaction solution is extremely non-uniform in its structure the alcohol cannot be directly involved in the rate-determining step, although it could be involved in a pre-equilibrium.

The activation parameters listed in Table 3 were obtained using different sets of apparatus and batches of reagents, yet they show only slight differences from each other. The activation enthalpies are small for all three trihalides and for the trichloride in two different solvent compositions. We believe that they indicate the cleavage of weak Te–X bonds in the rate-determining step. By contrast the entropy of activation is large and negative in all cases, indicative of observed rate constants that describe associative set of reactions.

The results of physical investigations by other workers provide strong support for these deductions. Solid-state studies of $RTeX_3$, X = Cl, Br, or, I, show that one Te–X bond is weaker than the others.[10,11] Nevertheless, unassisted heterolytic cleavage of the weak Te–Cl bond does not occur to any significant extent in these solvents, as conductivity and molecular weight studies of $RTeCl_3$ in organic solvents show that it is present in molecular form.[12]

In an organic solvent HCl should be a better leaving group than Cl^-, therefore protonation of a chloride will occur before its substitution. The small value of the observed activation enthalpy shows that the leaving group is only weakly bonded to the central tellurium atom, so indicating which Te–Cl bond is protonated. As the leaving group is only weakly attached to Te, the discrete step involving its loss is likely to be dissociative as the data of Table 3 indicate.

There are very few activation data for acid-catalysed solvolyses of *p*-block compounds quoted in the literature. The most relevant to us are those of Bøe[13] who obtained values of 38 kJ mol^{-1} and -192 J K^{-1} mol^{-1} for the enthalpy and entropy of activation for the acid-catalysed solvolysis of benzyloxosilanes in absolute ethanol containing chloroacetic acid. An associative mechanism [equations (5) and (6)] was suggested.

$$\mathrm{Me_2(XC_6H_4)SiOCH_2C_6H_4Y + EtOH \rightleftharpoons Me_2(XC_6H_4)Si(OH)CH_2C_6H_4Y^+ + EtO} \quad (5)$$

$$\mathrm{Me_2(XC_6H_4)Si(OH)CH_2C_6H_4Y^+ + EtOH \longrightarrow Me_2(XC_6H_4)SiOEt + HOCH_2C_6H_4Y + H^+} \quad (6)$$

Although the scheme describing the $RTeCl_3$ reaction may be broadly similar to this, it must differ in detail. Reactions (7)—(9), with (8) as the rate-determining step, represent a plausible mechanism. For most solvent compositions we believe that

$$\mathrm{RTeCl_3(MeOH)_\mathit{x} + MeOH_2{}^+ \overset{K_1}{\rightleftharpoons} [RTe(HCl)Cl_2(MeOH)_\mathit{x}]^+ + MeOH} \quad (7)$$

$$\mathrm{[RTe(HCl)Cl_2(MeOH)_\mathit{x}]^+ \xrightarrow{k_2} [RTeCl_2(MeOH)_\mathit{x}]^+ + HCl} \quad (8)$$

$$\mathrm{[RTeCl_2(MeOH)_\mathit{x}]^+ + \mathit{y}MeOH \xrightarrow{rapid} [RTeCl_2(MeOH)_{\mathit{x}+\mathit{y}}]^+} \quad (9)$$

$$\mathrm{[RTeCl_2(MeOH)_{\mathit{x}+\mathit{y}}]^+ \xrightarrow{rapid} \mathit{etc.}} \quad (10)$$

$x = 0$. This scheme gives equation (11) for the observed rate constant. If $K_1[H^+] \ll 1$ this simplifies to equation (12).

$$k_{obs.} = k_2\{K_1[H^+]/(1 + K_1[H^+])\} \quad (11)$$

$$k_{obs.} = K_1k_2[H^+] \quad (12)$$

We represent the protonation of $RTeCl_3$ as directly onto Cl in equation (7). The mathematical form of equation (12) would be unchanged if protonation initially occurred elsewhere and was followed by migration onto Cl; K_1 would merely be replaced by the product of appropriate equilibrium constants.

To include the possibility of solvation of the reagent we show the initial reagent as $RTeCl_3(MeOH)_x$. Unless two species with different values of x are present in significant concentrations such solvation will have no effect on equation (12), as is found at most solvent compositions. The most obvious explanation of the variations of rate with solvent composition which do occur is that x is non-zero only when the mole fraction of methanol in the solvent is close to unity. An inspection of the data of Table 4 shows that the rate constants at the extremes of the solvent range are approximately 2 400 and 5 000 $dm^3 mol^{-1} s^{-1}$ respectively. These probably correspond to the reactions of $RTeCl_3$ and $RTeCl_3(MeOH)$. That is, processes with $x = 0$, $y = 1$ and $x = 1$, $y = 0$ respectively.

In Table 9 we quote the observed rate data for reactions carried out in dioxane–methanol mixtures. The behaviour is qualitatively the same as that in benzene–methanol, but the rate constants tend to a markedly lower limit at the dioxane end of the solvent range. Very similar values are also seen in the restricted range of solvolysis data for aqueous dioxane quoted in Table 10. Therefore we deduce that this limit, approximately 300 $dm^3 mol^{-1} s^{-1}$, describes the conversion of $RTeCl_3$(dioxane) into an $RTeCl_2(dioxane)^+$ intermediate which then reacts rapidly with either MeOH or H_2O in a modified version of reactions (7) and (8). Experimental difficulties prevented our working at water:dioxane ratios above 1:5 (v/v), but it would appear that the rate constants for the same mole fractions of methanol and water are equal within experimental error. That is consistent with the proposed mechanism.

In conclusion, we believe that the mechanism of solvolysis in all the systems we have studied involves protonation at the most weakly bonded Te–X site of $RTeX_3$,[10,11] followed by the dissociative loss of HX in the rate-determining step. The subsequent formation of a Te–OMe or Te–OH bond, and the replacement of the other Te–X groups, follow rapidly.

Experimental

The preparation of aryltellurium trihalides was carried out using previously described methods,[1] and the purified products gave the expected analytical and spectral data. All other reagents used were of AnalaR grade and, if liquid, were dried and redistilled prior to their use. Two different reaction products were isolated and characterised as follows.

(p-*Ethoxyphenyl)tellurium Chloride Oxide*, RTe(O)Cl.—The colourless solution obtained by dissolving $RTeCl_3$ in pure methanol was reduced in volume under reduced pressure to approximately a tenth of its original volume, during which time a yellow precipitate formed. This was filtered off under a dry nitrogen atmosphere and fresh methanol was added. This process was repeated several times until the precipitate was pure white. After drying it was found to decompose without melting at 234 °C. Its i.r. spectrum and analytical data (32.2% C, 2.85% H, 11.5% Cl) are consistent with its identification as RTe(O)Cl (requires 32.0% C, 3.0% H, and 11.8% Cl).

(p-*Ethoxyphenyl)dimethoxotellurium Chloride*, $RTe(OMe)_2Cl$.—Sodium methoxide (3.1 mol ratio) was added to a methanolic solution of $RTeCl_3$ (1 mol ratio) and the volume reduced until a quantity of white precipitate had formed. This was filtered off, washed with cold, dry methanol, and the product then recrystallised from glacial acetic acid. This separates it from sodium chloride. The product is soluble in methanol, insoluble in pure benzene, dioxane, or nitrobenzene, and it reacts with water. It decomposes without melting at 185 °C and gave analytical data (32.3% C, 4.2% H, and 10.4% Cl) close to those calculated for $RTe(OMe)_2Cl$ (34.6% C, 4.4% H, and 10.2% Cl).

Kinetic experiments were carried out in a double-walled vessel. The temperature was kept constant by circulating water through the outer jacket. Readings were obtained by recording the signal from a Corning EEL model 12 pH meter fitted with glass and saturated calomel electrodes immersed in the reaction solution. Reactions were initiated by adding with stirring a thermostatted solution of the aryltellurium trihalide, in either benzene or dioxane, to the appropriate mixture of methanol and the same solvent. All reactions were followed to at least 75%, usually to 90% completion and data were then treated using a least-squares computer program written for an Apple IIe microcomputer.

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