Inorganica Chimica Acta, *180* (1991) 161–169

A kinetic and mechanistic study of the oxidation of a diarylditelluride by hydrogen peroxide in aqueous tetrahydrofuran

Neil K. Adlington and **J. David Miller***
Department of Applied Chemistry, Aston University, Birmingham B4 7ET (U.K.)

(Received September 3, 1990)

Abstract

When a diarylditelluride (RTeTeR), in solution in aqueous tetrahydrofuran, reacts with hydrogen peroxide it is first oxidised to RTeOH in a chain reaction involving RTe·(O_2H_2) and RTe radicals, which are in equilibrium with each other. If dioxygen is present a further equilibrium, involving RTe·O_2, slows the overall oxidation. The chain reaction, rather than a concerted four-centre mechanism, occurs because of the difference in Te–Te and O–O bond lengths. The subsequent two-electron oxidation of RTeOH to RTeO(OH) by another molecule of H_2O_2 occurs at a very similar rate. Finally there is a very slow oxidation to $RTe(OH)_3$. The effect of various experimental parameters on the rate of the first oxidation stage has been studied in detail and kinetic data have been determined. A mechanistic scheme is proposed.

Introduction

There are few reports in the literature of detailed mechanistic studies of compounds of the heavier p-block elements. Many of their reactions will be similar to those of the lighter elements, but the larger sizes of the atoms and the weaker bonds formed may lead to some differences; for example the involvement of radicals becomes more likely. We are working in this area, using aryltellurium species. They are a convenient group of compounds to study as the diarylditellurides exhibit strong absorptions in the visible region, and so can be followed spectrophotometrically. Here we describe the oxidation of the ditelluride RTeTeR, where R is the *para*-ethoxyphenyl group, by hydrogen peroxide.

In earlier papers in this series we have described the reduction of aryltelluriumtrihalides ($RTeCl_3$) to RTeTeR by SO_3^{2-}, Cr^{2+}, V^{2+}, and $[Ru(NH_3)_6]^{2+}$ [1, 2]. These reactions were carried out in mixtures of water and organic solvents; where hydrolysis to RTeO(OH), the tellurinic acid, is rapid [3]. The first reductive step from this is rate determining and, with the exception of the slow reduction by Ru(II), is inner-sphere. Because the preparation of some compounds of general formula RTeX has been reported [4, 5], we suggested that RTeOH is formed during these reductions; even though that particular compound has not yet been prepared. Therefore we decided to investigate the relationship of RTeOH to R_2Te_2 by studying the reverse process, the oxidation of the ditelluride.

Some mechanistic studies of the oxidation of ditellurides have already been reported. When I_2 is the oxidant the first discrete step is the formation of RTeI in what was assumed to be a four-centre reaction [6]. That is reasonable as both RTe–TeR and I–I bonds are similar in length [7], while square Te_4 transition states have been postulated during the formation of mixed diaryls in thermal decomposition reactions [8]. But the case under study here is very different, as the RTe–TeR bond is almost twice the length of the HO–OH bond. It is more likely that an inner-sphere reaction between these reagents would involve the addition of H_2O_2 to only one of the Te atoms. Asymmetrical bond cleavage might then occur.

When the Te–Te bond is broken during the oxidative addition of ditellurides to Vaska's compound [9], or during photochemical cleavage in solution [10], tellurium containing radicals are produced. Therefore radicals might also be involved here.

Previous workers have attempted to identify the products obtained from the oxidation of organotellurium compounds by hydrogen peroxide. For example, 30% hydrogen peroxide in alcoholic solution oxidises ditellurides to white solid products which were not fully characterised [11]. Characterisation

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

of the very insoluble oxidation products of ditellurides is nearly always a problem, as they can not usually be recrystallised or separated. Elemental analytical data often suggest that mixtures are formed, e.g. in the products from dimethyltelluride [12] and phenoxtellurine [13]. Both Te(IV) and Te(VI) are often included in formulae proposed. When t-butylhydroperoxide is used as the oxidant the products are unusually tractible, but mixtures still occur. Thus, Lee and Cava [14] found that the oxidation of an unsymmetrical diorganyltelluride gave a mixture of Te(IV) and Te(VI) species. During our kinetic studies we observed that the oxidation of the ditelluride occured in three consecutive, progressively slower, stages that we ascribe to changes in oxidation state through I (i.e. ditelluride), II, IV to VI. Such a sequence of reactions could easily lead to a mixed product.

In the cited oxidation studies, significant amounts of Te–C bond cleavage were not observed. That is usually the case in studies of organotellurium chemistry. Exceptions are known, e.g. the oxidation of RR'Te by air and hydrogen peroxide gives products of general formula RR'TeO·RTeOOH [15], but we found no evidence for Te–C cleavage in our work.

Results

The product of reaction

Solutions of the ditelluride in tetrahydrofuran are coloured orange ($\epsilon_{max} = 1080 \pm 12$ dm^3 mol^{-1} cm^{-1} at 400 nm in 3:1 THF:H_2O). This colour disappears within a few minutes when an aqueous solution of hydrogen peroxide is added. If the mixture is left standing for several days a white precipitate forms. We were unable to find a solvent from which we could carry out its recrystallisation. However the product is sufficiently soluble in chloroform for it to be spotted onto thin layer chromatographic sheets. Elution using a range of different solvents never gave more than one detectable spot. The product was stable up to 165 °C, when it decomposed. *Anal.* Found for the unpurified solid: C, 30.8; H, 4.15; Te, approx. 40%. This last determination proved difficult to carry out with precision. Calc. for $RTeO(OH)_3$: C, 30.4; H, 3.8; Te, 40.4%.

The product is sufficiently soluble in chloroform for its ^{1}H NMR spectrum to be measured. A series of broad bands are observed, with widths at half height of approximately 120 Hz. The centres of these bands, and their relative areas, are very similar to those found for the parent ditelluride. The values (with ditelluride data in parentheses) are 7.73 (7.67), 6.70 (6.71), 3.89 (3.97) and 1.27 (1.40) delta. No other signals due to protons were detected, while signal multiplicities were obscured due to the breadth of the bands. The origin of the broadening cannot be identified with certainty, but the general appearance of the spectrum suggests that the RTe group is retained in the product. The infrared spectrum also supports that deduction. With the exception of strong new bands at 750–550 (assigned to νTe–O) and 3500–3100 (νO–H) cm^{-1}, the infrared spectrum of the product is indistinguishable from that of the ditelluride.

Solutions of the product exhibit very weak, broad ESR signals, even though solutions sampled during the reaction show no such spectra. An identical and weak spectrum is obtained when a solution of $RTeCl_3$ undergoes base hydrolysis under aerobic conditions. Therefore a possible explanation of the broad NMR peaks is that a paramagnetic impurity is formed during the isolation of the product. Unfortunately neither that suggestion nor the formula of the product can be fully proved.

Reaction stoicheiometry

We investigated the stoicheiometry of the overall reaction in two sets of experiments summarised in Table 1. In each case the concentration of the reagent in excess was determined spectrophotometrically; using either its own colour in the case of the ditelluride, or that developed by adding acidified titanium(IV) chloride to an excess of hydrogen peroxide [16]. In one set of results the reaction solutions were stored in the dark under N_2 for several days while the determination was repeated from time to time until a constant value was obtained. In the other set of results (marked with an asterisk in the Table) the peroxide concentration was determined as soon as the ditelluride coloration had disappeared. The overall stoicheiometry varies with the initial ratio of reagent concentrations. When there is an excess of R_2Te_2 the ratio of $[H_2O_2]/[R_2Te_2]$ consumed is slightly greater than 1. As the concentration of peroxide increases so the ratio rises to 3. In the presence of a larger excess of H_2O_2 a value above 3 can be found.

In summary, in the first stage of the overall process, which has a 1:1 $[R_2Te_2]$:$[H_2O_2]$ stoicheiometry, the colour of the R_2Te_2 is lost. In a slightly slower second stage the ratio reaches 3:1. A very slow third stage follows that. In Table 2 we show the results of one of the experiments in which $[H_2O_2]$ was measured as a function of time after the ditelluride colour had completely disappeared. These results are discussed in more detail below, but are cited here to confirm the existence of the step giving a 3:1 stoicheiometry.

TABLE 1. The determination of reaction stoicheiometry in a 3:1 THF:water medium at 25 °C

Reagent concentrations		Reagent in excess[a]	Reagent consumption $[H_2O_2]/[R_2Te_2]$
$10^5 \times [H_2O_2]_0$ (M)	$10^5 \times [R_2Te_2]_0$ (M)		
895	201	H_2O_2	3.51
806	201	H_2O_2	3.41
672	201	H_2O_2	3.22
560	201	R_2Te_2	2.93
448	201	R_2Te_2	2.87
299	201	R_2Te_2	2.58
233	201	R_2Te_2	2.45
112	201	R_2Te_2	1.89
89.0	201	R_2Te_2	1.65
6.00	201	R_2Te_2	1.32
448	800	R_2Te_2	1.29
448	707	R_2Te_2	1.38
448	543	R_2Te_2	1.38
448	466	R_2Te_2	1.75
448	384	R_2Te_2	2.26
448	307	R_2Te_2	2.64
448	257	R_2Te_2	2.67
448	192	R_2Te_2	2.93
448	144	H_2O_2	3.04
448	96.0	H_2O_2	3.06
448	76.8	R_2Te_2	2.91
448	64.0	R_2Te_2	2.92
448	48.0	R_2Te_2	2.91
448	38.4	H_2O_2	3.28
448	108	H_2O_2*	2.35
448	87.5	H_2O_2*	2.11
448	64.5	H_2O_2*	1.52
448	49.0	H_2O_2*	1.20

[a] Data marked with an asterisk obtained immediately after the absorbance at 400 nm had dropped to 0.

TABLE 2. The variation of peroxide concentration with time for a reaction in 3:1 THF:water at 25 °C, with $[R_2Te_2]_0 = 4.26 \times 10^{-4}$ mol dm^{-3} and $[H_2O_2]_0 = 4.06 \times 10^{-3}$ mol dm^{-3}. The absorbance of the Ti(IV) complex at 410 nm (= 706 dm^3 mol^{-1} cm^{-1}) is used to determine residual H_2O_2

Time (min)	$10^3 \times [H_2O_2]$ (mol dm^{-3})	Consumed $[H_2O_2]/[R_2Te_2]_0$
16.5	3.20	2.02
19	3.07	2.32
22.5	3.02	2.44
34	2.97	2.56
38	2.92	2.68
49	2.86	2.82
61.5	2.85	2.84
120	2.78	3.00
1440	2.49	3.69

TABLE 3. The effect of $[R_2Te_2]_0$ on the rate of reaction at 25 °C in 3:1 THF:water with $[H_2O_2]_0 = 4.28 \times 10^{-3}$ mol dm^{-3}

$10^4 \times [R_2Te_2]_0$ (mol dm^{-3})	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})	$10^3 \times k_{comp}$ (s^{-1})
12.8	4.65	5.84	6.05
10.7	4.21	5.71	5.54
9.62	3.73	5.55	5.25
8.54	3.55	4.43	4.95
7.55	3.26	4.39	4.65
6.41	2.82	4.14	4.28
5.39	2.49	3.55	3.93
4.27	2.15	3.22	3.50
3.21	2.01	2.79	3.03
2.14	1.56	2.07	2.48
1.26	1.39	1.75	1.90

TABLE 4. The effect of $[H_2O_2]_0$ on the rate of reaction at 25 °C in 3:1 THF:water with $[R_2Te_2]_0 = 6.41 \times 10^{-4}$ mol dm^{-3}

$10^3 \times [H_2O_2]_0$ (mol dm^{-3})	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})	$10^3 \times k_{comp}$ (s^{-1})
22.8	13.3	20.7	21.3
19.1	10.5	18.5	18.1
15.2	7.33	14.7	14.6
11.4	6.30	11.0	11.1
9.97	5.77	9.76	9.75
8.57	4.24	8.94	8.43
7.62	3.96	8.45	7.53
6.53	3.41	6.76	6.48
4.28	2.82	4.14	4.28
3.13	0.94	2.03	3.15

TABLE 5. The effect of temperature on the rate of reaction in 3:1 THF:water with $[R_2Te_2]_0 = 5.02 \times 10^{-4}$ mol dm^{-3} and $[H_2O_2]_0 = 4.28 \times 10^{-3}$ mol dm^{-3}

Temperature (°C)	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})
20.0	1.95	2.74
25.0	2.97	3.89
30.0	4.11	5.12
35.0	5.66	6.57
40.0	7.43	8.87
45.0	9.65	11.1

Kinetic studies

Most of our kinetic experiments were concerned with the first stage of the reaction, and were carried out by following the disappearance of the ditelluride spectrophotometrically. The results are given in Tables 3–10. Typically, reaction was initiated by mixing a solution of the ditelluride in redistilled tetrahydrofuran with a freshly prepared solution of

TABLE 6. The effect of solvent composition on the rate of reaction at 25 °C with $[R_2Te_2]_0 = 4.00 \times 10^{-4}$ mol dm^{-3} and $[H_2O_2]_0 = 4.29 \times 10^{-3}$ mol dm^{-3}

THF (vol.%)	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})
50.0	3.61	3.88
55.0	2.91	3.49
60.0	1.98	2.48
65.0	2.26	2.99
70.0	2.88	3.12
75.0	2.50	3.27
80.0	2.90	3.27
85.0	2.36	3.71
90.0	2.14	4.01

TABLE 7. The effect of added $NaNO_3$ on the rate of reaction in 3:1 THF:water at 25 °C with $[R_2Te_2]_0 = 3.32 \times 10^{-4}$ mol dm^{-3} and $[H_2O_2]_0 = 4.26 \times 10^{-3}$ mol dm^{-3}

$10^4 \times [NaNO_3]$ (mol dm^{-3})	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})
100	2.70	2.91
90.0	2.73	2.98
70.0	2.59	2.78
50.0	2.58	2.78
30.0	2.68	2.89
10.0	2.71	2.93
5.0	2.51	2.72

hydrogen peroxide in the appropriate solvent mixture. The results were found to be reproducible. We also obtained essentially identical results when we used unpurified commercial THF as solvent; or when we allowed solutions of hydrogen peroxide in THF to stand before they were used in the experiments. Therefore we deduce that organic peroxides are not important in the reaction under study here. Nevertheless we tried to avoid their production for safety reasons.

In Fig. 1 we show the plot of absorbance versus time for a typical experiment. It has a sigmoid shape, which was unexpected as we are monitoring the disappearance of the initial Te-containing reagent. None of the common rate equations can be fitted to the whole reaction profile. Unexpectedly we found that the later portion of the curve can be described by a first order equation; the crosses of Fig. 1 show that fit (the squares show the integrated rate equation discussed below). That is especially surprising as the initial reagent ratio $[H_2O_2]_0/[R_2Te_2]_0$ is only 3.4 for the experiment illustrated. In the Tables the columns headed k'_{obs} refer to the pseudo-first order rate

TABLE 8. The effect of added HNO_3 or NaOH on the rate of reaction in 3:1 THF:water at 25 °C with $[R_2Te_2]_0 = 5.20 \times 10^{-4}$ mol dm^{-3} and $[H_2O_2]_0 = 4.48 \times 10^{-3}$ mol dm^{-3}. $NaNO_3$ being added to maintain a constant ionic strength of 1.40×10^{-2} mol dm^{-3}

$10^4 \times [HNO_3]$ (mol dm^{-3})	pH	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})
140	1.9	0.391	0.63
70.0	2.2	0.659	0.97
35.0	2.5	2.89	2.83
6.00	3.2	3.50	4.87
3.00	3.5	3.92	5.85
0.20	4.7	4.64	5.94
0.10	5.0	4.90	6.05
0	7.0	4.81	5.92
$10^4 \times$[NaOH] (mol dm^{-3})			
0.01	8.0	4.26	6.07
0.10	9.0	4.99	5.76
0.20	9.3	4.91	5.80
1.25	10.1	4.26	5.86
12.5	11.1	4.80	5.90
35.0	11.5	5.20	6.03
140	12.1	10.0	18.0

TABLE 9. The effect of added $[H_2O_2]$ on the rate of reaction in 3:1 THF:water at 25 °C with $[R_2Te_2]_0 = 4.50 \times 10^{-4}$ mol dm^{-3}. All reactions carried out under an atmosphere of O_2

$10^3 \times [H_2O_2]_0$ (mol dm^{-3})	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})	$10^3 \times k_{comp}$ (s^{-1})
74.7	30.5	23.8	23.5
56.0	25.5	18.6	18.0
37.3	17.2	11.9	12.2
22.4	10.2	6.04	7.47
11.2	4.24	2.75	3.78
6.17		1.28	2.10

TABLE 10. The effect of added $[H_2O_2]$ on the rate of reaction in 3:1 THF:water at 25 °C with $[R_2Te_2]_0 = 4.50 \times 10^{-4}$ mol dm^{-3}. All reactions carried out under an atmosphere of N_2

$10^3 \times [H_2O_2]_0$ (mol dm^{-3})	$10^3 \times k'_{obs}$ (s^{-1})	$10^3 \times k_{obs}$ (s^{-1})	$10^3 \times k_{comp}$ (s^{-1})
17.1	12.7	15.7	15.6
12.7	10.3	11.4	12.0
10.2	8.52	9.88	9.90
8.53	6.67	7.35	8.41
6.40	8.15	8.67	6.45

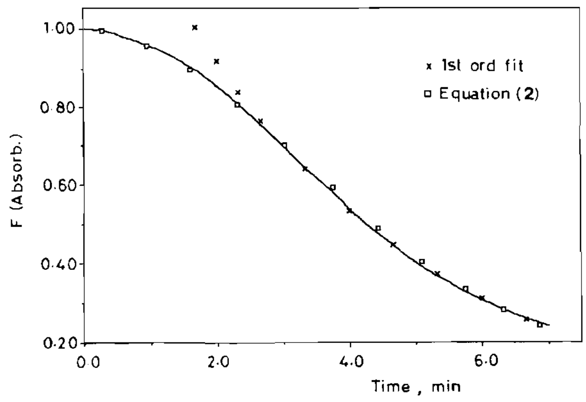

Fig. 1. Experimental data for disappearance of R_2Te_2. Plot of fractional absorbance against time. The fits to the data are for a pseudo-first order equation and eqn. (2).

constants obtained from this treatment. The variation of k'_{obs} with the initial reagent concentrations appears to be

$$k'_{obs} \propto [H_2O_2]_0^1[R_2Te_2]_0^{0.5} \qquad (1)$$

The true rate equation must be a more complicated mathematical function which simplifies to the first order equation under some conditions.

In order to gain a better understanding of this reaction we undertook some computer modelling of experiments with hydrogen peroxide in a large excess, using Euler's method [17]. We found a plausible short reaction scheme, a linear chain reaction, which in all cases could be fitted to give an excellent agreement with the experimental data from mixing up to at least 90% oxidation of the ditelluride. The rate constants obtained in this way vary smoothly and systematically as the experimental parameters are altered. In that way we settled on reactions (8), (9) and the forward part of (10) as the initiation and propagation steps. We tried various termination steps in association with them, but all were negligible over the range studied.

An integrated rate equation can be derived from these reactions as long as (i) the value of $[H_2O_2]$ remains constant; (ii) termination reactions are unimportant; and (iii) the ratio $[RTe\cdot(O_2H_2)]/[RTe]$ remains constant. The results of our computer modelling showed that when (i) is true (ii) and (iii) are applicable. Integration then leads to eqn. (2)

$$\log\{(2-f-2(1-f)^{0.5})/f\} = \text{constant} - k_{obs}t \qquad (2)$$

where the unreacted fraction $[R_2Te_2]/[R_2Te_2]_0$ is shown as f. This equation will apply to any linear chain reaction scheme where both the initiation and the propagation steps are first order in $[R_2Te_2]$. Notice also that as f becomes smaller the logarithmic term approaches $\log(1-f)$, and so the later part of the reaction can be described by a pseudo-first order rate equation.

We applied this equation to the results of all our experiments. We show the fit obtained by the squares in Fig. 1. In order to exclude inaccurate data, and also to allow the assumption that $[H_2O_2]$ remains constant, we always defined an upper limit for values of f used in computation. A limit corresponding either to 75% completion, or to a 10% drop from $[H_2O_2]_0$, whichever is less. In only three experiments was $f_{limit} < 0.5$. In the Tables all columns of data referring to k_{obs} cite data obtained using eqn. (2). The value of the integration constant is always very small.

Analysis of the listed data shows that, to a good approximation, k_{obs} depends on the initial reagent concentrations according to eqn. (1). To be consistent with the full mechanistic scheme described in the 'Discussion', it should be noted that a slightly better fit for the data of Tables 3 and 4 is

$$(k_{obs})^2 = \frac{\{1600[H_2O_2]_0^2[R_2Te_2]_0\}}{\{1+8.5[H_2O_2]_0\}} \qquad (3)$$

The value of k computed from eqn. (3) is listed in these Tables as k_{comp}.

From the data of Table 5, the activation parameters for k_{obs} are found to be $\Delta H^{\neq} = 39.5 \pm 2$ kJ mol^{-1} and $\Delta S^{\neq} = -87 \pm 5$ J K^{-1} mol^{-1}, essentially the same as those that can be derived from the pseudo-first order fit to the later part of the reaction profile.

Most of our experiments were carried out in air, but in Tables 9 and 10 we give results obtained when the reaction was carried out under atmospheres of essentially pure O_2 or N_2. In these experiments the reagent solutions were flushed out with the appropriate gas before they were mixed, and the atmosphere above the reaction mixture and in the spectrophotometer compartment was maintained throughout each kinetic run. The results of Tables 9 and 10 can be fitted to an extended form of eqn. (3), viz.

$$(k_{obs})^2 = \frac{\{2600[H_2O_2]_0^2[R_2Te_2]_0\}}{\{1+24[H_2O_2]_0+9a\}} \qquad (4)$$

where a is the ratio of dissolved oxygen under the experimental conditions to that under a pure oxygen atmosphere, i.e. $a = 1$ for Table 9, 0 for Table 10, 0.2 under air. We use this term as the solubility of dioxygen in aqueous THF is not known. If the solvent had been pure water, a would correspond to $[O_2] = 1.3 \times 10^{-3}$ mol dm^{-3} under pure O_2. Values computed for k_{obs} from eqn. (4) are included in Tables 9 and 10 as k_{comp}.

Subsequent oxidation stages

The first stage, presumably the oxidation of ditelluride to 2RTe(II), is followed by a slightly slower stage which took approximately 2 h to reach completion and led to an overall 3:1 stoicheiometry. We show it as

$$H_2O_2 + RTe(II) \longrightarrow RTe(IV) \qquad (5)$$

That is followed by a further, extremely slow reaction that continues for days.

We could only begin to measure the residual peroxide concentration when the orange colour of the ditelluride had disappeared. In the quoted experiment that is approximately 15 min after mixing. By then the ratio $[H_2O_2]_{consumed}$:$[R_2Te_2]_0$ had reached 2:1 and the second stage was already half complete. Therefore a rigorous analysis cannot be justified, and we restricted ourselves to identifying the rate equation for this stage, using a small number of experiments at one temperature.

When all the ditelluride has been oxidised, the further consumption of hydrogen peroxide can be treated as a single reaction; but one for which the time of initiation is unknown. The initial concentrations of reductant and oxidant for that single reaction can be taken to be $2[R_2Te_2]_0$ and $\{[H_2O_2]_0 - [RTe_2]_0\}$, respectively. In these experiments we measured A_t, the absorbance of the titanium–peroxo complex at time t. We found that the consumption of peroxide became extremely slow when a stoicheiometric ratio of 3:1 was reached. Until then the behaviour of A_t can be described by the usual second order rate equation

$$\log\{A_t/(A_f - A_t)\} = k_{obs}t + \text{constant} \qquad (6)$$

where A_f is the absorbance reading corresponding to 3:1 stoicheiometry, and

$$k_{obs} = k_5\{[H_2O_2]_0 - 3[R_2Te_2]_0\} \qquad (7)$$

From these data fits we found k_5, the second order rate constant for reaction (5), to be (0.3 ± 0.05) dm^3 mol^{-1} s^{-1}.

We made no attempt to investigate the very slow final oxidation stage, except to show that the final ratio of $[H_2O_2]$:$[R_2Te_2]$ consumption exceeds 3:1 but we never found a value beyond 5:1.

Discussion

The oxidation of the diarylditelluride by hydrogen peroxide occurs in three distinct stages, through the sequence of oxidation states II, IV and VI; the R–Te bond is not cleaved during the overall sequence.

$$R_2Te_2 \longrightarrow RTeOH \longrightarrow RTeO(OH) \longrightarrow RTeO(OH)_3$$

Our work has been concerned mainly with the first of these steps, which involves the reaction between equimolar amounts of R_2Te_2 and H_2O_2. We followed the reaction by monitoring the changes in the visible absorption of the ditelluride. The data obtained in such an experiment are illustrated in Fig. 1. This reaction profile was unexpected. Computer modelling allowed us to find an integrated rate equation that is a good description of the experimental data. Equation (2) derives from a linear chain reaction in which both the initiation and propagation steps are first order in $[R_2Te_2]$, and where termination steps can be ignored; under conditions where $[H_2O_2]$ remains essentially constant.

We used the following arguement to obtain a plausible mechanistic scheme. Since Te(II) is known [4, 5] in compounds with the formula RTeX, the first oxidation product is most likely to be RTeOH or a solvated form of that. Both Te–Te and O–O bonds must be broken during its formation. They cannot break in a four-centre transition state with the simultaneous formation of two separate Te–O bonds as that would follow second order kinetics, which are not observed. A four-centre transition state is also unlikely as there is such a large difference between the Te–Te and O–O bond lengths [7].

The involvement of organic peroxides was eliminated in comparison experiments. No significant change was observed in the rate of reaction as the reaction solvent was change either to unpurified commercial THF containing added stabilisers, or to a mixture of redistilled THF and hydrogen peroxide which had been left to stand for an hour before use.

We judge an outer-sphere mechanism to be unlikely for reaction between two p-block reagents, therefore a 1:1 R_2Te_2:H_2O_2 adduct in which both O atoms interact with one Te atom is indicated. Te–Te cleavage would then give RTe and $RTe\cdot(O_2H_2)$ radicals. Stoicheiometric data show that the first oxidation stage leads to Te(II) and not Te(IV). Therefore we suggested eqns. (8)–(10) as a plausible scheme, but initially we did not include the reverse of reaction (10). Those steps alone must be incomplete. While they predict the observed dependence of rate on $[R_2Te_2]$, they do not predict its dependence on $[H_2O_2]$ or on $[O_2]$.

The data of Tables 9 and 10 illustrate the unexpected feature that changes from nitrogen to air, and further to oxygen atmospheres, cause reductions in the rate of oxidation. The ratio of observed rate constants under pure N_2 and O_2 is 3:1. It is known that RTe and O_2 react rapidly to form the more stable $RTe\cdot O_2$ in aearated solutions [10]. The most reasonable way to complete our first reaction scheme is to add reaction (11) and the reverse of (10). Then RTe, $RTe \cdot (O_2H_2)$ and $RTe \cdot O_2$ are all in equilibrium with each other.

$$H_2O_2 + R_2Te_2 \longrightarrow RTe \cdot (O_2H_2) + RTe \quad k_1 \tag{8}$$

$$R_2Te_2 + RTe \cdot (O_2H_2) \longrightarrow 2RTe(OH) + RTe \quad k_2 \tag{9}$$

$$RTe + H_2O_2 \rightleftharpoons RTe \cdot (O_2H_2) \quad K_3 \tag{10}$$

$$RTe + O_2 \rightleftharpoons RTe \cdot O_2 \quad K_4 \tag{11}$$

If equilibria (10) and (11) are rapidly maintained, the observed rate constant for the scheme (8) to (11) is given by

$$(k_{obs})^2 = \frac{\{4k_1k_2K_3[R_2Te_2]_0[H_2O_2]_0^2\}}{\{1 + K_3[H_2O_2]_0 + K_4[O_2]\}} \tag{12}$$

It is not possible to determine accurate values for K_3 and K_4 because our control of the gaseous atmosphere was not precise, and the solubility of dioxygen in aqueous THF is not known. However, using eqn. (4) we can assign approximate values by assuming that the solubility of O_2 in aqueous THF is the same as that in water.

Thus we can set $K_3 = 24$ mol^{-1} dm^3, i.e. RTe and H_2O_2 form a weak adduct with equilibrium (10) always lying well over to the left. By contrast dioxygen forms an adduct more strongly. The ratio $[RTeO_2]/[RTe] = 1.8$ in solutions under air, and so (11) lies over to the right in aerobic conditions. Therefore we estimate K_4 to be 6×10^3 mol^{-1} dm^3, and k_1k_2 is approximately 30 mol^{-2} dm^6 s^{-2}.

The rate of reaction does not alter when the solvent is changed from 50% to 90% THF (Table 6), when its ionic strength is altered (Table 7), or when the pH varies between 3.5 and 11.5 (Table 8). These results imply that the reaction sequence involves neither solvent molecules nor charged species in the rate determining steps.

However the rate increases at the upper limit of our range, pH = 12. As the pK_a of H_2O_2 is 11.8 [18], that increase can be ascribed to the deprotonation of H_2O_2. At pH values below 3.5 the rate also changes, now decreasing markedly. Hydrogen peroxide is not protonated at that acidity, therefore the change must involve the protonation of a tellurium-containing species. Each reagent that could be affected by these protonation/deprotonation effects takes part in more than one reaction; therefore we are not certain where the effect occurs. Reaction (10) is the most likely step, as the reversible formation of a weak adduct will be very sensitive to any change in reactivity.

The assumed product of the chain reaction, RTe(OH), is not the final product. It undergoes further oxidation to Te(IV) which we write as the known tellurinic acid, RTeO(OH). Although we could not study it thoroughly, that step seems to be more straightforward. It is first order in each of RTe(OH) and H_2O_2, with a rate constant $k_5 = (0.3 \pm 0.05)$ dm^3 mol^{-1} s^{-1} at 25 °C in 25% aqueous THF. If we use the function $\{k_{obs}/[H_2O_2]_0\}$ as a simple measure of the rate of the first oxidation process, we see that the ratio $\{k_{obs}/[H_2O_2]_0\}:k_5$ is close to unity, at 2.5:1. That is why the formation of RTeO(OH) is well under way before all the R_2Te_2 has been consumed. It is easy to accept that hydrogen peroxide should attack the Te atoms in RTe–TeR and RTe–OH at similar rates, as the electron densities and steric crowding around Te are similar in the two cases.

By contrast the environment differs in RTeO(OH), which is oxidised much more slowly to $RTeO(OH)_3$. We estimate that the relevant second order rate constant for the formation of $RTeO(OH)_3$ is of the order of 2×10^{-3} dm^3 mol^{-1} s^{-1}; i.e. less than $k_5/100$.

Conclusions

Because of the great difference between the single Te–Te and O–O bond lengths, the oxidation of RTeTeR to 2RTe(OH) by H_2O_2 does not follow a concerted four-centre mechanism, even though both reagents undergo a two-electron change. Rather the O–O bond adds to only one Te atom. The subsequent two-electron oxidation of RTeOH by another molecule of H_2O_2, which again involves the interaction with only one Te atom occurs at a very similar rate. By contrast, further oxidation of RTeO(OH) is very much slower.

Experimental

Bis(*p*-ethoxyphenyl) ditelluride was prepared by the standard method [1] and its purity was established by elemental analysis, melting point and spectrophotometric measurement. All other reagents used were obtained commercially and were of Analytical Reagent quality. Tetrahydrofuran was redistilled and purified by the literature method [19].

All spectrophotometric measurements were carried out using a Pye Unicam SP8-100 spectrophotometer. When experiments under atmospheres of dinitrogen or dioxygen were carried out, the reagent solutions were flushed with the appropriate gas for half an hour in multinecked vessels fitted with air locks. Samples were taken by syringe through a septum and injected into the spectrophotometric cell again through a septum. The cell compartment of the spectrophotometer was also continually flushed with the gas during the experiment.

Elemental analyses for C and H were carried out by Butterworth Laboratories, Teddington, Middlesex. We determined hydrogen peroxide concentrations either by titration against acidified manganate(VII) or spectrophotometrically using titanium(IV) [16], and the tellurium content [20] of the oxidation product by literature methods. All instrumental and spectral data were obtained using standard instruments cited within the department.

Acknowledgement

One of us, N.K.A., thanks the University of Aston for providing support through a University Studentship.

References

1 J. D. Miller and T. A. Tahir, *J. Chem. Soc., Dalton Trans.,* (1987) 985.

2 J. D. Miller and T. A. Tahir, *Inorg. Chim. Acta, 161* (1989) 193.

3 N. K. Adlington, J. D. Miller and T. A. Tahir, *J. Chem. Soc., Dalton Trans.,* (1989) 457.

4 K. J. Irgolic, *The Organic Chemistry of Tellurium,* Gordon and Breach, New York, 1974, p. 84.

5 P. Schulz and G. Z. Klar, *Z. Naturforsch., Teil B, 30* (1975) 40.

6 R. T. Mehdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.,* (1983) 1071.

7 G. Llabres, O. Dideberg and L. Dupont, *Acta Crystallogr., Sect. B* **35** (1972) 2438.

8 D. H. R. Barton, S. A. Glover and S. V. Ley, *J. Chem. Soc., Chem. Commun.,* (1977) 266.

9 R. T. Mehdi and J. D. Miller, *J. Chem. Soc., Dalton Trans.,* (1984) 1083.

10 R. T. Mehdi, J. D. Miller and T. A. Tahir, *Inorg. Chim. Acta, 90* (1984) 85.

11 G. T. Morgan and R. T. Kellett, *J. Chem. Soc.,* (1926) 1080.

12 R. H. Vernon, *J. Chem. Soc.,* (1920) 889.

13 H. D. K. Drew, *J. Chem. Soc.,* (1926) 3054.

14 M. Lee and M. P. Cava, *J. Chem. Soc., Chem. Commun.,* (1981) 277.

15 M. P. Balfe, C. A. Chaplin and H. Phillips, *J. Chem. Soc.,* (1938) 441.

16 A. I. Vogel, *Quantitative Inorganic Analysis,* Longmans, London, 3rd edn., 1961.

17 W. H. Press, B. P. Flannery, S. A. Teukolsky and W. T. Vetterling, *Numerical Recipes,* Cambridge University Press, Cambridge, 1986.

18 N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements, Pergamon, Oxford, 1984.*

19 D. D. Perrin, W. L. F. Armarego and D. R. Perrin, *Purification of Laboratory Chemicals,* Pergamon, London, 2nd edn., 1980.

20 F. H. Kruse, R. W. Santer and J. F. Suttle, *Anal. Chem., 25* (1953) 500.

Appendix

Derivation of the rate equation cited in eqn. (2)

Consider the reaction scheme of (8) to (11) under conditions where $[H_2O_2]$ and $[O_2]$ remain constant. Let $k'_1 = k_1[H_2O_2]$, $K'_3 = K_3[H_2O_2]$ and $K'_4 = K_4[O_2]$.

If equilibria (10) and (11) are maintained, then the fraction of radicals present as $RTe\cdot(O_2H_2)$ is constant

$$[RTe\cdot(O_2H_2)]/\{[RTe]+[RTe\cdot(O_2H_2)]+[RTe\cdot O_2]\}$$
$$=K'_3/\{1+K'_3+K'_4\}=A$$

The only reaction in which radicals are formed or consumed is (8), and therefore

$$d[RTe\cdot(O_2H_2)]/dt = 2k'_1A[R_2Te_2] \qquad (13)$$

If $k_2[RTe\cdot(O_2H_2)][R_2Te_2] \gg k'_1[R_2Te_2]$ as would be the case in a chain reaction, then

$$-d[R_2Te_2]/dt = k_2[RTe\cdot(O_2H_2)][R_2Te_2] \qquad (14)$$

The integrated rate equation derived from eqns. (13) and (14) was discovered by considering trial solutions. Thus, consider the solution eventually found

$$[R_2Te_2] = ze/\{x+e\}^2 \qquad (15)$$

where x, y and z are constants, and e represents $\exp(-yt)$. From this

$$d[R_2Te_2]/dt =$$

$$z\{(x+e)^2(-ye) - e(2(x+e)(-ye))\}/(x+e)^4$$

i.e.

$$d[R_2Te_2]/dt = -yze(x-e)/(x+e)^3 \qquad (16)$$

Equations (14) and (16) must be equivalent, and therefore

$$yze(x-e)/(x+e)^3 = k_2[RTe\cdot(O_2H_2)][R_2Te_2]$$

i.e.

$$[RTe\cdot(O_2H_2)] = y(x-e)/k_2(x+e) \qquad (17)$$

But the differential of this must also be the same as eqn. (8) i.e.

$$2k'_1A[R_2Te_2] = y\{(x+e)(ye) - (x-e)(-ye)\}/\{k_2(x+e)^2\}$$

i.e.

$$2k'_1A[R_2Te_2] = 2xy^2e/\{k_2(x+e)^2\}$$

$$2k'_1Az = 2xy^2/k_2$$

or

$$xy^2 = k'_1 k_2 A z \qquad (18)$$

The trial solution of eqn. (15) is therefore acceptable, and the values of the constants x, y and z must be selected to fit the boundary conditions of the reaction. At time $t=0$, $[R_2Te_2] = [R_2Te_2]_0$ and $[RTe \cdot (O_2H_2)] = 0$.

Substitution of these values into eqns. (15) and (18) gives $x=1$, $y^2 = 4k'_1 k_2 A[R_2Te_2]_0$ and $z = 4[R_2Te_2]_0$.

Equation (15) can now be rewritten as

$$[R_2Te_2]/[R_2Te_2]_0 = f$$

$$= 4\exp(-yt)/\{1+\exp(-yt)\}^2 \qquad (19)$$

In order to obtain the rate equation quoted in the text, eqn. (19) should be expanded to a quadratic equation in $\exp(-yt)$ as

$$f \cdot exp(-2yt) + (2f-4)\exp(-yt) + f = 0 \qquad (20)$$

As f is a positive fraction, the unique solution of this equation is

$$\exp(-yt) = \{(2-f)2(1-f)^{0.5}\{/f \qquad (21)$$

When logarithms are taken, this is eqn. (2) with the observed rate constant $= y$. On substitution that can be rewritten as

$$(k_{obs})^2 = 4k_1 k_2 K_3 [R_2Te_2]_0 [H_2O_2]^2 / \{1$$

$$+ K_3[H_2O_2] + K_4[O_2]\} \qquad (22)$$

Note. This derivation relates to our particular reaction scheme, but it is applicable with appropriate changes to the constants A, x, y and z to the generalised scheme for a chain reaction

$$R \longrightarrow I$$

$$R + I \longrightarrow I + P$$

where R, I and P represent reagent, intermediate and product species.