MECHANISTIC STUDIES OF ORGANOTELLURIUM CHEMISTRY

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SUMMARY

THE UNIVERSITY OF ASTON IN BIRMINGHAM
MECHANISTIC STUDIES OF ORGANOTELLURIUM CHEMISTRY
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The oxidation of bis(p-ethoxyphenyl) ditelluride by hydrogen peroxide has been studied kinetically. The reaction monitored was an oxidation from tellurium(I) to tellurium(II). The reaction stoichiometry ratio was found to depend upon the initial reagent concentrations. The presence of dioxygen was found to retard the rate and attributed to a dioxygen-ditelluride adduct. The rate varies in the following order of different atmospheres N_2 > Air >> O_2. The final product obtained from the oxidation has been characterised by IR, NMR and ESR spectroscopy. A mechanism for the oxidation has been suggested.

The reduction of p-$EtOPhTeCl_3$ by the hydrazinium ion has been studied kinetically. The stoichiometric measurements show that four moles p-$EtOPhTeCl_3$ are equivalent to three moles hydrazinium ion. The kinetics were studied under pseudo first order conditions. No ammonia was detected as a nitrogen containing product. The reduction proceeds via a two-electron process which indicates that it is inner-sphere in nature. A mechanism for the reduction is suggested.

The solvolysis of p-$EtOPhTeCl_3$ by methanol in benzene/methanol media has been studied. The study shows that the solvolysis is a reversible, acid catalysed reaction. Replacement of the chlorides on tellurium by methanol is agreed to be associative and replacement of the first chloride is rate determining. The rate of solvolysis varies in the order trichloride > tribromide > triiodide. A mechanism for the solvolysis is suggested.

The synthesis of some tellurium heterocyclics is reported. The synthesis and characterisation of telluranthrene is reported. The attempted synthesis of telluraxanthene was unsuccessful.

KEY WORDS

Tellurium
Kinetics
Oxidation

Solvolysis
Reduction

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LIST OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER ONE

INTRODUCTION

1 INTRODUCTION

Tellurium was discovered in 1782 and its name is derived from the latin "Tellus" meaning "Earth". Tellurium belongs to group 16 with an electronic structure of $[Kr]4d^{10}5s^{2}5d^{4}$ and has an electronegativity of 2.01 (Pauling scale). The metallic character of this group increases as the atomic weight increases from Oxygen to Polonium. However, although Tellurium shows some metallic properties, it is predominantly non-metallic in character.

Tellurium has an atomic weight of 127.6 and an atomic number of 52, together with twenty-two known isotopes with atomic masses ranging from 114 to 135. The element, unlike Oxygen, has s, p and d orbitals available for use in bonding and thus it can form more than four sigma bonds to other atoms. The most common oxidation states are II and IV represented by TeO and $TeCl_4$. Other oxidation states include -II, I and VI represented by H_2Te,$(p\text{-}EtOPh)_2Te_2$ and TeF_6.

Tellurium has numerous established uses, for example in glass and ceramics for colouring and in rubber technology as a vulcanizing agent. Other uses include an additive to improve the machinability of steel and copper. It has also been used as a catalyst in the oxidation of propylene to acrylic acid and as an anti-oxidant in lubricating oils.

In this thesis I describe the kinetics and mechanistic aspects of the oxidation of bis(p-ethoxyphenyl)ditelluride, $[(p\text{-}EtOPh)_2Te_2]$, by hydrogen peroxide, reduction of p-ethoxyphenyltelluriumtrichloride ($p\text{-}EtOPhTeCl_3$) by the hydrazinium ion

($N_2H_5^+$), the solvolysis of p-EtOPhTeX_3 (X=Cl, Br, I) by methanol in methanol/benzene mixtures, and the synthesis of Telluranthrene. It is hoped that this work will help to provide a general understanding of the mechanistic aspects of this particular group of organotellurium compounds. Thus, while the mechanisms of reactions involving transition metal complexes and of several typical elements especially the lighter ones have been extensively studied, little attention has been given to the heavier elements such as tellurium.

Organotellurium compounds have a history dating back to 1840[1] when Wohler prepared some dialkyltellurides. These were the first organic compounds of tellurium. The principal organotellurium compounds used in this study are p-ethoxyphenyl telluriumtrichloride, (p-EtOPhTeCl_3) and bis(p-ethoxyphenyl) ditelluride, [(p-EtOPh)$_2$Te$_2$].

Morgan and Drew[2] in 1925 first synthesised an aryltellurium trichloride by treating tellurium tetrachloride ($TeCl_4$) with phenetole in the presence of a solvent, chloroform.

$$TeCl_4 + C_2H_5OC_6H_5 \longrightarrow C_2H_5OC_6H_4TeCl_3 + HCl$$

The mechanism of this reaction probably involves electrophilic attack by $TeCl_3^+$ at the activated position of the aromatic nucleus. A more general method, which does not depend on the reactivity of the aromatic nucleus, involves reaction of arylmercuric halides with $TeCl_4$.[3]

$$RHgCl + TeCl_4 \longrightarrow RTeCl_3 + HgCl_2$$

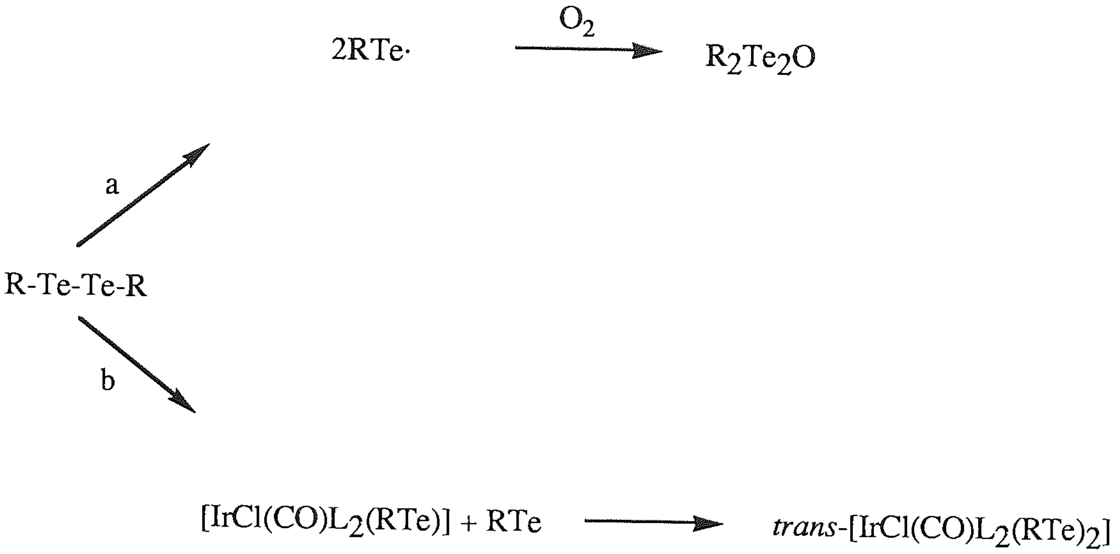
R=Aryl group

The advantage of this method lies in the possibility of obtaining compounds with any relative arrangement of substituents. Petragnani[4], Rheinboldt and Vincentini[5], and Reichel and co-workers[6,7] have described the preparation of a large number of aryltellurium trichlorides employing the method mentioned.

The principal methods for the synthesis of aromatic ditellurides involve the reduction of the corresponding aryltellurium trihalides. The most common reducing agents used are Na_2S, $Na_2S_2O_5$, and hydrazine[8,9,10]. The corresponding ditellurides are formed in quantitative yield. A few other modes of formation of ditellurides have been found but are of very limited interest for preparative work.

Although to date, little work has been published on the kinetics and mechanisms of reactions of organotellurium compounds, Mehdi[11] and Tahir[12] have begun to throw light on the mechanistic aspects involving the diaryl ditellurides and aryltellurium trichlorides.

Mehdi carried out some mechanistic studies of diaryl ditellurides. These included studying the effect of visible irradiation[13] on diaryditellurides in a solution containing alcohol, the reaction of iodine with diaryl ditelluride[14] through attack on the tellurium-tellurium bond, and the reaction of diaryl ditellurides with a transition metal complex, Vaska's compound[15].The reactions involving ditellurides involve the cleavage of the weak Te-Te bond. It was found that with irradiation by light and oxidative addition to Vaska's compound, free radical species were detected resulting, it was proposed, from homolytic cleavage of the Te-Te bond. In the reaction with iodine however an intermediate species, RTeI, was formed by non-radical cleavage



a = hν

b = Vaska's compound $[IrCl(CO)L_2]$, $L = PPh_3$

$$\text{R-Te-Te-R} \xrightarrow{I_2} 2RTeI \xrightarrow{2I_2} 2RTe(I_3) \longrightarrow 2RTe(I)_3$$

The reduction of aryltellurium trihalides to yield the ditellurides was studied by Tahir using sulphite ($Na_2S_2O_5$ and Na_2SO_3)[16] and two transition metal reductants (V(II) and Cr(II)) as reducing agents. In both sets of reductions an inner-sphere mechanism was proposed with an oxygen in the sulphite and chloride in the transition metal reductants as the bridging ligands. The interpretation of these reductions was that tellurium in p-EtOPhTeX_3 prefers an inner-sphere mechanism in its reactions. Also, the methanolysis of aryltellurium trihalides was briefly studied in aqueous and non-aqueous media.

Diaryl ditellurides are useful intermediates for the synthesis of some classes of organotellurium compounds (Fig 1-1). The aryl compounds are more stable and much easier to handle than the aliphatic members which, in addition their relative instability, possess an obnoxious, persistent odour. Additionally the diaryl ditellurides exhibit strong colours, orange to red, which makes it easier to study the disappearance or appearance of the ditelluride by means of a spectrophotometer.

The work concerning organotellurium compounds, which had been carried out up to 1971, has been reviewed by Irgolic[17]. Research during the period 1971-79[18-23] has also been reviewed by Irgolic. In 1971, Cooper published a book dealing with all aspects of tellurium titled "Tellurium".

A major one step route to diaryl ditellurides involves the reaction of a Grignard reagent with tellurium in THF

$$\mathrm{PhMgBr} + \mathrm{Te} \longrightarrow \mathrm{PhTeMgBr} \xrightarrow{O_2} \mathrm{Ph_2Te_2}$$

However when the reaction is carried out in diethylether, diaryltellurides as well as the ditellurides are formed. Petragnani and de Moura Campos[24] have explained the formation of these products on the basis of the following mechanism which is, however, only supported by the observation of the final products, Ph_2Te_2 , Ph_2Te and $Te(MgBr)_2$, accompanied by the possibility of radical dissociation of the ditelluride. The reaction is complex and variable ratios of products are obtained

$$\mathrm{PhMgBr} + \mathrm{Te} \longrightarrow \mathrm{PhTeMgBr}$$

$$\mathrm{PhTeMgBr} \longrightarrow \mathrm{PhTe} + \mathrm{MgBr}$$

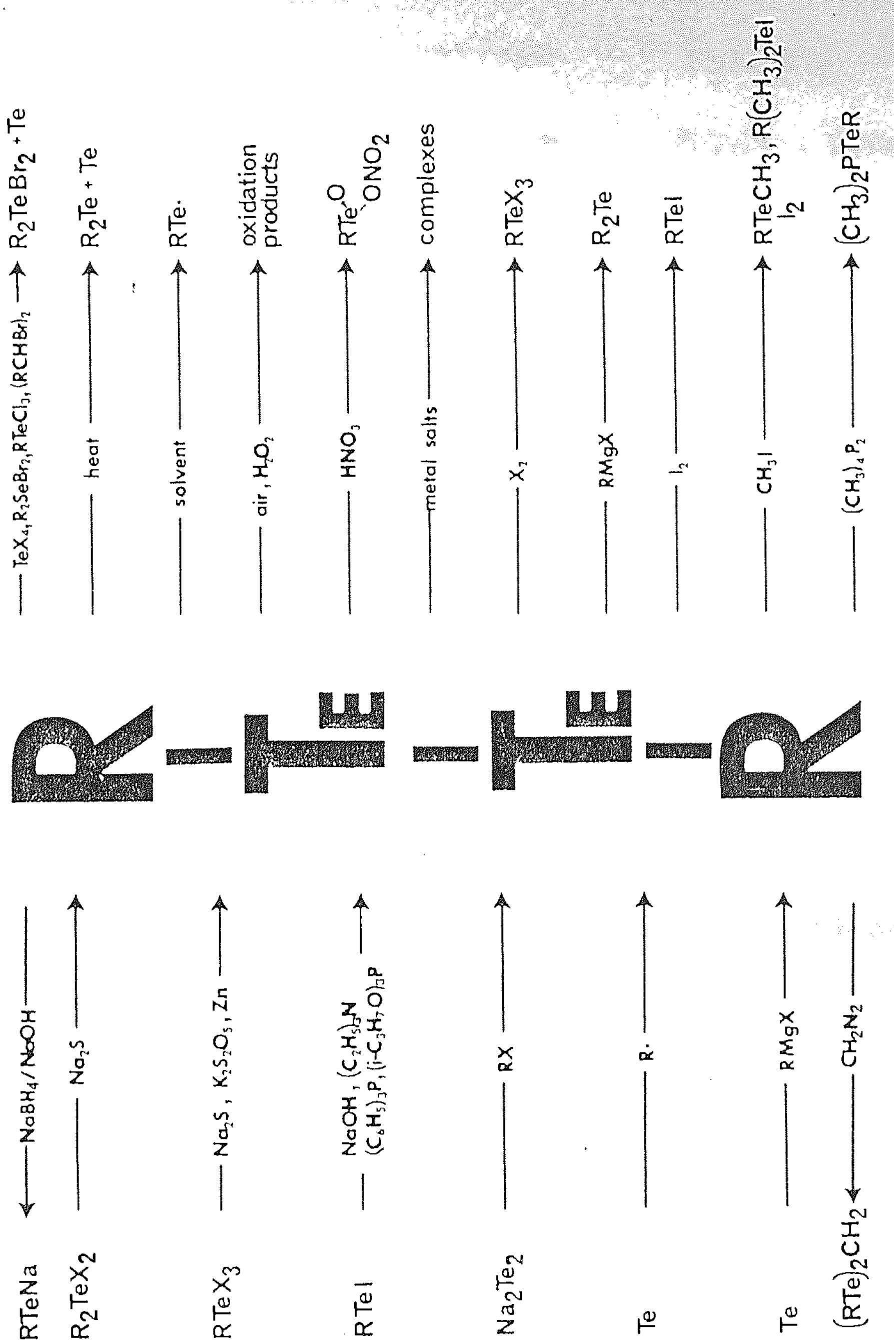


Fig 1-1 Synthesis and reactions of diorganyl ditellurides

$$2PhTe \longrightarrow Ph_2Te_2$$

$$2MgBr + Te \longrightarrow Te(MgBr)_2$$

$$PhTe\text{-}TePh + PhMgBr \longrightarrow PhTePh + PhTeMgBr$$

Many attempts have been made to prepare unsymmetrical ditellurides. Thavornytikarn[25] reduced a mixture of two aryltellurium trichlorides using $Na_2S.9H_2O$ and $K_2S_2O_5$, and by irradiating a benzene solution containing diphenyl ditelluride and p-ethoxyphenyl ditelluride. His conclusion was that the ditelluride is not dissociated into radicals in organic solvents. The failure to obtain the unsymmetrical diorganyl ditellurides, R'-Te-Te-R, led to the investigation of the properties of solutions containing mixtures of symmetric ditellurides, R_2Te_2.

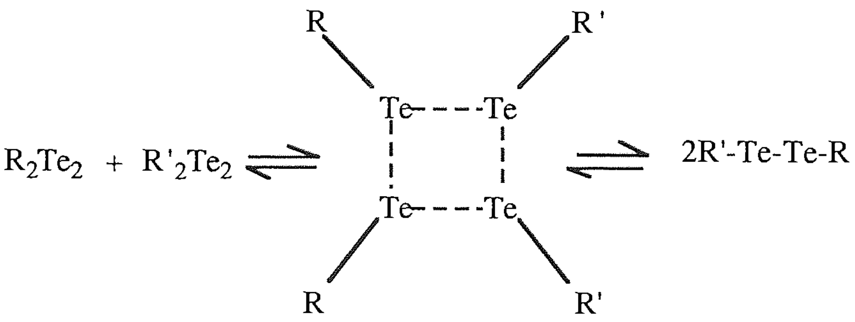
Recent[26] work has demonstrated an exchange between ditellurides R_2Te_2 and R'_2Te_2 which provides the first evidence of unsymmetrical diaryl ditellurides, R-Te-Te-R', from proton NMR spectroscopy. One possible mechanism for the redistribution of R groups would proceed via a radical mechanism

$$R_2Te_2 \rightleftharpoons 2RTe$$

$$R'_2Te_2 \rightleftharpoons 2R'Te$$

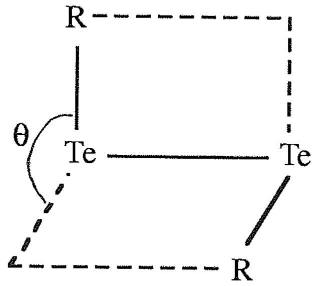
$$R'Te + RTe \rightleftharpoons R\text{-}Te\text{-}Te\text{-}R'$$

Alternatively a dimeric intermediate might occur



Dance[26] found no evidence that ditellurides spontaneously produce RTe radicals indicating that the dimeric structure is a distinct possibility. In the presence of dioxygen, however, evidence for radical species is found, but this has been shown to be due to a photochemically promoted reaction between the ditelluride and dioxygen. The ditelluride exchange reaction for the above process was calculated to be close to 4 $mol^{-1}\ dm^3$ and is independent of temperature implying that the process is under entropy control.

Structural details of diorganylditellurides have been determined from X-ray crystallographic studies[27-29]. In all the ditellurides examined, the "hydrogen peroxide" structure is observed with a dihedral angle θ



The dihedral angles, θ, have been found to be 70-75° whereas the C-Te-Te bond angles have been found to be 90-100° indicating that Te-C bonds have a higher degree of p-character. In the case of p-p'-dichlorophenylditelluride, the two organic groups bonded to the tellurium atoms form a dihedral angle of 72° and the tellurium-tellurium bond length is 2.70A whereas the C-Te bond length is 2.131A.

The crystal structures[30] of p-EtOPhTeX_3 (X=Cl,Br,I) show that the tellurium atom has a square pyramidal co-ordination with each tellurium lying almost exactly in the basal planes formed by the four chlorine atoms, whilst the p-EtOPh group is in the apical position. The pyramids are linked in chains through cis-basal chlorine atoms, and there is an acute angle between the basal planes of the pyramids. This has been suggested to result from weak bonding indicated by short distances between adjacent tellurium atoms. The trichloride crystallises as a polymer.

The tribromide and triiodide both crystallise with a dimeric molecular unit. The coordination at tellurium is square pyramidal with the halogen atoms in the basal positions and the organic group in the apical position. The pyramids are linked in pairs by two symmetrically bridging atoms. In general Te-X terminal distances are slightly shorter than Te-X bridging distances. The Te-aryl distances range between 2.09 and 2.16A among the three compounds.

McWhinnie and Thavornytikarn[31] made a spectroscopic examination of solid phenyltellurium trihalides. It was found that $PhTeBr_3$ may differ from the other two members of the group. The IR spectrum of the triiodide and trichloride indicated that the structure is based on "$PhTeX_2^+$" units (X=Cl or I) associated via halide bridges to give 5-coordinated tellurium atoms. Although there is no evidence that the above structures are ionic, McWhinnie considered that they might be built up from donor-acceptor interactions between $PhTeX_2^+$ and X^- to give the molecular structure illustrated (Fig1-2). The conclusion was that $PhTeCl_3$ and $PhTeI_3$ are at least dimeric, $PhTeBr_3$ may even be trimeric as illustrated in Fig 1-3

Rania and Khandelwal[32] obtained the IR and NMR spectra of $p\text{-EtOPhTeCl}_3$. They also made conductance and molecular weight measurements on their compounds.

They found that both compounds are present in molecular form in organic solvents and the $TeCl_3$ group is in the para position to the ethoxy or methoxy groups in the ring.

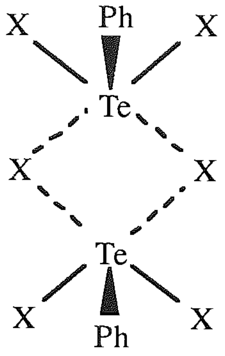


Fig 1-2

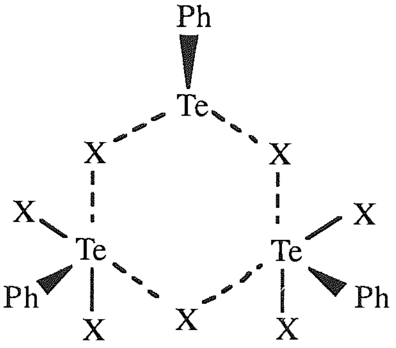


Fig 1-3

1-1 Solvent Effects on Reaction Rates

In my kinetic studies the effect of varying the ionic strength and dielectric constant of the reaction medium was used to in an attempt to gain information about the nature of the reacting species in solution.

The dependence of rates of reactions on the ionic strength of the reaction solutions has been used to provide evidence concerning mechanisms of many reactions. The Debye-Huckel[33] theory has been applied to the influence of neutral salts upon the rates of reactions in solution by Bronsted[34], Bjerrum[35] and Christiansen[36].

In dilute solutions, the activity coefficient is in accord with the Debye-Huckel limiting law. Thus the variation of the logarithm of the rate constant(log k) for a reaction between ions varies with the square root of the ionic strength.

ie

$$\log k_r = \log k_o + 1.02\, z_A z_B \sqrt{u}$$

Where k_o = rate constant at zero ionic strength

This equation has been tested a considerable number of times particularly by Bronsted, La Mer and Davies. For reactions involving an ion and a neutral molecule $Z_A Z_B$ is zero, and the rate is expected to be independant of ionic strength. This is true, for example, for the base-catalysed hydrolysis of ethyl acetate. However, at higher concentrations the rate may change because of changes in the activity coefficient of the ions which are not accounted for by the Debye-Huckel theory and also because the activity coefficient of neutral molecules are effected by higher ionic strength.

Using a more elaborate treatment of the effects of ionic strength for reactions between ions and neutral molecules, Huckel[37] proposed that the logarithm of the rate constant should vary with the first power of the ionic strength . This conclusion has received experimental evidence from Bronsted and Wynne-Jones, although the effect is small. However salt effects maybe eliminated from consideration by dealing with rate constants under conditions of zero ionic strength.

Variation of the rate constant with dielectric constant(D) of the solvent medium has long been used as evidence concerning mechanisms. Scatchard[38] predicted that the logarithm of the rate constant should vary with the reciprocal of the dielectric constant of the solvent for reactions between ions. Amis and La Mer[39] plotted log k at zero ionic strength versus (1/D) for the reaction between negative divalent tetrabromophenol and negative univalent hydroxide ions in water-methanol and water-ethanol mixtures. Straight lines with negative slopes were obtained down to a dielectric constant of around 65. In the water-methanol case there was a slight deviation in the region of pure water, attributed to the preferential absorption of water by the ions. Marked deviations at low dielectric constants of the solvent in the relationship have been attributed to the approximations used in deriving the equation.

Huckel[40] and Debye and McUlay[41] tend to the view that the ionic strength effect is negligible compared to the influence of the solvent in reactions between ions and dipolar molecules. Eyring[42] pointed out that sets of data, describing variation of the rate constant with dielectric constant, that can be extrapolated to zero ionic strength are scarce. Since Huckel, Debye and McUlay tend to discount the effect of ionic strength, Eyring predicted that the plot of log k versus 1/D should be a straight line with a positive slope irrespective of the sign of the ion, since they are governed by the square of the charge. Using the N-Chloroacetanilide and N-Chloropropionanilide conversions to the p-chloro compounds, straight lines with positive slopes were obtained as required[43].

Eyring and Laider[42], using data from Martin and co-workers, have plotted log k versus (D-1)/(2D+1) for dipole-dipole reactions. They obtained straight lines from such plots, with deviation from linearity found only at low values of the dielectric constant.

Kinetic studies in mixed solvents offer advantages and disadvantages compared with those in single solvents. For example, it is not possible to study the role of the solvent in the aquation reactions of octahedral complexes without recourse to mixed solvent. In this kind of work it appears to be disadvantageous to work with a mixed solvents. Firstly, it is difficult or even impossible to decide on the composition of the intermediate environment of the reaction centre. Thus, for complex formation in mixed solvents containing water and another solvating solvent such as methanol or ethanol, the reactant distribution is in general, unknown.

The second difficulty is that of product distribution. In the solvolysis of complexes in mixed solvents, there is no clear evidence whether both solvents enter the primary co-ordination shell, or whether there is selectivity in the displacement of the leaving group by the components.

The third difficulty lies in the imprecise picture and limited physical data available for many mixed solvents. This is particularly relevant to mixed aqueous solvents where inter- and intra-component interactions have an important effect on the overall structure and properties of the solvent mixture.

However, in the kinetic studies described in my thesis mixed solvents were a necessity as diaryl ditellurides are insoluble in aqueous media. The mixed solvent, THF:H_2O, used gave a homogenous solution as required for kinetic studies. This also, however, placed limits on the available kinetic experiments. For example, in the reduction of the trichloride by the hydrazinium ion, a limiting concentration of hydrazinium chloride was reached at ~0.1mol dm^{-3} in which immisciblility occured, that is a cloudy appearance as opposed to a clear single solution. Also, the same problem occurred when varying the solvent composition as at 90% by volume THF immiscibility occurred.

In my kinetic studies involving the oxidation of bis(p-ethoxyphenyl) ditelluride by hydrogen peroxide, and the reduction of p-ethoxyphenyltellurium trichloride by the hydrazinium ion, the non-aqueous component of the solvent used was THF. Although THF is similar structurally to 1,4-dioxane, the mixing properties with water are superior and it takes a considerably a shorter time to produce a homogeneous solution than 1,4-dioxane does upon mixing with water. THF was also chosen because it is completely miscible in all proportions with water.

CHAPTER TWO

EXPERIMENTAL

2 EXPERIMENTAL

2-1 Chemicals

All chemicals used were obtained from the usual commerical sources and "AnalaR" grades were used when necessary. Tellurium tetrachloride ($TeCl_4$), the important starting material, was supplied by the British Drug House (BDH) in a sealed bottle and used without further purification.

2-2 Solvents

All solvents used were obtained from commercial sources. If further purification was required, they were purified according to the literature method[44]. When deoxygenated solvent was required, the solvent was purged through with dinitrogen 30 minutes prior to use in a 3 necked flask and sealed. Solutions under deoxgyenated atmospheres were transfered using glass graduated hypodermic syringes fitted with stainless steel needles. THF was refluxed and distilled under nitrogen, prior to use, over $LiAlH_4$. THF used in the reduction studies was stored under nitrogen.

2-3 Physical Measurements

2-3-1 Visible Absorption

Visible absorption spectra and kinetic studies were taken on a Pye-Unicam SP8-100 spectrophotometer. The solution spectra were measured in the range 800-350nm. The solution and the reference solvent were both contained in 1cm glass cells. The cell compartment of the spectrophotometer is equipped with water jackets so that temperature control can be achieved simply by circulating water at the desired temperature through the cell holder.

2-3-2 Infra-red spectroscopy

Infra-red absorption spectra were recorded on a Perkin-Elmer 1710 Infrared Fourier Transform Spectrometer which covers the range 4000-220cm^{-1}. The samples were recorded as potassium bromide discs and the spectra printed on a Perkin-Elmer Model PP-1 plotter printer.

2-3-3 Electron Spin Resonance(ESR) spectroscopy

The ESR spectra were recorded at room temperature using a JEOL JES-PE-1 spectrometer. Solid samples were examined by placing the solid in a capillary tube sealing both ends and placing in the quartz tube.

2-3-4 Nuclear Magnetic Resonance

The ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ solution by a Bruker Spectrospin AC 300MHz FTNMR instrument using tetramethylsilane(TMS) as an internal standard.

2-3-5 pH Measurements

pH measurements were obtained using a Corning-EEL Model 12 pH, operating range pH (O) to (14) with an accuracy of ±0.02. For the methanolysis kinetic studies, pH measurements were obtained by pH meter model 38B in conjunction with a Servoscribe RE 511.20 potentiometric recorder.

2-3-6 Melting Points

The melting points of all solid compounds were determined using a Gallenkamp melting point apparatus which is heated electrically and the temperature recorded using a mercury thermometer.

2-3-7 Thin Layer Chromatography(T.L.C)

T.L.C on silica was used to determine the number of species present in certain solutions and the chromatograms were developed with iodine.

2-3-8 Mass Spectra

Mass spectra on Telluranthrene was carried out using a AE1 MS9 spectrometer at an ionising potential of 70 eV. Measurements were carried out using the ^{130}Te isotope, which has the largest mass number and highest relative abundance (compared to other Te isotopes).

2-4 Computation

All computer programmes were written in BASIC and run on an Apple IIe microcomputer at the University of Aston.

2-5 Analysis.[45]

Micro-analysis for carbon and hydrogen were performed by the microanalytical laboratory of the chemistry department at the university of Aston. The solvolysis product (Section 2-7-9) was analysed by Butterworths Laboratories Ltd, Teddington, Middlesex. Hydrogen peroxide was standardised by titration with acidified potassium permanganate and hydrazinium chloride by titration with potassium iodate under Andrew's conditions. The absence of ammonia, from the reduction of p-EtOPhTeCl_3 by N_2H_5Cl, was shown as follows:

p-EtOPhTeCl_3 (1g) was mixed with 200cm^3 distilled water. 50cm^3 Hydrazinium Chloride solution (0.1 mol dm^{-3}) was added and stirred overnight. The precipitate of unreacted p-EtOPhTeCl_3 and product ditelluride was filtered and concentrated perchloric acid (10cm^3) was added to the solution, then potassium iodate added. The formation of iodine was observed and this was removed by the addition of chloroform (50cm^3). The chloroform was separated and the aqueous layer treated with a few drops of Nessler's reagent (Section 2-7-10). No red colouration or precipitate was observed. This experiment shows that ammonia is not a by-product from the hydrazinium ion when it is oxidised by p-EtOPhTeCl_3.

2-6 Stoichiometry

2-6-1 Determination of H_2O_2 consumed by (p-EtOPh)$_2$Te$_2$

Two sets of experiments were carried out using different initial ditelluride and H_2O_2 concentrations. Solutions of the ditelluride (p-EtOPh)$_2$Te$_2$ in THF were added to freshly prepared H_2O_2 solutions in THF : water to give a final reaction mixture of three volumes THF to one volume water. The solutions were left overnight in the dark and under a nitrogen atmosphere(dry box). The excess ditelluride concentration was determined spectrophotometrically from its absorbance at 400nm. The excess H_2O_2 concentration was determined[45] by adding an equal volume of acidified titanium(IV)chloride solution to the reaction solution, and reading the absorbance spectrophotometry at 410nm (ε =706 dm^3 $mol^{-1}cm^{-1}$).

2-6-2 Determination of N_2H_5Cl consumed by p-$EtOPhTeCl_3$

A series of graduated flasks were purged out with nitrogen and stored in an atmosphere of nitrogen(dry box). In each flask 50cm^3 of p-$EtOPhTeCl_3$ (4.02 x10^{-3} mol dm^{-3}) was added. To each flask, fleshly made solutions of different hydrazinium chloride concentrations (6.51 to 3.18 x10^{-3} mol dm^{-3}) in THF/water (1:1 by volume) were added, and shaken then left overnight in the dark. The ditelluride produced was determined spectrophotometrically from its absorbance at 400nm.

2-7 Preparations

2-7-1 p-Ethoxylphenyltelluriumtrichloride (p-$EtOPhTeCl_3$)^2

Tellurium tetrachloride (12g), phenetole (17g), and dry chloroform (75cm^3) were mixed and heated under reflux for two hours with the exclusion of moist air. Hydrogen chloride was evolved and the solid dissolved. During heating a copious precipitate of glistening yellow flakes, consisting of practically pure p-$EtOPhTeCl_3$ was observed. This was removed after one day, washed with a little cold chloroform and dried. Yellow crystals were obtained in quantitative yield, which melted to a red liquid at 181-182^{o}C (lit 182-183^{o}C)^2 without further recrystallisation. (Found C,27.0%;H,2.6%: $C_8H_9TeCl_3$ requires ; C,27%; H,2.5%).

2-7-2 Bis(p-ethoxyphenyl)ditelluride (p-$EtOPh)_2Te_2$^{10}

p-Ethoxylphenyltelluriumtrichloride (6g) was stirred in distilled water and potassium metabisulphite (5g) in water (50cm^3) was added portion wise over 30 minutes. The red/brown product was filtered and washed with water, and recrystallised from petroleum ether (60-80) producing fluffy masses of brilliant golden-orange plates, melting at 104-105°C to a deep red liquid. (lit. 107-8°C)[10]. (Found C,38.4%; H,3.6%: requires : C,38.6%; H,3.6%).

2-7-3 p-Ethoxyphenyltelluriumtribromide[46]

Bromine in carbon tetrachloride (0.5g) was added dropwise with stirring to a solution of $(p\text{-}EtOPh)_2Te_2$ (0.5g) at room temperature and magnetically stirred. The solution of ditelluride changed from orange-red to yellow with precipitation of a yellow compound. The mixture was continously stirred for another 30 minutes. The precipitate was filtered and dried, and recrystallised from glacial acetic acid. Yellow crystals were obtained which melted at 196-205°dec (lit.195-205°C)[46]. (Found:C,19.7%;H,1.7% $C_8H_9OTeBr_3$ requires C,19.7%; H,1.8%)

2-7-4 p-Ethoxyphenyltelluriumtriiodide[46]

The procedure was similar to that used for the corresponding tribromide, ditelluride (1g) reacted with iodine (1.6g) in carbon tetrachloride. The product obtained was recrystallised from benzene and afforded a black powder which melted at 133-4°C (lit. 133-4°C)[46] (Found: C,15.3%; H,1.5%; $C_8H_9TeI_3$ requires : C,15.3%; H,1.45%).

2-7-5 o-Phenylenemercury(II)[47]

Sodium metal (7g) was added to 50cm^3 mercury in a 250cm^3 stoppered flask under nitrogen over a period of 2 hours. The flask was kept at 55°C throughout by immersing in a water bath and a steady stream of nitrogen was passed through the apparatus during this time. The flask is cooled to room temperature and

150cm^3 diethylether and 50g o-dibromobenzene is added. The flask was stoppered and placed on a shaker for 10 days. The flask is then opened under nitrogen and 25cm^3 of water added carefully to destroy any excess sodium metal. At this stage the flask comprises of a grey semi-solid with beads of mercury suspended with the aqueous and ethereal layers above it. The contents were filtered, and the aqueous and ethereal layers discarded. The solid is allowed to dry then placed in a dry nylon bag and squeezed until no more mercury comes through the cloth. The remaining solid is washed twice with water and twice with ether. The solid is dryed at 80^{o}C for two hours and divided into two portions. Each portion is successively stirred with 100cm^3 1-methylpyrolindin-2-one at 120^{o}C for 20 minutes. The suspensions obtained are centrifuged to remove any remaining traces of mercury. The red-brown liquors are combined and filtered. The filtrate is added to methanol (300cm^3). This causes the precipitation of a creamy-white finely divided o-phenylenemercury(II) which was removed by filteration. The product was recrystallised from DMF as small thin needles and dried at 110^{o}C for 24 hours melting at 332^{o}C (Lit.332-4^{o}C)[47]. Yield 12g. (Found C,26.2%; H,1.79% requires C,26.04%; H,1.46%)

2-7-6 Telluranthrene[48]

o-Phenylenemercury(II) (3g) and finely powdered tellurium (3g) were ground together and placed in a well of a sublimation apparatus. The pressure was reduced to 1mm or less and the cold finger cooled by means of dry-ice . The well of the apparatus, containing the reaction mixture, was taken to 250^{o}C and maintained at this temperature for 7 hours in a bath of Wood's metal. During this time both elemental mercury and a crystalline material condensed on the cold finger. The sublimed solids are dissolved in chloroform and filtered to remove the mercury.

Evaporation of the solvent leaves light yellow crystals which were recrystallised from ethanol/benzene melting at 168-9°C (Lit.169-70°C)[48]. (Found C,35.1%; H,2.01% : requires C,35.4%; H,1.96%).

2-7-7 Telluraxanthene

The attempted synthesis of Telluraxanthene was by the method of Lohner and Praefcke. This required the starting material 2,2'-dibromodiphenylmethane which was prepared as follows[49] :

2-7-7-1 Dibromobenzil

A solution of 2-bromobenzaldehyde (50cm^3) in ethanol (65cm^3) and sodium cyanide (5g) in water (50cm^3) was refluxed for 30 minutes. The mixture was cooled and a dark orange oily material separated. (Since the oily material could not be crystallised it was used crude for the next stage). The oil was placed in an evaporating dish on a steam bath. Concentrated nitric acid (570cm^3) was added slowy with stirring. When the addition was completed, heating was continued for a further 7 hours and afterwards the mixture was poured into water (1 litre). The yellow precipitate was recrystallised from ethanol giving yellow crystals which melted at 127-8°C (Lit. 127-8°C)[49]. Yield 55% based on 2-bromobenzaldehyde.

2-7-7-2 2,2'-Dibromobenzilic acid

A mixture of benzil (30g), ethanol (45cm^3), KOH (18g) and water (35cm^3) was refluxed for 15 minutes and then diluted with water (500cm^3). Dilute HCl was added and the precipitate formed upon neutralisation was filtered and recrystallised from benzene giving light brown crystals which melted at 151-3°C (Lit.152-4°C)[49]. Yield 65%.

2-7-7-3 2,2'-Dibrombenzophenone

2,2'-Dibromobenzilic acid (20g) in glacial acetic acid (65cm^3) was stirred violently with sodium bismuthate (15g) at 50-60°C for 6 hours. After cooling, 85% phosphoric acid(9cm^3) ,water(13cm^3) was added and left standing overnight. Diethylether (250cm^3) was added and washed successively with water, dilute NaOH solution and water again. The ether was removed and the residue recrystallised from ethanol giving pale yellow plates melting at 85°C (Lit. 84-5°C)[49]. The yield was 15g (75%).

2-7-7-4 2,2'-Dibromodiphenylmethane

A mixture of the dibromobenzophenone (15g), red phosphorus (31g), 57% HI (33cm^3) was refluxed for 48 hours. The mixture was cooledthen diluted with water and extracted twice with toluene (50cm^3). The organic layer was washed several times with water, dried with sodium sulphate and the solvent removed. The crude product was vacuum distilled (boiling point 164°C at 5mmHg). Yield 70%. (Found C,47.7%;H,3.0%; $C_{13}H_{10}Br_2$ requires C,48.1%; H,3.3%).The product was also confirmed by its IR spectra.

2-7-7-5 Telluraxanthene[50]

A solution of 2,2'-dibromodiphenylmethane (6cm^3) in 250cm^3 diethylether under nitrogen was stirred in a 3 necked flask containing a nitrogen inlet and one neck having a rubber suba seal. 25cm^3 t-Butyl lithium(15% in hexane) solution was added with stirring over an hour. The solution was stirred for a further one and half hours by which time it took on a red tint. Tellurium powder (3.2g) was added portionwise over 30 minutes with stirring. After the addition the solution was refluxed for 2 hours then cooled and left open to the atmosphere overnight. Chloroform ($50cm^3$) was added then water($50cm^3$), upon which tellurium metal precipitated, and filtered. The chloroform was separated then removed leaving a red gum. Evaporation of the water resulted in a pale brown solid.

2-7-8 p-Ethoxyphenyltellurinic acid

A solution of ditelluride (0.5g in $50cm^3$ THF) was added dropwise with stirring, to a solution of H_2O_2 (1:1 by volume THF:H_2O), containing a ten molar excess over a period of 30 minutes. The reaction solution was then allowed to stand overnight and the solvent removed leaving a white precipitate which was dried in vacuum over P_2O_5. The product had no melting point but decomposed at 165-6°C.(Lit. 234-6°C)[51] (Found C,30.8%; H,4.1% ; $C_8H_{10}O_3Te$ requires C,33.9%; H,3.5%).

2-7-9 Methanolysis product

Dry methanol ($30cm^3$) was added to p-ethoxyphenyltelluriumtrichloride (0.2g) in a $100cm^3$ beaker and left in a dessicator overnight. A white precipitate was observed and the liquor was drawn off and more methanol ($30cm^3$) added. This procedure was repeated for a week until vacuum drying of the white precipitate gave no yellow colour (which was observed if the precipitate is dried after the addition of methanol first time). The product decomposed at 234°C. (Found C,32.2% ; H,2.87%; Cl,11.5%)

2-7-10 Nessler's Reagent[45]

This was used in section 2-5. 23g Mercuric iodide and 16g potassium hydroxide was made up in ammonia free water to a volume of $100cm^3$. $100cm^3$ sodium hydroxide solution (6M) was added and the mixture allowed to stand for 24 hours. The solution was decanted from any precipitate that may have formed and transferred to a dark bottle. The reagent was stored in the dark until use.

2-8 Kinetic Studies

2-8-1 Procedure for H_2O_2/(p-EtOPh)$_2$Te$_2$ and N_2H_5Cl/p-EtOPhTeCl$_3$ systems

This involves using an SP8-100 UV visible spectrophotometer in conjunction with a thermostated water bath. The thermostating assembly of the water bath is adjusted to the required temperature and switched on and monitored using a thermometer. The glass cell (1cm length) was filled with 1.5cm^3 of (p-EtOPh)$_2$Te$_2$ solution in THF and kept in the cell holder for at least 20 minutes. A solution of H_2O_2 in THF/water (1:1 by volume) in a graduated flask was placed in the water bath for the same period. 1.5cm^3 of the H_2O_2 solution was transferred to the glass cell, quickly stoppered and replaced into the cell holder of the spectrophotometer. This procedure found to to be satisfactory even though the first reading was taken 10-20 seconds later.

In the reduction of p-EtOPhTeCl$_3$ by N_2H_5Cl the same procedure was used as explained above with the ditelluride solution replaced by p-EtOPhTeCl$_3$ and the H_2O_2 solution by N_2H_5Cl.

When the kinetic experiments were conducted under an atmosphere of either dinitrogen or dioxgyen the following procedure was used. A solution of ditelluride in THF, in a 3 necked flask, was purged through with dinitrogen or dioxgyen for at least 30 minutes and then sealed with one neck having a rubber suba seal.

Solutions of H_2O_2 were similarly treated and placed on a water bath prior to use. 2cm^3 of ditelluride solution was transferred to the cell (sealed under the appropriate atmosphere with a rubber suba seal), by means of a glass graduated hypodermic syringe fitted with a stainless steel needle. The cell was replaced in the cell holder for 20 minutes and then H_2O_2 solution (1cm^3) transferred into the cell by the same means as the ditelluride solution was transferred. The cell was shaken before being replaced in the cell holder and the absorbance-time curve obtained.

2-8-2 Methanolysis of p-$EtOPhTeCl_3$

The methanolysis of p-$EtOPhTeCl_3$ in methanol/benzene mixed solvent was determined at controlled temperatures. The apparatus consisted of a 250cm^3 beaker enclosed in a glass jacket. The system is kept at a constant temperature by circulating water through the water jacket of the beaker from the water bath.

The mixed solvent in the thermostated beaker was stirred continuously by a magnetic stirrer. The pH of the mixed solvent was measured using a pH meter mentioned in section 2-3-5. The solvents were supplied commerically and distilled prior to use.

The mixed solvent was left in the beaker for 20-30 minutes until the desired temperature was reached (usually 25^{o}C). At the same time the electrode of the pH meter was immersed in the mixed solvent and left until it gave a constant reading. A concentrated solution of p-$EtOPhTeCl_3$ in benzene (1cm^3) was added to the mixed solvent, stirred rapidly and the pH-time curve was obtained.

CHAPTER THREE

OXIDATION OF BIS(para-ETHOXYPHENYL) DITELLURIDE BY HYDROGEN PEROXIDE

3-1 INTRODUCTION

In this chapter I describe the oxidation of bis(p-ethoxyphenyl) ditelluride by hydrogen peroxide over a range of reagent concentrations, hydrogen ion concentrations, ionic strengths and solvent compositions.

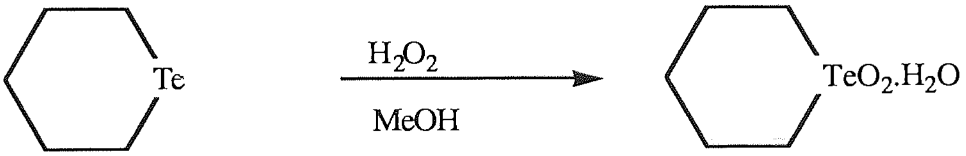
This particular reaction has been reported twice in the literature. Morgan and Kellet reported that the ditelluride was oxidised by a 30% hydrogen peroxide solution in alcohol to a white substance which was not further characterised[10]. Tahir[16], when investigating the reduction of p-ethoxyphenyltellurium trichloride by sulphite, undertook a cursory investigation of the ditelluride reaction with hydrogen peroxide using 1,4-dioxane and water (3:1 by volume) as the solvent. He found a short induction period relative to the time taken for the reaction to go to completion, followed by a reaction which appeared to show first order dependence on the concentration of ditelluride. His deduction from the data was that the presence of hydrogen peroxide catalyses the destruction of ditelluride, via a radical chain reaction.

3.1.1 Reactions of organotellurium compounds with Hydrogen Peroxide

Reactions involving organotellurides and ditellurides with hydrogen peroxide have been reported since 1920 when Vernon[52] claimed to have prepared dimethyltellurone, by reacting dimethyltelluride with hydrogen peroxide

$$(CH_3)_2\,Te \xrightarrow{H_2O_2} (CH_3)_2Te\,O_2$$

However it was pointed that analysis for the tellurone were not in close agreement but the product was reported to possess all the characteristics of a peroxide. The reaction between tellurocyclopentane and hydrogen peroxide in methanol, gave a white amorphous powder. However the product was insoluble in common organic solvents and liberated chlorine from hydrochloric acid and decolourised acidified potassium permanganate. On the basis of the tellurium analysis and the above properties the authors[53] suggested the product to be tellurocyclopentane 1,1-dioxide monohydrate



Balfe[54] and co-workers treated bis(carbonomenthoxymethyl) telluride with a 30 per cent hydrogen peroxide solution and obtained a white solid, which liberated iodine from HI and decolourised acidified permanganate. The authors thought that their compound was the hydrogen peroxide adduct of the telluroxide

$$R_2Te(OH)(OOH).$$

Other oxidations using air and hydrogen peroxide on unsymmetrical tellurides, lead to isolation of addition products of telluroxides with tellurinic acids of the general formula

$$RR'TeO.RTeOOH$$

where $R = C_4H_9$ and $R' = CH_2CO_2C_2H_5$

The tellurinic acid product was attributed to the instability of the telluroxides in their enol form, which were then further oxidised to give the tellurinic and carboxylic acids.

Bird and Challenger[55] obtained similar results when they oxidised dimethyl selenide with hydrogen peroxide. Balfe also suggested that the chemical properties observed for the tellurone were in fact due to the presence of a hydroxyl perhydrate
Viz:

$$R_2Te(OH){\cdot}O_2H$$

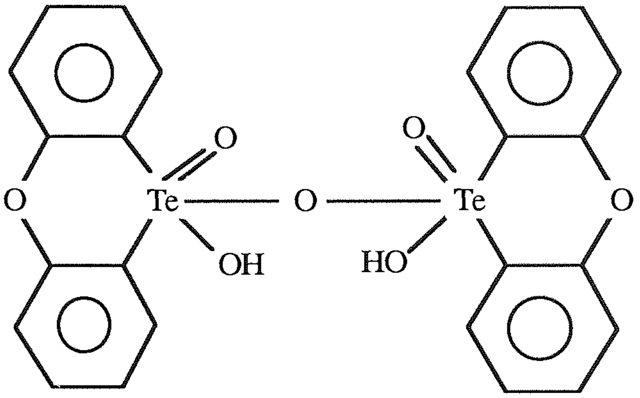
formed because the telluroxide, the primary product with hydrogen peroxide and n-$BuTeCH_2CO_2Et$, is stabilized by further combination with hydrogen peroxide forming a derivative analogous to $Bu_2Te(OH)_2$. Only when the oxidants were air and hyperol, were the products single compounds whereas HNO_3 and hydrogen peroxide gave double compounds. On this basis the cyclo-telluropentane product could be formulated as

$$C_5H_{10}\ Te(OH)O_2H$$

and Vernon's compound was probably similar

ie $(CH_3)_2TeO.CH_3TeO_2H$

The oxidation of phenoxtellurine by hydrogen peroxide was reported by Drew[56]. The results indicated that the compound was a mixture of products and possibly a double compound. It was soluble in alkaline media and liberated chlorine from hydrochloric acid. The tellurone was suggested on the above chemical properties, and after vacuum drying at 110°C the analysis suggested the half-anhydride of the semi-ortho form was obtained.



When stoichiometric quantities of hydrogen peroxide and phenoxtellurine were used, the product obtained was consistent with tellurone formation[3].

Hollimann and Mann[57] oxidised telluroisochroman with hydrogen peroxide and the reaction proceeded beyond the tellurone without, however, complete conversion. The authors suggested the hydroxy-perhydrate formation, $R_2Te(OH)OOH$, from the elemental analysis.

The phenoxtellurine and tellurisochroman products are examples of Tellurium (VI) compounds. In all the earlier work discussed, elemental analysis and chemical properties were used to confirm the composition of the product. The products were not, however, recrystallised due to their insolubility. This together with Balfe and co-worker's observations cast doubts upon the interpretations that the tellurium is present in the oxidation state +6.

Recent work however, using t-butylhydroperoxide as the oxidant, show that several tellurides gave tellurium (VI) species as the product[58]

$$RTeC_6H_4OCH_3 \xrightarrow{\text{t-BuOOH}} RTe(O)_2C_6H_4OCH_3$$

$R = n\text{-}C_{12}H_{35}$

thus confirming that tellurium (VI) is a possible reaction product by oxidation with peroxides.

The results from the reaction stoichiometry also indicated that a mixture of tellurium(IV) and tellurium (VI) products were possible. Lee and Cava[58] reported a similar occurence when t-butylhydroperoxide oxidised telluride (1), in equal molar concentrations, to give the oxide (2) and dioxide (3) and unreacted telluride (1) in a 1:2:1 molar ratio

$$\begin{array}{ccll} RTeC_6H_4OCH_3 & \xrightarrow{\text{t-BuOOH}} & RTe(O)_2C_6H_4OCH_3 & (2) \\ (1) & & + & \\ & & RTe(O)C_6H_4OCH_3 & (3) \end{array}$$

Reactions involving organoselenium compounds with hydrogen peroxide are reported to give two products, selenoxides and seleninic acids with selenium (IV) and not selenium (VI) present in the products. It was reported that selenoxides are the products with diaryl selenides[59], whilst seleninic acids occur with alkylaryl, dialkyl selenides [60] and diaryl diselenides[61, 62].

The product described in this chapter is believed to be tellurinic acid, p-EtOPhTe(O)OH. This compound has been prepared by hydrolysis of the acid chloride, p-EtOPhTe(O)Cl, in 70-80% sodium hydroxide solution[6].This is a general preparation of tellurinic acids, the other method involves oxidation of diorganyl tellurides. Tellurinic acids[17] are not a well characterised group but the acid chlorides, bromides, iodides, nitrates and anhydrides are known derivatives.

3.1.2 Organotellurium and selenium radical species

The reaction described here was initially believed to involve radicals. Pulse radiolysis of diaryl diselenides, selenides, tellurides and ditellurides in neutral and acidic methanolic solutions were reported to involve radicals[63]. In the diselenide and selenide system two transients were observed, assigned to the radicals RSeSe' and RSe'. However only one transient was observed in the telluride and ditelluride system, assigned to RTe, thus indicating little tellurium-carbon bond cleavage occurs in the ditelluride system.

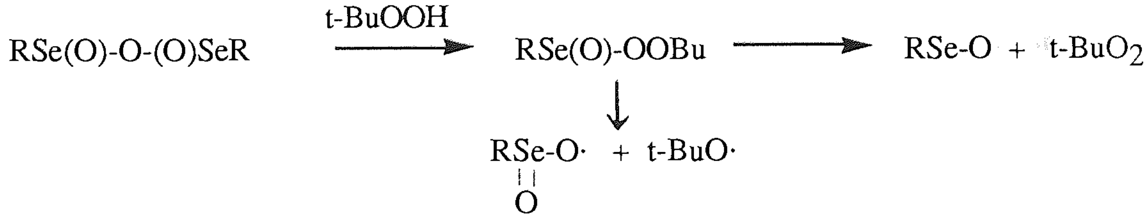
Spencer and Cava[64] reported that photoreactions involving dibenzyl ditelluride and the same diselenide behave similarly upon u.v. irradiation. In the absence of oxygen, elemental selenium or tellurium and dibenzyl selenide and telluride are produced quantitatively. In the presence of oxygen, elemental selenium and tellurium together with benzaldehyde, benzyl alcohol, toluene and 1,2-diphenylethane are the products.

Mehdi's photochemical investigation of diaryl ditellurides, demonstrated that radicals could be detected by ESR. The radicals were suggested to come from homolytic cleavage of Te-Te bond producing RTe. The reaction showed a dependence on the presence of dissolved dioxygen to give a telluroxide, bis(p-phenetyl) telluryl oxide, R_2Te_2O, as the product[13].

Reactions involving diselenides with peroxides have been reported to involve radicals. Dialkyl diselenides react with a stoichiometric quantity of t-butyl hydroperoxide in benzene at room temperature to give seleninic anhydride

$$\mathrm{RSeSeR} + \text{3t-BuOOH} \longrightarrow \mathrm{RSe(O){-}O{-}(O)SeR} + \text{3t-BuOH}$$

This reaction is believed to be non-radical in nature[65]. However when the reaction is carried at 75°C, the products are ultimately SeO_2, O_2 and t-butyl alcohol. It was suggested[67] that the first formed seleninic anhydride reacts with t-butyl hydroperoxide to form a perester, which then undergoes homolytic decomposition

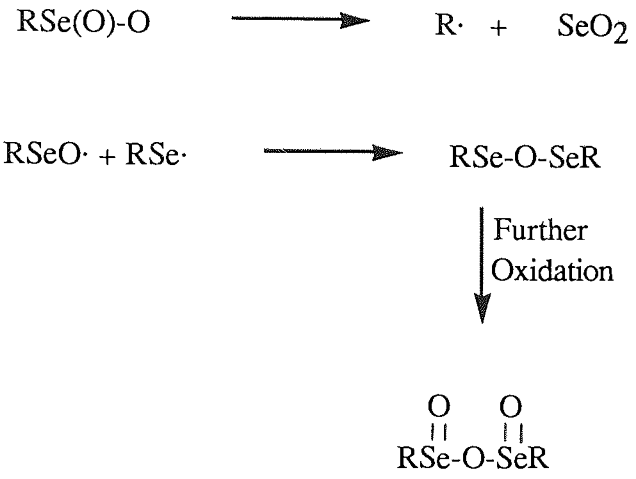


$$\mathrm{RSe(O){-}O{-}(O)SeR} \xrightarrow{\text{t-BuOOH}} \mathrm{RSe(O){-}OOBu} \longrightarrow \mathrm{RSe{-}O} + \text{t-BuO}_2$$

$$\downarrow$$

$$\underset{\overset{\parallel}{\mathrm{O}}}{\mathrm{RSe}}\mathrm{{-}O\cdot} + \text{t-BuO}\cdot$$

The fate of the oganoselenium radicals is not known. Since SeO_2 is formed it is possible that the selenoxyl-type radicals may be converted into seleninic anhydride



$$RSe(O)\text{-}O \longrightarrow R\cdot + SeO_2$$

$$RSeO\cdot + RSe\cdot \longrightarrow RSe\text{-}O\text{-}SeR \xrightarrow{\text{Further Oxidation}} R\overset{O}{\overset{\|}{Se}}\text{-}O\text{-}\overset{O}{\overset{\|}{Se}}R$$

Woodbridge also found that dialkyl selenide catalytically decomposes at least 50 moles of hydroperoxide, and the decomposition was found to be zero order in hydroperoxide and first order in seleninic acid.

3.1.3 Intermediates in Organotellurium and Selenium Chemistry

The first reaction scheme postulated for the reaction understudy here involved RTeOH as an intermediate. Compounds of the type ArTeX (X= Cl, Br,I, CNS etc), where Ar= aromatic group, have been prepared from the reduction of aryltellurium trichlorides but not so far for X= OH[17, 67]. Hydrolysis of ArTeX (X=Cl, Br, I) in basic media produces a mixture of ditellurides and tellurinic acid derivatives. One probable intermediate, ArTeOH was not isolated, probably due to the fact it is too co-ordinatively unsaturated to allow isolation. ArTeOH has been postulated to explain thermolysis of $RCH_2CH_2Te(O)Ar$ (R= n-$C_{12}H_{35}$- and Ar = aryl group). The products were found to be tellurinic acid ArTe(O)OH, telluride RCH_2CH_2TeAr and alkene $RCH{=}CH_2$. The authors suggested ArTeOH as an intermediate which reduced half the orginal oxide back to the corresponding telluride. The presence of ditelluride was consistent with competitive thermal disproportionation of ArTeOH

Viz

$$\mathrm{3ArTeOH} \longrightarrow \mathrm{Ar_2Te_2} + \mathrm{ArTe(O)OH} + \mathrm{H_2O}$$

$$\mathrm{ArTeOH} + \mathrm{RCH_2CH_2Te(O)Ar} \longrightarrow \mathrm{RCH_2CH_2TeAr} + \mathrm{ArTe(O)OH}$$

Consideration was given to the discussion of the lower reaction stoichiometry results, when the possibility of

$$\begin{array}{ccccc} 3\,\mathrm{Te}^{\mathrm{II}} & \rightleftharpoons & \mathrm{Te_2} & + & \mathrm{Te}^{\mathrm{IV}} \\ \text{Intermediate} & & \text{Ditelluride} & & \text{Product} \end{array}$$

was considered.

Disproportionation is known to occur in organoselenium chemistry. When seleninic acids and diselenides are mixed together an intermediate (PhSeOH) is believed to be in equilibrium with $PhSeO_2H$ and Ph_2Se_2[68].

Viz

$$\mathrm{PhSeO_2H} + \mathrm{Ph_2Se_2} \rightleftharpoons 3[\mathrm{PhSeOH}]$$

This intermediate is known to add to alkenes to give allylic alcohols.[69] However Gancarz has deduced from ^{19}F NMR that the intermediate could be ArSeOSeAr in equilibrium with ArSe(O)O(O)SeAr and Ar_2Se_2 from the reaction of equal molar amounts of t-Butylhydroperoxide and diselenide (Ar_2Se_2), Ar= p-FC_6H_4.

The decomposition of hydrogen peroxide is known to be catalysed by a variety of species. My finding of higher reaction stoichiometry results than the expected 3:1 stoichiometry (H_2O_2:R_2Te_2) also suggested this possibility. Reich[70] reported that hydrogen peroxide is catalytically decomposed by selenoxides in mixed solvent systems. It was found that decomposition was rapid in aqueous methanol but much slower in aqueous THF using methylphenyl selenoxide (CH_3SeOPh). However it was reported that phenyl seleninic acid (PhSe(O)OH) does not decompose hydrogen peroxide under the same conditions. The observation that seleninic acid did not decompose hydrogen peroxide in aqueous THF was similar to the results obtained in my work. I therefore suggest that the higher stoichiometry results were due to the formation of Te^{VI} as the final product.

3.1.4 Hydrogen Peroxide

Hydrogen peroxide has been known since 1818 when Louis-Jacques Thernard treated nitric acid with barium peroxide. The standard redox potentials of hydrogen peroxide for one-electron equivalent oxidations are

$$H_2O_2 + H^+ + e^- \longrightarrow HO\cdot + H_2O \qquad E^o = 0.80V \quad \text{---(3-8)}$$

$$HO\cdot + H^+ + e^- \longrightarrow H_2O \qquad E^o = 2.74V \quad \text{---(3-9)}$$

For two-electron equivalent oxidation in acidic and basic solution the standard redox potentials are[71]

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad E^o = 1.77V \qquad \text{---(3-10)}$$

$$HO_2^- + H_2O + 2e^- \longrightarrow 3OH^- \qquad E^o = 0.87V \qquad \text{---(3-11)}$$

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \qquad E^o = 0.68V \qquad \text{---(3-12)}$$

from which it can be seen that hydrogen peroxide is a strong oxidizing agent in either acid or basic solution. It also acts as a reducing agent (3-12) but only towards strong oxidizing agents such as potassium permanganate.

Reactions between hydrogen peroxide and various oxidants and reductants, together with the metal-ion catalysed decomposition involving hydrogen peroxide in solution, can give rise to radicals of which the hydroxyl(HO) and the perhydroxyl (HO_2) radicals are most important.

The oxygen evolved during catalytic[72] decomposition of hydrogen peroxide has been shown by ^{18}O tracer studies to come from the hydrogen peroxide molecule and not from the water (solvent). The same has been found in oxidation and reduction reactions of hydrogen peroxide, for example, the oxygen does not come from potassium permanganate.

The one-electron equivalent oxidation and reduction of hydrogen peroxide gives rise to the hydroxyl and the perhydroxyl radicals. The perhydroxyl radical has been reported in aqueous solutions by Saito and Bidski[73] in the interaction of ceric sulphate with hydrogen peroxide

$$\mathrm{Ce^{IV}} + \mathrm{H_2O_2} \longrightarrow \mathrm{Ce^{III}} + \mathrm{HO_2} + \mathrm{H^+} \qquad \text{---(3-13)}$$

$$\mathrm{Ce^{IV}} + \mathrm{HO_2} \longrightarrow \mathrm{Ce^{III}} + \mathrm{O_2} + \mathrm{H^+} \qquad \text{---(3-14)}$$

It was later confirmed[74], however, that the electron spin resonance (ESR) signal came from a ceric(III)-complex, [$\mathrm{Ce^{III}}$-OOH], as suggested by earlier workers .

The hydroxyl radical has been identified in solutions of titanium(III) and hydrogen peroxide. Initially only one signal was observed, but this was later found to be a superposition of two signals. It is believed that the interaction of hydrogen peroxide with titanium(III) gives the hydroxyl radicals which then react with titanium(IV) to give ESR signals of two relativity unreactive species[75].

$$\mathrm{Ti^{III}} + \mathrm{H_2O_2} + \mathrm{H^+} \longrightarrow \mathrm{Ti^{IV}} + \mathrm{HO\cdot} + \mathrm{H_2O} \qquad \text{---(3-15)}$$

$$\mathrm{Ti^{IV}} + \mathrm{HO\cdot} \longrightarrow [\mathrm{Ti^{IV}\text{-}OH}] \qquad \text{---(3-16)}$$

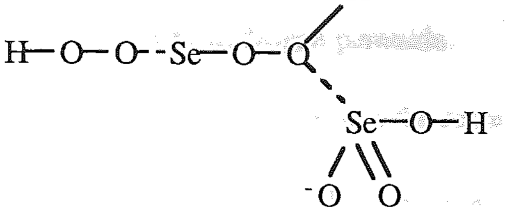
Thus, depending on whether hydrogen peroxide is acting as an oxidizing or reducing agent, two different radicals are produced by a one-electron step. Acting as an oxidant gives the hydroxyl radical, whereas acting as a reductant gives the perhydroxyl radical.

3.1.5 Mechanistic aspects of oxidations by hydrogen peroxide

In the reaction studied in this chapter, the oxidation monitored involved oxidation from tellurium(I) in the ditelluride, to tellurium(II). Thus the possibility of hydroxyl radicals present as an intermediate must be considered. However, this depends on whether hydrogen peroxide oxidises the ditelluride by a one- or two-electron equivalent reaction.

Oxidations involving hydrogen peroxide with transition metals involve mainly one-electron equivalent reactions. However, Higginson and Marshall[76] state that oxidation-reduction reactions between simple compounds of non-transition elements usually occur in two-electron equivalent steps. Since hydrogen peroxide and the ditelluride are compounds derived from p-block elements the reaction might be expected to go via a two-electron process. Oxidation-reduction reactions between a compound of a non-transition element and a transition metal ion or compound, on the other hand, may occur via a one- or two-electron equivalent. It is generally found that the one-electron equivalent process dominates.

The oxidation of tin(IV) and selenious acid (H_2SeO_3) by hydrogen peroxide proceeds via a two-electron equivalent. The oxidation of selenious acid by hydrogen peroxide in strong acid media was reported by Hughes and Martin[77]. Two possible mechanisms were suggested. One involves the nucleophilic replacement of $HSeO_3^-$ from peroxyselenious acid by a biselenite ion with the following transition state



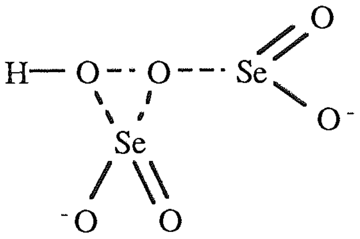
---(3-17)

In this mechanism one peroxide would go to the selenate (H_2SeO_4) whereas the other ends up in the selenite ($HSeO_3^-$). The selenite exchanges oxygen with water

$$H_2SeO_3 \rightleftharpoons SeO_2 + H_2O \qquad \text{---(3-18)}$$

and as such half the peroxide oxygen atoms end up in the selenate.

The other pathway suggested was based on the analogous sulphur system. It was found that both peroxide oxygen atoms appear in the same sulphate (product) using ^{18}O labelled hydrogen peroxide. Thus attack on the hydrogen peroxy-group, HO_2^- , in a hydrogen peroxy selenite ion by SeO_2 was suggested. Both the O-O, from the peroxide and the Se-O bonds break simultaneously to give the biselenate. The transition state in this case would have the form



The SeO_2^- comes from the dehydration equilibria 3-18. This reaction is a two-electron equivalent and also involves oxidation of selenium(IV) to selenium(VI).

The reactions of organoselenium compounds with hydrogen peroxide are reported to give selenium(IV) products, so this reaction demonstrates that it is possible to get selenium(VI) from oxidation by hydrogen peroxide.

Another interesting feature of this reaction was the report of decomposition of hydrogen peroxide. The authors reported that low concentrations of selenious acid inhibit the thermal decomposition of hydrogen peroxide (reaction was carried out at 67.7 and 75°C). It was suggested that the inhibition occurs via a chain-carrying radical reacting with selenious acid to give a selenium radical which terminates the chain. It was clear, however, that the decomposition does not involve a combined oxidation and reduction of hydrogen peroxide by the H_2SeO_3-H_2SeO_4 couple. This conclusion is similar to that I reached in my reaction stoichiometry studies. This was despite the fact that thermodynamic data indicate that a tellurium(IV)-tellurium(VI) couple would be capable of decomposing hydrogen peroxide. The reaction stoichiometry ratios were less than those expected for decomposition of hydrogen peroxide. Also, the tellurium(VI) species (H_6TeO_6) is six co-ordinate and for decomposition to occur by an inner-sphere two-electron equivalent reduction of tellurium(VI) a co-ordination number of seven would be required. Since this is expected to be difficult the decomposition could be very slow.

The reaction of tin(II) and hydrogen peroxide has been studied in hydrochloric acid media[78]. The authors showed that the reaction involved a two-electron equivalent reaction; no induced reaction from tin(III) with trioxalatocobaltate(III) was observed. Tin(III) is expected if one-electron oxidation of tin(II) occurs. The reaction stoichiometry was found to be 1:1 ($[Sn(II)]/[H_2O_2]$) using the spectrophotometric method of determining the hydrogen peroxide concentration, which was in excess in 1M HCl media. No consumption of Co(III) was observed under all the experimental conditions.

$$Sn^{II} + H_2O_2 \longrightarrow Sn^{IV}O^{2+} + H_2O \qquad \text{---(3-19)}$$

The last two examples demonstrate that reactions of non-transition element compounds react with hydrogen peroxide via a two-electron equivalent. However, in each case the difference in the oxidation states was two, whereas in my system the oxidation observed was tellurium(I) to tellurium(II), that is difference of the oxidation states of only one; however the change is also dimer to monomer.

The oxidation of the chromous ion by hydrogen peroxide was reported to involve both one and two-electron equivalents. The chromium products are $[Cr(H_2O)_6]^{3+}$ and an appreciable amount of a dinuclear complex[79]. Some 14% of the chromium was found to be present in this dinuclear complex. The $[Cr(H_2O)_6]^{3+}$ product is formed by a one-electron equivalent reaction

Viz:

$$\underset{}{Cr^{II}} + H_2O_2 \xrightarrow{\text{1-eqv}} \underset{\text{mononuclear}}{Cr^{III}} + HO\cdot \qquad \text{---(3-20)}$$

The dinuclear species is formed by a two-electron equivalent process

$$Cr^{II} + H_2O_2 \xrightarrow{\text{1-eqv}} Cr^{IV}\ \text{species}$$

$$Cr^{IV} + Cr^{II} \longrightarrow \text{dinuclear species}$$

$$\text{---(3-21)}$$

The one-electron equivalent process, however, is predominant as 70% of the oxidation to chromium(III) goes via this pathway. The oxidation by molecular oxygen also involves a dinuclear species

$$Cr^{II} + O_2 \longrightarrow [CrO_2]^{2+} \qquad \text{---(3-22)}$$

$$[CrO_2] + Cr^{III} \longrightarrow \underbrace{[Cr^{III}\text{-}O\text{-}O\text{-}Cr^{III}]^{4+}}_{\text{Dinuclear species}} \qquad \text{---(3-23)}$$

The dinuclear species in the O_2 system (3-23) is shown to have an O-O bridge. The species derived from the hydrogen peroxide system also probably involves an O-O bridged dimeric species. The oxidation by molecular oxygen, however, goes entirely via this dinuclear complex, whereas the hydrogen peroxide system has two competing reactions taking place.

The oxidation of vanadium(II) by hydrogen peroxide and molecular oxygen was described by Swinehart[80]. An intermediate was detected spectroscopically during the course of the reaction, while the vanadium product was vanadium(III). The oxidation of excess vanadium(II) occurs by rapid oxidation to give VO^{2+} followed by the reaction of VO^{2+} with V^{2+} yielding V^{3+}

$$V^{2+} + H_2O_2 \text{ or } O_2 \longrightarrow VO^{2+}$$

$$VO^{2+} + V^{2+} \longrightarrow VOV^{2+} \longrightarrow VO^{+} + V^{3+}$$

$$\text{---(3-24)}$$

The direct one-electron equivalent step,vanadium(II) to vanadium(III) was also reported to occur. However, the process going via the two-electron equivalent accounted for 30% of the total pathway for hydrogen peroxide and 60% for molecular oxygen. Thus the predominant path in hydrogen peroxide oxidation is the one-electron equivalent. Now, in the molecular oxygen reaction it is possible that VO^{2+} is formed from a $[V\text{-}O\text{-}O\text{-}V]^{2+}$ species in which the O-O bridge undergoes homolytic fission to give the vanadium(IV) species, VO^{2+}. The hydrogen peroxide oxidation, however, could either give VO^{2+} from a simple bimolecular reaction

$$V^{2+} + H_2O_2 \longrightarrow VO^{2+} + H_2O$$

or involves the $[V\text{-}O\text{-}O\text{-}V]^{2+}$ species. In both cases a two-equivalent reaction is occuring and the overall oxidation state change for the vanadium(II) is one.

The chromium(II) and vanadium(II) examples show that oxidation then reduction can occur with the metal ion species. This is similar to my postulated scheme which involves oxidation from tellurium(I) to tellurium(III) then reduction by tellurium(I) to give the initial tellurium(II) product.

The rate of reaction for the oxidation of the ditelluride by hydrogen peroxide was found to be inhibited by acid at $pH<3$ and above $pH>11.5$ the rate increased. Between these values the rate was independent of the pH. Now in the oxidation of ditelluride by hydrogen peroxide, we can consider the ditelluride acting as a nucleophile.

Generally, oxidations involving hydrogen peroxide with nucleophiles are slower in acidic solution than in alkali solution. This must be a kinetic effect. Equation (3-11) shows that, as the acidity increases, the oxidation by hydrogen peroxide becomes more favourable. When the acid concentration is high, $pH>1$, acid catalysis is known without exception for reactions involving hydrogen peroxide with nucleophiles. The acid catalysis term normally appears as a second term[82,83] in the rate law giving the law over a range of pH values as

$$\text{Rate} = k_2[H_2O_2][\text{Nuc}] + k_3[H_2O_2][\text{Nuc}][H^+] \qquad \text{--(3-25)}$$

where Nuc = Nucleophile

Within the nucleophilic attack scheme for oxidations by hydrogen peroxide, it is generally accepted that the rate law expressed above results from protonation of hydrogen peroxide. Water is a better leaving group than OH^- and therefore protonation of hydrogen peroxide promotes nucleophilic cleavage of the O-O bond

Viz:

$$H_2O_2 + H^+ \longrightarrow H_3O_2^+ \qquad \text{Fast} \qquad \text{---(3-26)}$$

$$H_3O_2^+ + Nu \longrightarrow H_2O + HONu \qquad \text{Slow} \qquad \text{---(3-27)}$$

The pK_a of the step 3-26, has been estimated as -4.7, thus only when the acid concentration is high $pH<1$ does the concentration of $H_3O_2^+$ become significant. Indeed many reactions show that the above scheme is valid as acid catalysis occurs at high acidities.

In my work the rate was found to drop at acidities below $pH<3$ indicating that some other protonation equilibrium is occurring. Also the lowest pH I worked at was 1.74, which is less than that expected for the observation of acid catalysis. It was not possible to study at lower pH values due to the immiscibility of the ditelluride and hydrogen peroxide solutions.

The reaction proposed for the ditelluride oxidation involves a ditelluride-dioxygen adduct which retards the rate of reaction. Molecular oxygen reacts reversibly with some metal complexes and the greatest number of dioxygen-metal complexes are based on cobalt. The hexamminecobalt(II) ion was the first example to be investigated and is oxygenated in aqueous ammonia with the dioxygen displacing one of the ammonia ligands[83].

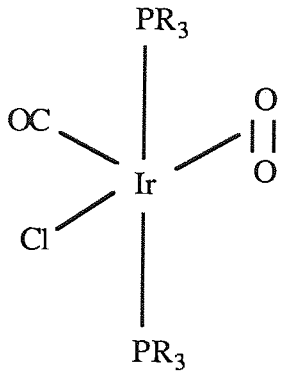
$$2[Co(NH_3)_6]^{2+} + O_2 \longrightarrow [(NH_3)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{4+} + 2NH_3 \qquad \text{---(3-28)}$$

A decrease in the dioxygen pressure or increase of the ammonia concentration deoxygenates the complex.

Oxygen complexes with other transition metals are restricted mainly to the groups VIII and IX. Vaska's compound reversibly takes up molecular oxygen in benzene solution and can be isolated

$$\textit{trans}\text{-}Ir^{I}CO[P(C_6H_5)_3]_2Cl + O_2 \longrightarrow Ir^{III}CO[P(C_6H_5)_3]_2(Cl)O_2 \qquad \text{---(3-29)}$$

The entry of the O_2 molecule into the coordination sphere of the complex leads to an approximately trigonal bipyramidal structure[84]. The O_2 bond distance increases from 1.21 to 1.30A in the adduct which is consistent with a superoxo species(O_2^-).



Although a ditelluride-dioxygen adduct is proposed, it takes no part in the reaction as no radical species are believed to be present. Nevertheless the fact that the rate of reaction is a quarter of that under air, indicates that an adduct may be occurring in my system.

Now, turning to my work a brief summary is given.

The oxidation of bis(p-ethoxyphenyl) ditelluride by hydrogen peroxide has been studied. The oxidation consists of three distinct stages, tellurium(I) to tellurium(II) then tellurium(II) to tellurium(IV) and lastly tellurium(IV) to tellurium(VI). Each successive stage is slower than the last and as a result the kinetic studies presented refer to the fast stage, tellurium(I) to tellurium(II). The reaction profile is characterised by an induction period followed by a stage profile which fitted well to a first order rate equation in its later stages.

An integrated rate equation was derived which could fit the whole kinetic data from the start to at least 70% completion of the reaction, that is including the induction period, and continuing to a stage where I decided that the accuracy of the data did not warrant further use. The integrated rate constant varies under different gaseous atmospheres in the following order

$$N_2 \; > \; \text{Air} \; >> \; O_2$$

therefore the interaction of the tellurium species with dioxygen needs to be considered. Evidence was found to show that further oxidation occurs from tellurium(II) to tellurium(IV), and tellurium(IV) to tellurium(VI). These oxidations are very slow and can be treated separately from the earlier oxidation. The first step is believed to be a second order reaction.

The product exhibits a broad band between 750-550cm^{-1} in its infra-red spectrum. This indicates that a Te-O bond is present. The ^{1}H nmr spectrum of the product is very broad and the product gives an ESR signal. The elemental analysis for carbon and hydrogen content of the product are lower than that expected for the tellurinic acid and the anhydride formulation. The product appears to be a mixture of p-ethoxyphenyl tellurinic acid(p-EtOPhTe(O)OH) and a tellurium(VI) product,on the basis of the avaliable evidence.

3-2 RESULTS

The reaction between bis(p-ethoxyphenyl) ditelluride (p-EtOPh)$_2$Te$_2$, and hydrogen peroxide (H_2O_2), using a 3:1 by volume THF : water mixture as the solvent, has been studied. The results obtained from individual experiments were always reproducible under the same conditions over the whole reagent concentration, solvent and temperature ranges studied.

The absorbance maximum of the ditelluride, over the range 800-350nm, occurs at 400nm. A solution of hydrogen peroxide in the same solvent gave no absorbance at this wavelength, thus the absorbance maximium (400nm) of the ditelluride represented the best wavelength to follow the reaction.

It was found that the ditelluride, in a 3:1 by volume THF:water solvent, obeys the Beer-Lambert law over the concentration range studied in the kinetic studies. A plot of absorbance versus concentration of (p-EtOPh)$_2$Te$_2$ is a straight line as shown in fig 3-1 and the slope corresponds to the molar extinction coefficient of (p-EtOPh)$_2$Te$_2$. The value obtained from the slope was 1082 ± 12 dm^3 mol^{-1} cm^{-1} .

The kinetic studies for the reaction were made by measuring the decrease in the concentration of one of the reactants, (p-EtOPh)$_2$Te$_2$, with time. The reaction was monitored at 400nm using an SP8-100 uv-visible spectrophotometer. The reaction profile was followed until the reaction was 90% complete, that is 10% of the initial absorbance at which stage the observation was stopped. A reaction profile is shown in fig 3-2 from an original kinetic run and shows two distinct stages. Initially there is an induction period which lasts around 2-3 minutes. The rate of observed loss for the of reagent then increases giving a reaction profile as shown in fig 3-2.

The absorbance-time graphs could be fitted, for the second stage of the reaction profile, to an integrated form of a first order rate equation. The reaction was found to be first order with respect to the ditelluride concentration and thus the rate equation can be expressed as

$$-\frac{d[(p\text{-EtOPh})_2Te_2]}{dt} = k_{obs}[(p\text{-EtOPh})_2Te_2)] \qquad \text{---(3-30)}$$

Integration of equation 3-30 leads to equation 3-31

$$\log_e [A_t - A_{oo}] = k_{obs}t + \text{Constant} \qquad \text{---(3-31)}$$

where the subscripts A_t and A_{oo} refer to the absorbance at time t and infinity. Thus a plot of $\log_e [A_t - A_{oo}]$ versus time gives a straight line giving k_{obs} (observed rate constant) for each kinetic run. A computer program in BASIC for the Apple IIe, shown in appendix I, was used to obtain the individual rate constants (k_{obs}) in all the kinetic runs undertaken, and a typical fit of the data with this treatment is shown by the crosses on fig 3-2 (The circles indicate the treatment of the integrated rate equation discussed later). Surprisingly the rate of this part of the reaction, as determined from equation 3-31, appeared to be zero order in hydrogen peroxide even when the peroxide was not in a large excess although H_2O_2 is needed and consumed during the reaction.

The effect on the observed rate constant (k_{obs}) using different initial ditelluride concentrations was studied (table 3-2). The initial hydrogen peroxide concentration used in these runs was 4.28 x 10^{-3} mol dm^{-3} whilst the ditelluride concentration was varied from 12.8 to 1.26 x 10^{-4} mol dm^{-3}. A plot of the natural logs of the observed rate constant and initial ditelluride concentrations gave a straight line graph, whose slope was 0.5 ± 0.04. Also a plot of the observed rate constant versus the square root of the initial ditelluride concentration gave a straight line graph (fig 3-3).

The effect on the observed rate constant (k_{obs}) using different initial hydrogen peroxide concentrations was studied (table 3-3). The ditelluride concentration was kept at 6.41 x 10^{-4} mol dm^{-3}, whilst the hydrogen peroxide concentration was varied from 22.8 to 3.13 x 10^{-3} mol dm^{-3}. A plot of the natural logs of k_{obs} and the initial hydrogen peroxide concentration gave a straight line graph of slope unity. A plot of the observed rate constant versus the initial hydrogen peroxide concentration is linear as shown in fig 3-4.

On investigating the effect of temperature on k_{obs} it was found that the reaction followed an Arrhenius plot, fig 3-5. The data for the temperature runs are shown in table 3-4. The concentrations of hydrogen peroxide and ditelluride used throughout were 4.48 x 10^{-3} and 4.54 x 10^{-4} mol dm^{-3}.

The Arrhenius equation

$$k = A \exp(-\Delta E^*/RT) \qquad \text{---(3-32)}$$

where A = Frequency factor, R is the gas constant (8.314 J K^{-1} $mole^{-1}$). A plot of ln k_{obs} versus K/T is linear as shown in figure 3-5. The slope corresponds to $-\Delta E^*/R$ and a least squares computer program (Appendix II) was used to determine the slope.

The activation energy is related to the enthalpy of activation by the equation

$$\Delta H^* = \Delta E^* - nRT \qquad \text{---(3-33)}$$

where n is unity for unimolecular reactions and liquid phase reactions. The entropy of activation was calculated from the following equation

$$k_{obs} = (K_B T/h)\ \exp(\Delta S^*/R)\ \exp(-\Delta H^*/RT) \qquad \text{--- (3-34)}$$

where K_B is the Boltzmann constant and h is Planck's constant .

The observed data of ΔE^*, ΔH^* and ΔS^* are;

$$\Delta E^* = 49.1 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta H^* = 46.6 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta S^* = -137 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$$

Experiments were carried out in which the solvent composition was varied. Data after the addition of an inert salt (sodium nitrate, $NaNO_3$) also gave similar results, tables 3-5 and 3-6 . In both cases the observed rate constant showed a small change indicating that there was no significant effect on the reaction rate (k_{obs}) by varying the dielectric medium and ionic atmosphere.

The effect of pH on the observed rate constant was investigated over the pH range 1.74 to 12.10 (table 3-7 and fig 3-6), using sodium nitrate to maintain a constant ionic strength throughout. The plot of ln k_{obs} versus pH indicates that there is a region where k_{obs} is independent of pH (3.5 to 11) and shows a inverse H^+ effect around 3.5 and 11.5.

The effect of different gaseous atmospheres was investigated. In Mehdi's photochemical studies it was found that molecular oxygen was involved in the reaction, and the rate varied in the following order of different atmospheres O_2 > Air >> N_2 . The rate profile was qualitatively similar to my system. A short induction period was followed by a rate profile showing a half-order rate equation dependance upon [ditelluride] (the length of the induction period varied as N_2>> Air > O_2).

However, I found that in my system, the rate varied in the following order of different atmospheres

$$N_2 > \text{Air} >> O_2$$

The induction period under dinitrogen was very short, whilst under dioxygen it lasted up to a fifth of the reaction time (that is the time taken to reach 90% completion). A comparison of rate profiles are shown in fig 3-7.

The effect of varying the hydrogen peroxide concentrations under a gaseous dinitrogen or dioxygen atmosphere was investigated. The dioxygen data, table 3-8, gave a linear plot from a log plot of the observed rate constant and initial hydrogen peroxide concentration whose slope was unity and a plot of k_{obs} versus the initial hydrogen peroxide concentration is linear shown in fig 3-8. The range of initial hydrogen peroxide concentrations used were 6.17 to 74.7 $\times 10^{-3}$ mol dm^{-3}, which was three times the maximum concentration used under air. The ditelluride concentration was 4.50 $\times 10^{-4}$ mol dm^{-3} throughout these runs. In these runs the induction period was still observed up to the maximum concentration of hydrogen peroxide used, whereas in air it was unobserved at the largest concentration of hydrogen peroxide used (22.4 x10^{-3} mol dm^{-3}).

The data under dinitrogen, table 3-9, gave a linear plot of slope unity from a log plot of the observed rate constant and initial hydrogen peroxide concentration. The range of initial hydrogen peroxide concentrations used were 17.1 to 6.40 x 10^{-3} mol dm^{-3} and the ditelluride concentration kept at 4.55 x10^{-4} mol dm^{-3} throughout these runs.

Stoichiometry experiments were undertaken to determine the reagent ratios. Two sets of experiments were undertaken using different initial ditelluride and hydrogen peroxide concentrations. The excess ditelluride was determined from the absorbance of the remaining ditelluride, and excess hydrogen peroxide was determined from the Ti(IV)-peroxy complex (ε = 706 mol^{-1} dm^{3} cm^{-1} at 410nm), obtained by adding equal volumes of reaction solution and acidified titanium (IV) sulphate solution.

The first set of experiments used constant ditelluride concentrations (table 3-10), and the second set constant hydrogen peroxide concentrations (table 3-11). Both sets of data follow the same pattern. I found that the stoichiometry depends on the initial ratio of the two reagent concentrations. When there is an excess of ditelluride the stoichiometry lies between one and two. When there is up to three molar excess of hydrogen peroxide, the stoichiometry lies between two and three. Finally when the hydrogen peroxide is above three molar excess the reaction stoichiometry is above three.

Using the Ti(IV)-peroxy complex it was possible to determine the stoichiometric ratio at the end of the disappearance of the ditelluride. The results are presented in table 3-12, and they show that the reaction stoichiometry is less than $3[H_2O_2]$: $[(p\text{-}EtOPh)_2Te_2]$, the last run having the lowest ratio 1.20:1. This implies that the disappearance of the ditelluride involves oxidation from Te(I) to Te(II). If this is correct then in the last run the main tellurium species is in the form Te(II).

Tables 3-13 and 3-14 show the progress of the reaction after the disappearance of the ditelluride by following the hydrogen peroxide concentration via the Ti(IV)-peroxy complex. The results show that the hydrogen peroxide is decreasing with time. The infinity reading, listed in table 3-13, gave a reaction stoichiometry of 3.05. However 24 hours later it was found to be 3.30. The data presented in tables 3-13 and 3-14 were treated with the integrated form of a second order rate equation in which the oxidant is in excess

Viz:

$$k_{obs}\,t = \log_e\,[(A_f - A_t / X)/ (A_f - A_t)] \qquad \text{---(3-35)}$$

where the subscripts A_f, A_t correspond to final absorbance and absorbance at time t. X is the ratio

$$X = 4\,[(p\text{-}EtOPh)_2Te_2)]_o / 2\,[H_2O_2]_o \qquad \text{---(3-36)}$$

The concentration of the tellurium species is taken as twice the initial ditelluride concentration and H_2O_2 as $[H_2O_2]_o$ - $[(p\text{-}EtOPh)_2Te_2]_o$, and the treatment shown in figs 3-10 and 3-11. The observed rate constants for the two runs were found to be 6.2 and 3.4 $x10^{-4}$ s^{-1}, which is approximately a fifth of the value of the first order rate constant for the disappearance of the ditelluride, ie Te(I) to Te(II) under similar conditions of initial reagent concentrations. These results imply that oxidation of Te(I) to Te(II) is faster than oxidation of Te(II) to Te(IV). The second order rate constant was calculated to be 0.11 and 0.18 mol^{-1} dm^3 S^{-1} respectively.

The reaction product was a white powder which, using thin layer chromatographic analysis, gave only one spot with a variety of solvents. The product decomposed at 165-6^{o}C and the IR spectrum, fig 3-12, as a KBr disc showed a Te-O bond mode at 750-550 (strong) cm^{-1} and a broad band between 3600-2800 cm^{-1} implying O-H present. For comparison the IR spectrum of the ditelluride is shown in fig 3-13.

The ^{1}H NMR spectrum of the reaction product in deuterochloroform ($CDCl_3$) is shown in fig 3-15 and that of the starting ditelluride in fig 3-14. The ditelluride ^{1}H spectrum is consistent with the para-ethoxyphenyl grouping. The signals observed with splitting characteristics are a set of doublets at 7.67δ and 6.71δ, a quartet at 3.97δ, and a triplet at 1.40δ. However, the reaction product spectrum is broad and no fine structure is observed. The signals observed are at 7.73δ, 6.70δ, 3.89δ and 1.27δ.

The elemental analysis for carbon and hydrogen gave figures of 30.8% and 4.15%. Tellurium analysis proved difficult due to the difficulty of dissolving the sample. The reaction was thought to involve radicals, so several attempts to obtain an electron spin resonance (ESR) spectrum were made. Solutions of hydrogen peroxide and ditelluride were mixed in an ESR tube under air or a dioxygen atmosphere. No signal was obtained.

The ESR spectrum of the reaction product, p-ethoxyphenyl tellurinic acid (p-EtOPhTe(O)OH), and the anhydride $(p\text{-EtOPhTeO})_2O$ were recorded. The ESR spectrum of the reaction product is shown on fig 3-16 and that of the acid fig 3-17. The anhydride was found to have the same spectrum as fig 3-17. Due to the absence of the standard (Mn^{3+}) I was unable to record a g-value of the signals. However, it appears that each signal is the same indicating they have the same g-value.

Although I was unable to obtain an ESR signal from the reaction solution, the reaction was still considered to go via a free radical mechanism. A computer numerical integration involving the scheme below was carried out on all the kinetic runs presented, in an attempt to obtain more detailed information.

(R = p-EtOPh)

$$H_2O_2 + R_2Te_2 \xrightarrow{k_a} RTe + RTe(OH)_2 \qquad (3\text{-}37)$$

$$R_2Te_2 + RTe(OH)_2 \xrightarrow{k_b} RTe + 2RTeOH \qquad (3\text{-}38)$$

$$RTe + H_2O_2 \xrightarrow{k_c} RTe(OH)_2 \qquad (3\text{-}39)$$

$$RTe + RTe(OH)_2 \xrightarrow{k_d} \text{Inert} \qquad (3\text{-}40)$$

(Steady state applies to RTe)

The computer program is shown in appendix III.

The fit obtained from the computer runs were good with the sum of the squared differences being very low, in the order of 10^{-3} to 10^{-5}. The computer numerical integration could fit the kinetic data from the start of the reaction up to 90% completion. I found that in all the computer trials carried out, the reaction was sensitive to the product term, k_ak_b, rather than the individual values of k_a and k_b. The values of k_ak_b, ratio k_d/k_c and k_a and k_b are listed in tables 3-15 and 3-16. The computer results for runs at different temperatures gave a straight line Arrhenius plot. The implication from the temperature results is that the scheme computed holds at other temperatures.The varied solvent composition data is presented in table 3-16. I found that k_b was virtually constant throughout the range studied, 50% to 90% THF by volume solvent.

The pseudo first order rate equation gives the rate constants for the second stage of the reaction, however little information is available for the first stage of the reaction. Using a scheme based on the following

$$H_2O_2 + R_2Te_2 \longrightarrow RTe + RTe(OH)_2 \qquad (3\text{-}41)$$

$$RTe(OH)_2 + R_2Te_2 \longrightarrow 2RTeOH + RTe \qquad (3\text{-}42)$$

$$RTe + H_2O_2 \longrightarrow RTe(OH)_2 \qquad (3\text{-}43)$$

(Applying the steady state to RTe)

it was possible to derive an integrated rate equation from the trial solution

$$A = Ze^{-yt} / (x + e^{-yt})^2 \qquad \text{---}(3\text{-}44)$$

which upon integration, shown in appendix IV gave equation 3-45

$$\mathrm{Log}_e \frac{2 - f - 2\sqrt{1 - f}}{f} = \text{Constant} - yt \qquad \text{---(3-45)}$$

where $f = [(p\text{-EtOPh})_2Te_2]_t \,/\, [(p\text{-EtOPh})_2Te_2]_o$ ---(3-46)

ie the ratio of the concentrations of ditelluride at time t and initially and $y = k_{obs}$

where k_{obs}

$$k_{obs} = \sqrt{4k_o [R_2Te_2]_o [H_2O_2]_o^2} \qquad \text{---(3-47)}$$

A computer program shown in appendix V was used to get the individual values of k_o, k_{obs} and the constant.

It was found that the data fitted the integrated rate equation over the reagent concentration and temperature range studied, from t=0 up to 70% completion or a 10% change in the hydrogen peroxide concentration. The same data used to determine the pseudo first order rate constants was treated using the form of the integrated rate equation to get values of k_{obs}, k_o and the constant.

The variable ditelluride concentration data are shown in table 3-17 and a plot of the square root of the initial ditelluride concentration versus the observed rate constant gives a straight line graph, fig 3-18. The slope is given by slope = $k_o / (2\,[(p\text{-EtOPh})_2Te_2]^{0.5})$ giving the rate constant, k_o, as 19.1 $mol^{-3/2}\ dm^{9/2}\ s^{-1}$.

The variable hydrogen peroxide concentration data, table 3-18, gives a linear graph when the initial hydrogen peroxide concentration is plotted against the observed rate constant , fig 3-19. The slope in this case is given by slope =

$k_o / (2 [H_2O_2]_o)$ giving the rate constant, k_o, as 19.1 $mol^{-3/2}$ $dm^{9/2}$ s^{-1}.

The rate constants under dinitrogen and dioxygen were calculated. The data under dinitrogen, table 3-20, gave a linear graph when the initial hydrogen peroxide concentration is plotted against the observed rate constant, fig 3-21. The slope is given by slope $= k_o / (2 [H_2O_2]_o)$ giving a rate constant of 21.5 $mol^{3/2}$ $dm^{-9/2}$ s^{-1}.

The data under a dioxygen atmosphere, table 3-21, also gave a linear plot when the initial hydrogen peroxide concentration is plotted against the observed rate constant, fig 3-22. The slope is given by slope $= k_o / (2[H_2O_2]_o)$ which gives the rate constant as 7.80 $mol^{-3/2}$ $dm^{9/2}$ s^{-1}.

The temperature data, table 3-19, were found to obey an Arrhenius plot over the temperature range studied, fig 3-20. The slope from the Arrhenius plot gave the following data

$$\Delta E^* = 42.0 \pm 2 \ \text{kJ mol}^{-1}$$

$$\Delta H^* = 39.5 \pm 2 \ \text{kJ mol}^{-1}$$

$$\Delta S^* = -87 \pm 5 \ \text{J K}^{-1} \text{mol}^{-1}$$

These values are similar in magnitude to those derived from the pseudo first order rate constant.

The rate constants for the solvent composition and inert salt studies are listed in tables 3-22 and 3-23. The solvent composition, table 3-22, work shows little effect on the rate, whilst the inert salt effect, table 3-23, is constant within experimental error over the range studied (figs 3-23 and 3-24). The pH data, table 3-24, shows the same effect as was shown by the pseudo first order rate constant variation, fig 3-25.

$[(p\text{-}EtOPh)_2Te_2]$ $/10^{-4}$ mol dm^{-3}	ABSORBANCE
16.9	1.82
14.2	1.53
12.7	1.36
11.3	1.25
9.71	1.10
8.50	0.940
7.55	0.821
6.80	0.750
5.67	0.615
5.07	0.543
4.25	0.447
3.40	0.370
2.43	0.264

Table 3-1 Absorbance of various molar solutions of $(p\text{-}EtOPh)_2Te_2$ in aqueous THF (1: 3 by volume) at 25°C .

$[(p\text{-EtOPh})_2Te_2]_o$ $/10^{-4}$ mol dm^{-3}	$\log_e[R_2Te_2]_o$	Rate constant $k_{obs}/10^{-3}$ s^{-1}	$\log_e k_{obs}$
12.8	-6.66	4.65	-5.37
10.7	-6.84	4.21	-5.47
9.62	-6.95	3.73	-5.59
8.54	-7.07	3.55	-5.64
7.55	-7.19	3.26	-5.73
6.41	-7.35	2.82	-5.87
5.39	-7.53	2.49	-5.99
4.27	-7.76	2.15	-6.14
3.21	-8.04	2.01	-6.21
2.14	-8.45	1.56	-6.46
1.26	-8.98	1.39	-6.58

Table 3-2 Variation in the the pseudo 1st order rate constant for the reaction of H_2O_2 (4.28 x10^{-3}M) with different initial molar concentrations $(p\text{-EtOPh})_2Te_2$ at 25^{o}C in aqueous THF .

$[H_2O_2]_o$ /10^{-3} mol dm^{-3}	$\log_e[H_2O_2]_o$	Rate constant $k_{obs}/10^{-3}s^{-1}$	$\log_e k_{obs}$
22.8	-3.78	13.3	-4.32
19.1	-3.96	10.5	-4.56
15.2	-4.19	7.33	-4.92
11.4	-4.47	6.30	-5.07
9.97	-4.61	5.77	-5.16
8.57	-4.76	4.24	-5.46
7.62	-4.88	3.96	-5.53
6.53	-5.03	3.41	-5.68
4.28	-5.45	2.82	-5.87
3.13	-5.77	0.94	-6.97

Table 3-3 Variation in the pseudo 1st order rate constant for the reaction of $(p\text{-EtOPh})_2Te_2$ (6.41×10^{-4} M) with different initial molar concentrations H_2O_2 at 25°C in aqueous THF .

Temp/K	T/K x10^3	Rate constant k_{obs} /$10^{-3}s^{-1}$	$\log_e k_{obs}$
293	3.43	1.95	-6.24
298	3.35	2.97	-5.82
303	3.30	4.11	-5.49
308	3.25	5.66	-5.17
313	3.19	7.43	-4.90
318	3.14	9.65	-4.64

Table 3-4 Variation in the pseudo 1st order rate constant at different temperatures for the reaction of $(p\text{-}EtOPh)_2Te_2$ (5.02 x10^{-4} M) with H_2O_2 (4.28 x10^{-3} M) in aqueous THF .

%THF by volume	Rate constant k_{obs} /$10^{-3}s^{-1}$
50	3.61
55	2.91
60	1.98
65	2.26
70	2.88
75	2.50
80	2.90
85	2.36
90	2.14

Table 3-5 Variation in the pseudo 1st order rate constant for the reaction of $(p\text{-}EtOPh)_2Te_2$ (4×10^{-4} M) and H_2O_2 (4.29×10^{-3} M) in different solvent compositions .

$[NaNO_3]$ /10^{-4} mol dm^{-3}	k_{obs} /10^{-3} s^{-1}
100	2.70
90	2.73
70	2.59
50	2.58
30	2.68
10	2.71
5	2.51

Table 3-6 Variation in the pseudo 1st order rate constant for the reaction of H_2O_2 (4.26 x10^{-3}M) with (p-EtOPh)$_2$Te$_2$ (3.32 x10^{-4}M) at different ionic strength.

$\times 10^4$ [HNO_3] /mol dm^{-3}	pH	Rate constant k_{obs} /10^{-4} s^{-1}
140	1.74	3.91
70	2.29	6.59
35	2.94	28.9
6.0	3.23	35.0
3.0	3.97	39.2
0.2	5.14	46.4
0.1	5.71	49.0
—	6.41	48.1
$\times 10^4$ [NaOH] /mol dm^{-3}		
0.01	7.59	42.6
0.1	8.56	49.9
0.2	8.82	49.1
1.25	9.83	42.6
12.5	10.81	48.0
35	11.23	52.0
140	12.1	100

Table 3-7 Variation in the pseudo 1st order rate constant for the reaction of H_2O_2 (4.48×10^{-3} M) with $(p\text{-EtOPh})_2Te_2$ (5.20×10^{-4} M) for reactions carried out at different pH at constant ionic strength of 0.014 mol dm^{-3}.

$[H_2O_2]_o$ x10^3 /mol dm^{-3}	$\log_e[H_2O_2]_o$	Rate constant k_{obs} /$10^{-3}s^{-1}$	$\log_e k_{obs}$
74.7	-2.59	30.5	-3.49
56.0	-2.88	25.5	-3.67
37.3	-3.29	17.2	-4.06
22.4	-3.80	10.2	-4.59
11.2	-4.49	4.24	-5.46

Table 3-8 Variation in the pseudo 1st order rate constant for the reaction of $(p\text{-EtOPh})_2Te_2$ (4.50 x10^{-4} M) with different initial molar concentrations of H_2O_2 in aqueous THF at 25°C under a dioxgen atmosphere .

$[H_2O_2]_o$ x10^3 /mol dm^{-3}	$\log_e[H_2O_2]_o$	Rate constant k_{obs} /$10^{-3}s^{-1}$	$\log_e k_{obs}$
17.1	-4.07	12.7	-4.37
12.7	-4.37	10.3	-4.58
10.2	-4.57	8.52	-4.77
8.53	-4.76	6.67	-5.01
6.40	-5.05	8.15	-5.81

Table 3-9 Variation in the pseudo 1st order rate constant for the reaction of $(p\text{-}EtOPh)_2Te_2$ (4.50 X10^{-4} M) with different initial molar concentrations of H_2O_2 in aqueous THF at 25°C under a dinitrogen atmosphere.

$\times 10^4$ $[H_2O_2]$ /mol dm^{-3}	Reaction Stoichiometry
89.5	3.51
80.6	3.41
67.2	3.22
56.0	2.93
44.8	2.87
29.9	2.58
23.3	2.45
11.2	1.89
8.90	1.65
6.00	1.32

Table 3-10 Experimental data for the reaction stoichiometry determinations for the reaction between different molar H_2O_2 concentrations with constant $(p\text{-}EtOPh)_2Te_2$ concentration (20.1×10^{-4} M) in aqueous THF .

$[(p\text{-EtOPh})_2Te_2]$ $/10^{-4}$ mol dm^{-3}	Reaction stoichiometry
80.0	1.29
70.7	1.38
54.3	1.38
46.6	1.75
38.4	2.26
30.7	2.67
25.7	2.64
20.1	2.87
19.2	2.93
14.4	3.04
9.60	3.06
7.68	2.91
6.40	2.92
4.80	2.91
3.84	3.28

Table 3-11 Experimental data for the reaction stoichiometry determinations for the reaction between different initial molar $(p\text{-EtOPh})_2Te_2$ concentrations with constant H_2O_2 concentration (4.48×10^{-3} M) in aqueous THF .

$[(p\text{-}EtOPh)_2Te_2]$ $/10^{-4}$ mol dm^3	Reaction Stoichiometry
10.8	2.35
8.75	2.11
6.45	1.52
4.90	1.20

Table 3-12 Experimental data for the reaction stoichiometry determinations at the end of the observation of disappearance of $(p\text{-}EtOPh)_2Te_2$ with constant H_2O_2 concentration (4.48×10^{-3} M).

Time (mins)	Absorbance of Ti(IV)-complex	Reaction stoichiometry	$\log_e Y$
16.5	1.290	1.94	3.29
19	1.238	2.28	3.61
22.5	1.218	2.42	3.78
34	1.198	2.55	4.00
38	1.178	2.68	4.29
49	1.154	2.84	4.83
61.5	1.149	2.88	5.00
Infinity	1.123	3.05	——
24 hours	1.005	3.30	——

Table 3-13 Data for the rate of reaction after the first stage completed (ditelluride disappearance) by following H_2O_2 concentration via the Ti(IV)-peroxy complex in aqueous THF at 25°C .

$[Te(II)] = 8.52 \times 10^{-4}$ mol dm^{-3}

$[H_2O_2] = 3.63 \times 10^{-3}$ mol dm^{-3}

$\log_e Y = \ln_e[(A_f - A_t / X) / (A_f - A_t)]$

$X = 4\,[(p\text{-EtOPh})_2Te_2]_o \;/\; 2\,[H_2O_2]_o$

Time (mins)	Absorbance of Ti(IV)-complex	Reaction Stoichiometry	$\log_e Y$
35.5	0.532	1.37	1.60
38.5	0.497	1.48	1.83
46.5	0.441	1.80	2.18
49.5	0.435	1.85	2.22
56	0.419	2.01	2.32
60.5	0.410	2.13	2.38
68.5	0.396	2.38	2.46
77	0.390	2.51	2.50
Infinity	0.357	—	—

Table 3-14 Data for the reaction after the first stage completed (ditelluride disappearance) by following the H_2O_2 concentration via the Ti(IV)-complex in aqueous THF at 25°C .

[Te(II)] = 9.08×10^{-4} mol dm $^{-3}$

[H_2O_2] = 1.79×10^{-3} mol dm^{-3}

AIR ATMOSPHERE

$[(p\text{-EtOPh})_2Te_2]_o$ $/10^{-4}$ mol dm^{-3}	k_a $/s^{-1}$	k_b $/s^{-1}$	k_d/k_c	k_ak_b $/s^{-2}$
12.8	0.037	57	5.6	2.11
9.62	0.042	59	8	2.48
8.54	0.061	51	9.6	3.11
6.41	0.038	30	10.9	1.90
3.21	0.032	40	13.4	3.31
Average	0.042	52	9.5	2.17

$[H_2O_2]_o = 4.29 \times 10^{-3}$ mol dm^{-3}

TEMPERATURE

Temp/^oC	k_a $/s^{-1}$	k_b $/s^{-1}$	k_d/k_c	k_ak_b $/s^{-2}$
25	0.042	52	9.5	2.17
30	0.105	35	4.33	3.67
35	0.240	20	0.36	4.80
40	0.400	20	1.00	8.00
45	0.660	18	0.10	11.9

$[(p\text{-EtOPh})_2Te_2]_o = 4.54 \times 10^{-4}$ mol dm^{-3}
$[H_2O_2]_o = 4.48 \times 10^{-3}$ mol dm^{-3}

Table 3-15 Computer numerical integration data for the variable ditelluride concentration and temperature runs .

Solvent Composition data

%THF	k_a $/s^{-1}$	k_b $/s^{-1}$	k_d/k_c	k_ak_b $/s^{-2}$
50	0.047	35	1	1.65
55	0.038	28	0.0001	1.06
60	0.020	30	.001	0.60
65	0.027	30	.001	0.81
70	0.027	35	.0001	0.95
75	0.030	35	.0001	1.02
80	0.042	25	.001	1.05
85	0.045	34	1	1.53
90	0.094	33	12.5	3.10
Average	Various	32	——	Various

$[(p\text{-EtOPh})_2Te_2]_o = 4.00 \times 10^{-4}$ mol dm^{-3}

$[H_2O_2]_o = 4.29 \times 10^{-3}$ mol dm^{-3}

Table 3-16 Computer numerical integration data for the variation in solvent composition .

$[(p\text{-EtOPh})_2Te_2]_o$ /10^{-4} mol dm^{-3}	Observed rate constant /$10^{-3}s^{-1}$	k_o /mol$^{-1/2}$dm$^{9/2}$s^{-1}	Constant
12.8	5.84	19.1	-0.187
10.7	5.71	20.4	-0.150
9.62	5.55	20.9	-0.164
8.54	4.43	17.7	-0.153
7.55	4.39	18.7	-0.127
6.41	4.14	19.1	-0.127
5.39	3.55	17.9	-0.150
4.27	3.22	18.2	-0.150
3.21	2.79	18.2	-0.150
2.14	2.07	16.5	-0.150
1.26	1.75	18.2	-0.190
	Average	18.7	-0.150

Table 3-17 Data from the integrated rate equation for the reaction between different initial molar concentrations $(p\text{-EtOPh})_2Te_2$ with H_2O_2 (4.28×10^{-3} mol dm^{-3}) in aqueous THF

.

$$k_o = k_{obs} / (2 [H_2O_2]_o [(p\text{-EtOPh})_2Te_2]^{1/2})$$

$x10^3[H_2O_2]_o$ / mol dm^{-3}	Observed rate constant /$10^{-3}s^{-1}$	k_o / $mol^{-1/2}dm^{9/2}s^{-1}$	Constant
22.8	20.7	18.3	-0.085
19.1	18.5	19.1	-0.200
15.2	14.7	19.1	-0.108
11.4	11.0	19.1	-0.209
9.97	9.76	19.3	-0.065
8.57	8.94	20.6	-0.113
7.62	8.45	21.9	-0.076
6.53	6.76	20.4	-0.262
4.28	4.14	19.1	-0.182
3.13	2.03	12.8	-0.240
	Average	19.0	-0.154

Table 3-18 Data from the integrated rate equation for the reaction between different initial molar concentrations H_2O_2 with $(p\text{-EtOPh})_2Te_2$ (6.41×10^{-4} M) in aqueous THF .

$k_o = k_{obs} / (2[H_2O_2]_o [(p\text{-EtOPh})_2Te_2]^{1/2})$

Temp/K	Rate constant k_{obs} /$10^{-3}s^{-1}$	k_o / $mol^{-1/2}dm^{9/2}s^{-1}$	Constant
293	2.74	13.4	-0.052
298	3.89	19.1	-0.120
303	5.12	25.1	-0.150
308	6.57	32.2	-0.170
313	8.87	43.4	-0.180
318	11.1	54.3	-0.140

Table 3-19 Data from the integrated rate equation for the reaction of $(p\text{-EtOPh})_2Te_2$ (5.02×10^{-4} M) with H_2O_2 (4.28×10^{-3} M) in aqueous THF at different temperatures.

$x10^3[H_2O_2]_o$ /mol dm^{-3}	Observed rate k_{obs} /$10^{-3}s^{-1}$	k_o / $mol^{-1/2}dm^{9/2}s^{-1}$	Constant
17.1	15.7	21.6	0.003
12.7	11.4	21.2	0.360
10.2	9.88	22.8	0.300
8.53	7.35	20.3	0.040
6.40	8.67	31..9	0.100
	Average	23.6	0.161

Table 3-20 Data from the integrated rate equation for the reaction of $(p\text{-}EtOPh)_2Te_2$ (4.50×10^{-4} M) with different molar concentrations H_2O_2 in aqueous THF under a dinitrogen atmosphere.

x10^3 $[H_2O_2]_o$ /mol dm^{-3}	Observed rate Constant /10^{-3} s^{-1}	k_o /mol$^{-1/2}$dm$^{9/2}$s^{-1}	Constant
74.7	23.8	7.50	0.045
56.0	18.6	7.79	0.003
37.3	11.9	7.48	-0.038
22.4	6.04	6.32	0.053
11.2	2.75	5.76	0.110
6.17	1.28	4.86	0.207
	Average	6.62	0.063

Table 3-21 Data from the integrated rate equation for the reaction of $(p\text{-EtOPh})_2Te_2$ (4.50 x10^{-4} M) with different molar concentrations H_2O_2 in aqueous THF under a dioxygen atmosphere.

%THF by volume	Observed rate Constant /$10^{-3}s^{-1}$	k_o /$mol^{-1/2}dm^{9/2}s^{-1}$	Constant
50	3.88	22.6	0.13
55	3.49	20.3	0.28
60	2.48	14.5	0.21
65	2.99	17.4	0.31
70	3.12	18.2	0.23
75	3.27	19.1	0.12
80	3.27	19.1	0.084 0.12
85	3.71	21.6	0.03
90	4.01	23.4	-0.19

Table 3-22 Data from the integrated rate equation for the reaction of $(p\text{-EtOPh})_2Te_2$ (4 x10^{-4} M) with H_2O_2 (4.29 x10^{-3} M) in different solvent compositions.

[Sodium nitrate] added /10^{-4}M	Observed rate Constant /10^{-3} s^{-1}	k_o /$mol^{-1/2}dm^{9/2}s^{-1}$	Constant
100	2.91	18.8	0.173
90	2.98	19.2	0.110
70	2.78	17.9	0.051
50	2.78	17.9	0.073
30	2.89	18.6	0.089
10	2.93	18.8	0.039
5	2.72	17.5	0.083
	Average	18.4	0.089

Table 3-23 Data from the integrated rate equation for the reaction of $(p\text{-}EtOPh)_2Te_2$ (6.12×10^{-4}M) with H_2O_2 (4.85×10^{-3}M) in different ionic strength solutions.

$\times 10^4$ [HNO_3] /mol dm^{-3}	pH	Observed rate Constant /$10^{-3}s^{-1}$	k_o /mol$^{-1/2}$dm$^{9/2}$s^{-1}
140	1.74	0.63	2.61
70	2.29	0.97	4.04
35	2.94	2.83	11.8
6.0	3.23	4.87	20.3
3.0	3.97	5.85	24.4
0.2	5.14	5.94	24.7
0.1	5.71	6.05	25.2
——	6.41	5.92	24.7
$\times 10^{-4}$ [NaOH] mol dm^{-3}			
0.01	7.59	6.07	25.3
0.10	8.56	5.76	24.0
0.20	8.82	5.80	24.2
1.25	9.83	5.86	24.4
12.5	10.81	5.90	24.6
35.0	11.23	6.03	25.1
140	12.10	18.0	75.0

Table 3-24 Data from the integrated rate equation for the reaction of (p-EtOPh)$_2$Te$_2$ (5.20 x10^{-4}M) with H_2O_2 (4.48 x10^{-3}M) at different hydrogen ion concentration at constant ionic strength of 0.014 mol dm^{-3}.

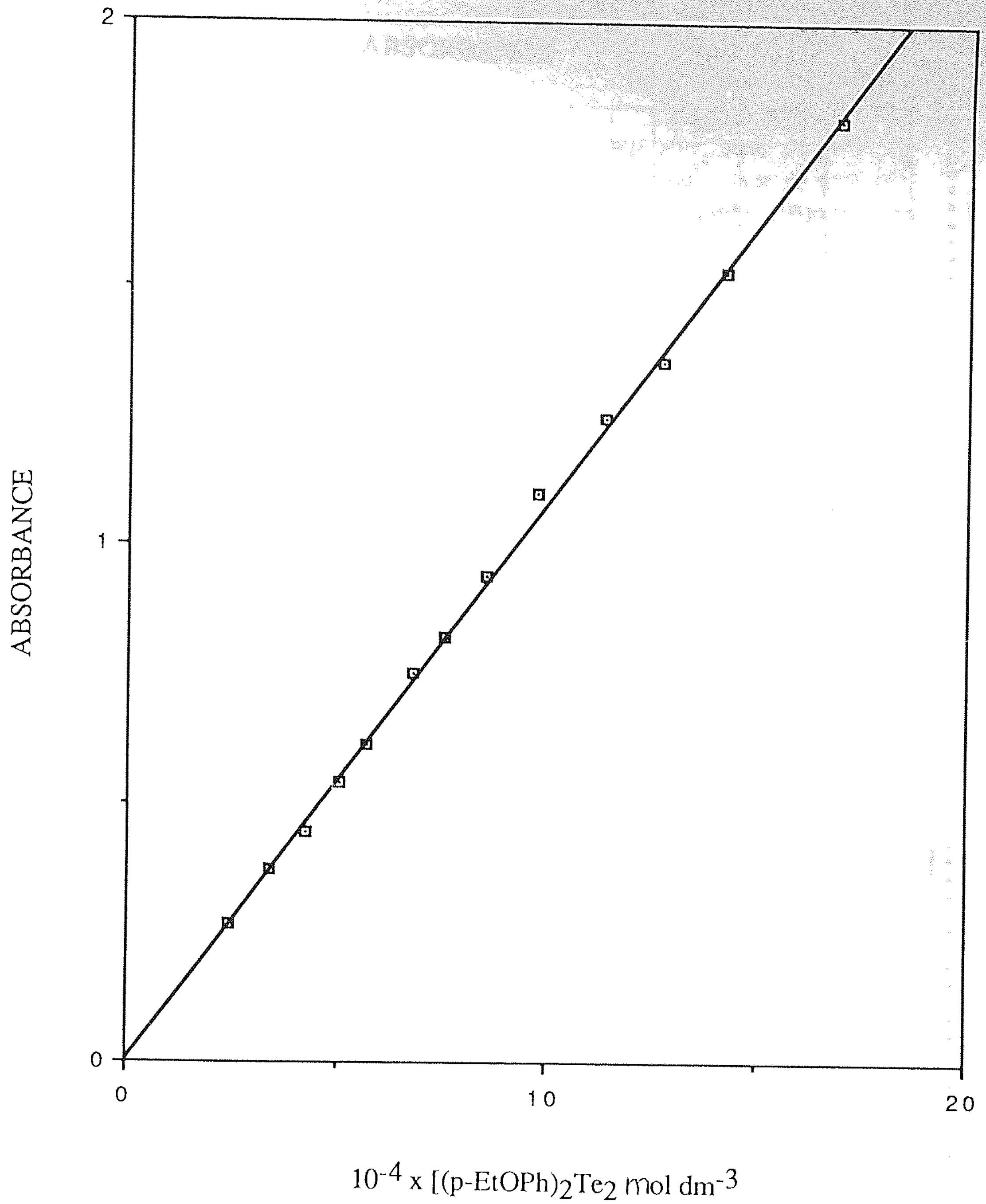


Fig 3-1 Plot of absorbance against concentration of (p-EtOPh)$_2$Te$_2$

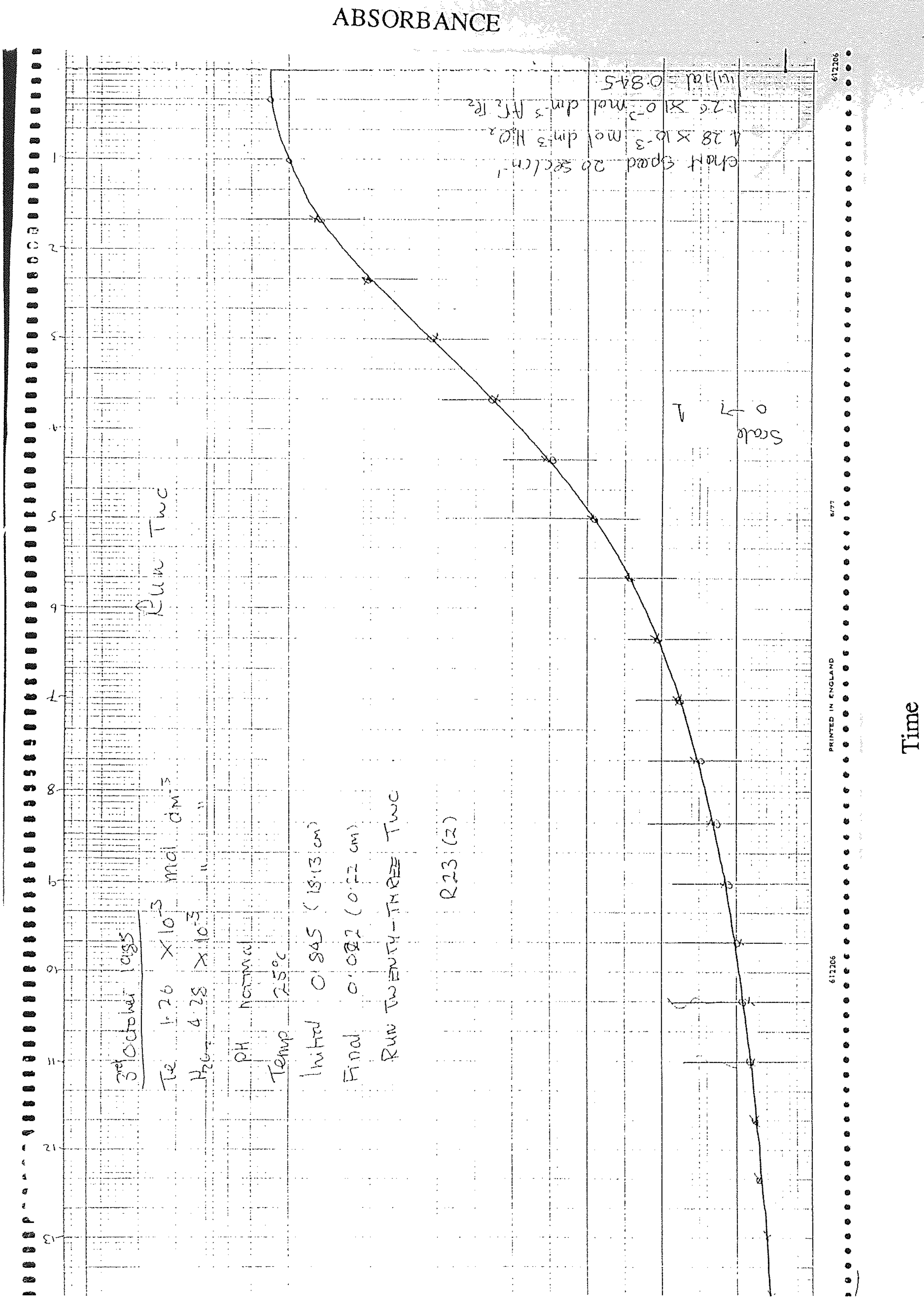


Fig 3-2 Reaction profile of absorbance against time

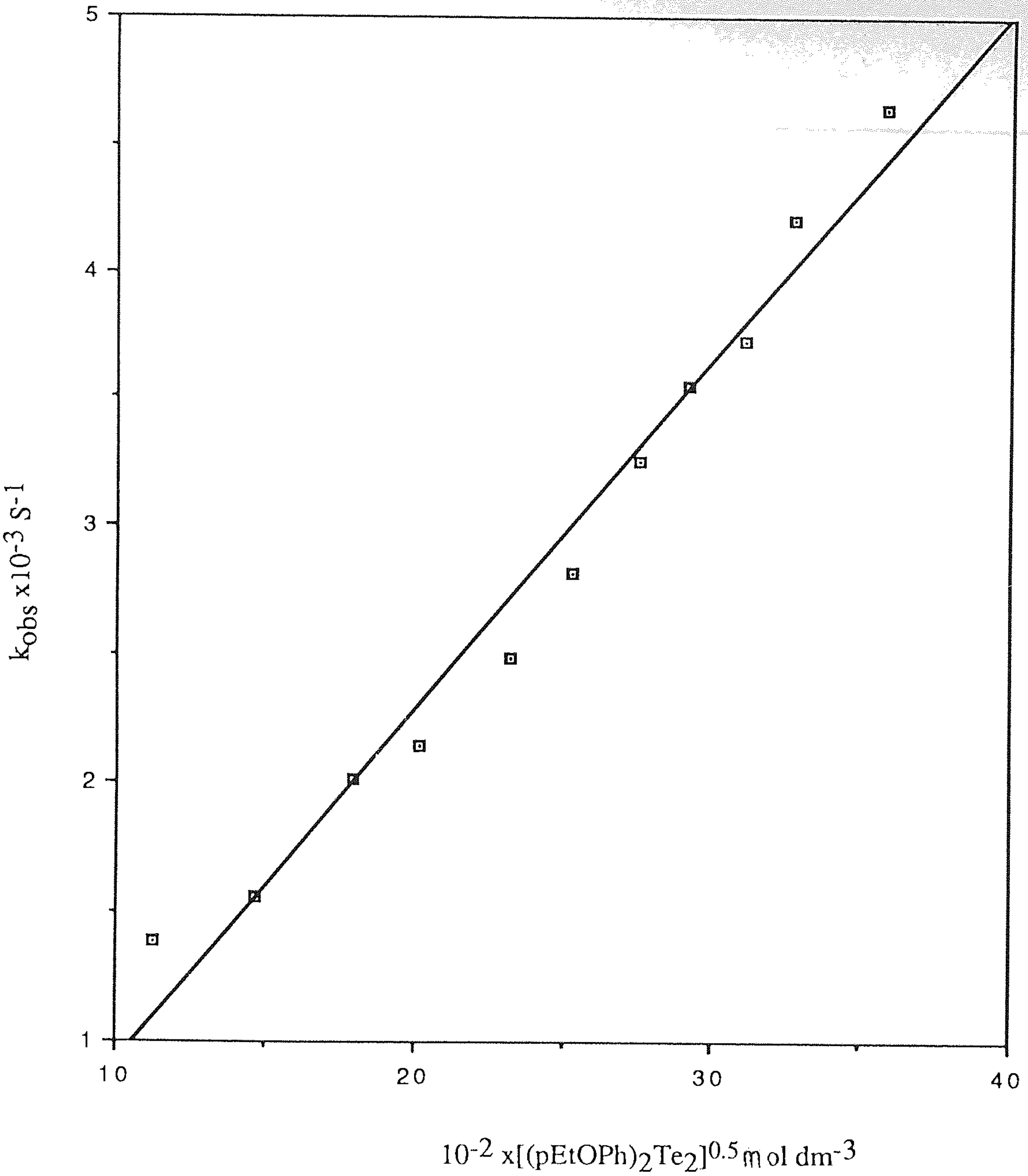


Fig 3-3 Plot of k_{obs} versus square root of initial $(p\text{-}EtOPh)_2Te_2$ concentration at 25°C for data from pseudo 1st order rate equation.

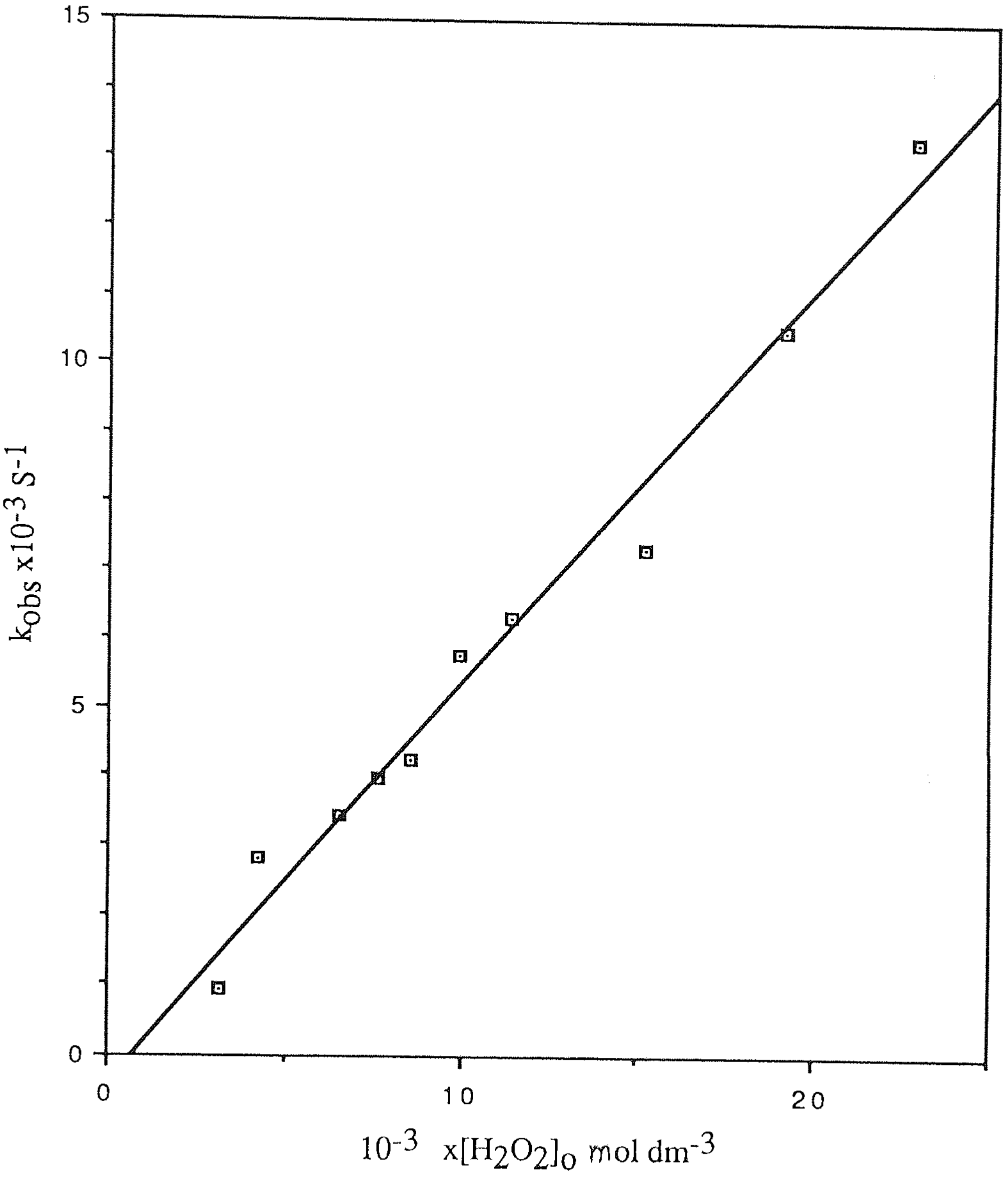


Fig 3-4 Plot of k_{obs} versus initial H_2O_2 concentration at 25°C for data from pseudo 1st order rate equation.

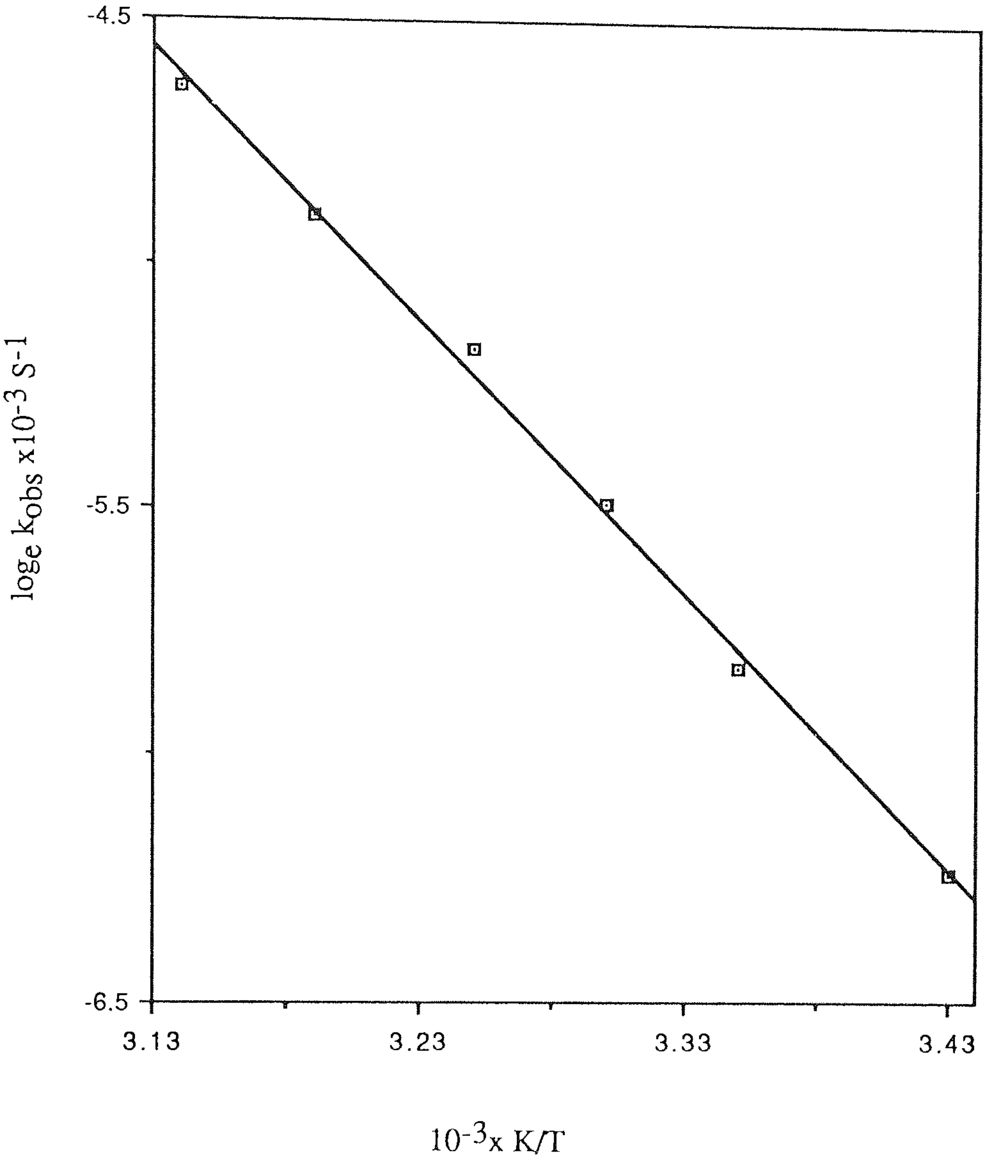


Fig 3-5 Plot of $\log_e k_{obs}$ versus K/T for the reaction of $(p\text{-EtOPh})_2Te_2$ with H_2O_2 in aqueous THF for data from pseudo 1st order rate equation.

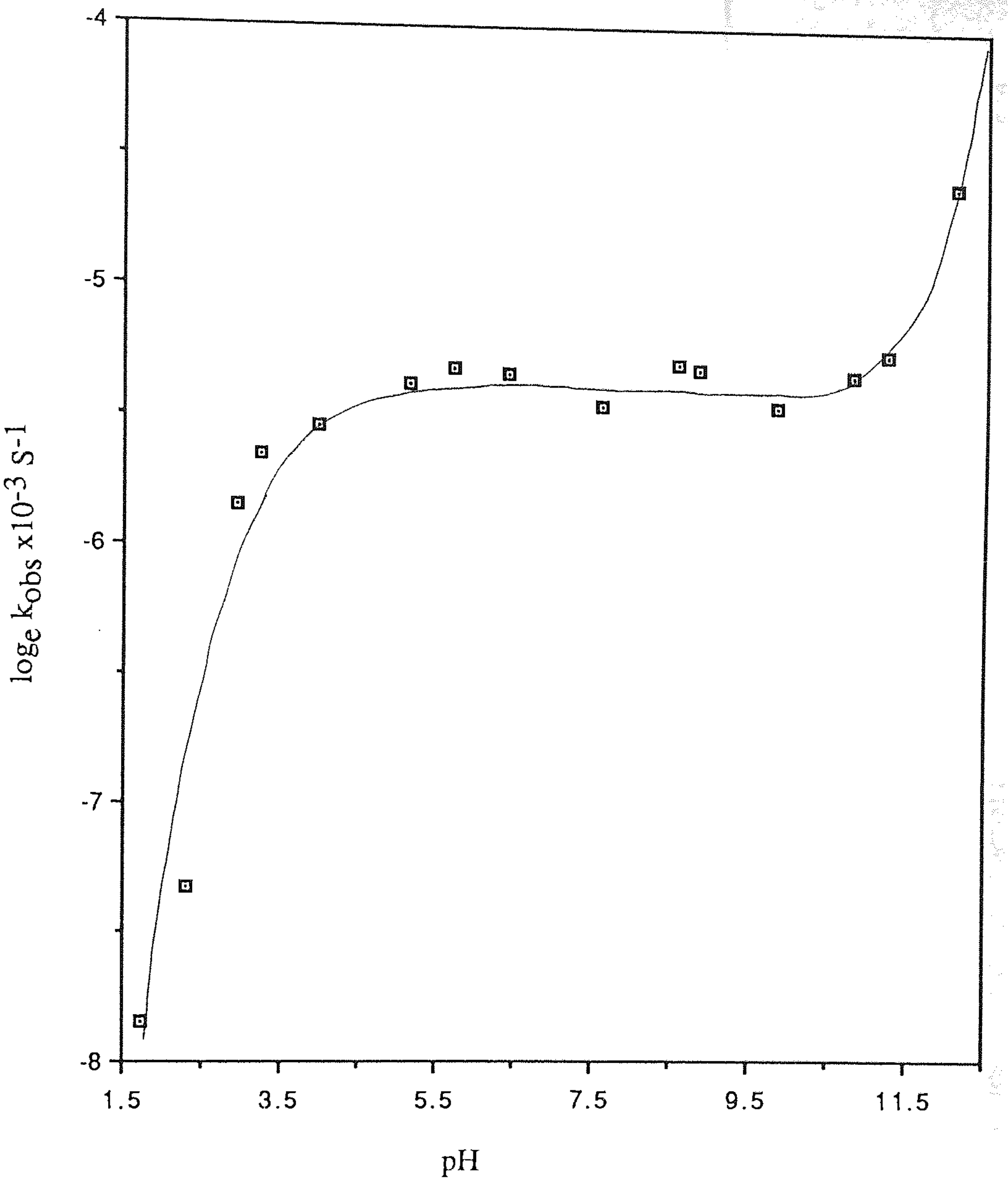


Fig 3-6 $\log_e k_{obs}$ versus pH for the reaction of $(p\text{-EtOPh})_2Te_2$ with H_2O_2 at 25°C and at ionic strength of 0.1 mol dm^{-3} in aqueous THF for data from pseudo 1st order rate equation.

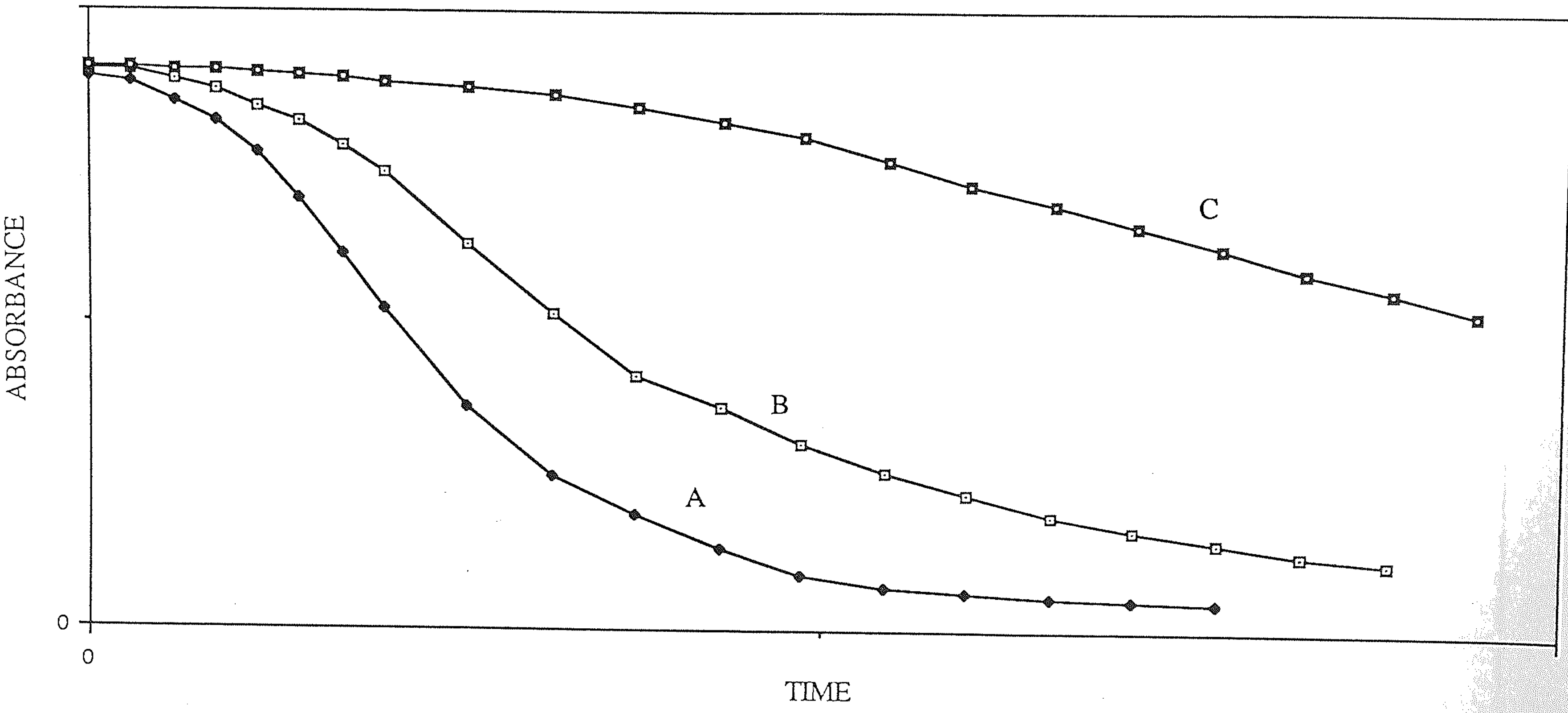


Fig 3-7 Comparison of the reaction profiles under different aerial atmospheres. A = Dinitrogen, B = Air and C = Dioxygen.

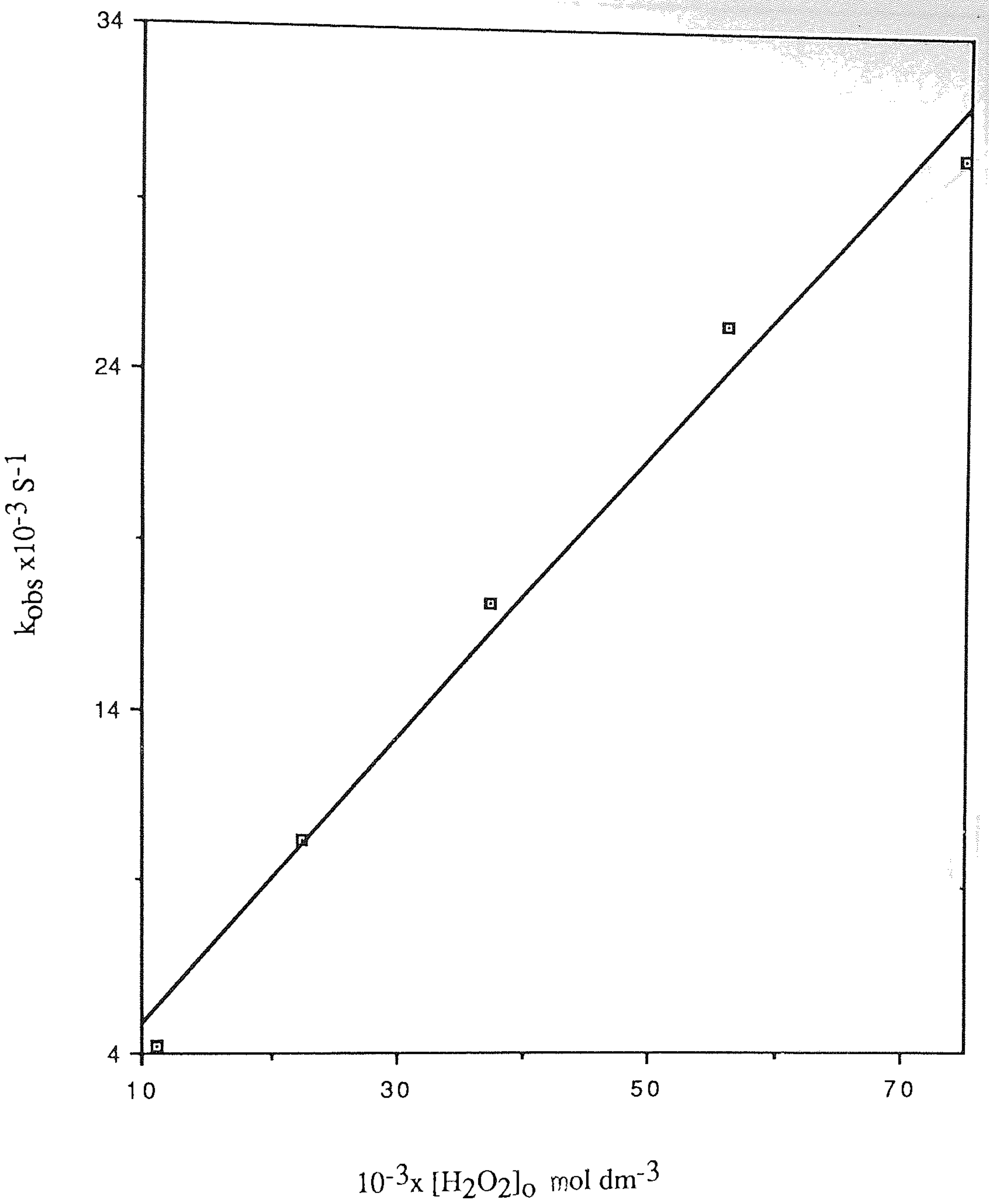


Fig 3-8 Plot of k_{obs} versus initial H_2O_2 concentration at 25^{o}C for reaction under a dioxygen atmosphere in aqueous THF for data from pseudo 1st order rate equation.

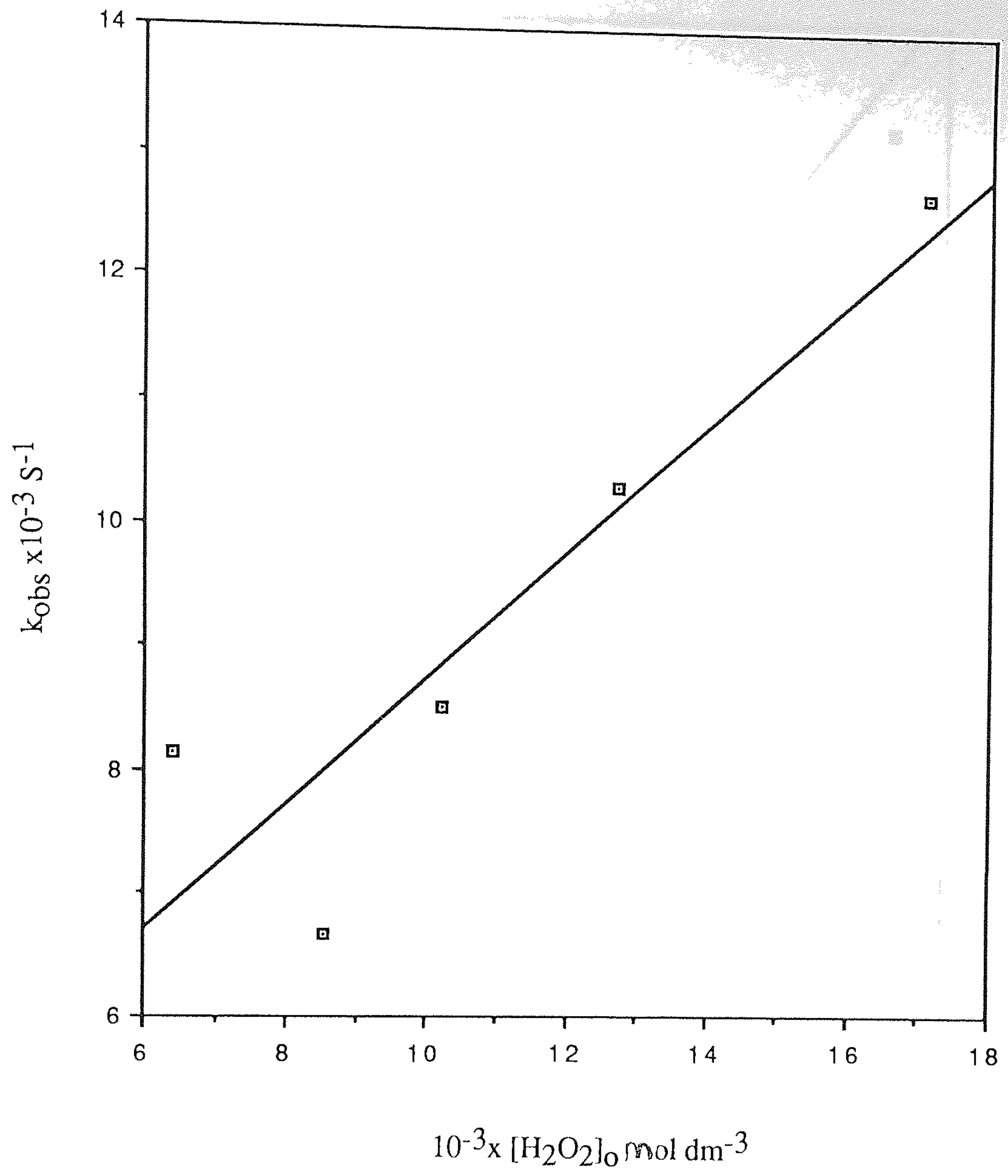


Fig 3-9 Plot of k_{obs} versus initial H_2O_2 concentration at 25°C for reaction under a dinitrogen atmosphere in aqueous THF for data from pseudo 1st order rate equation.

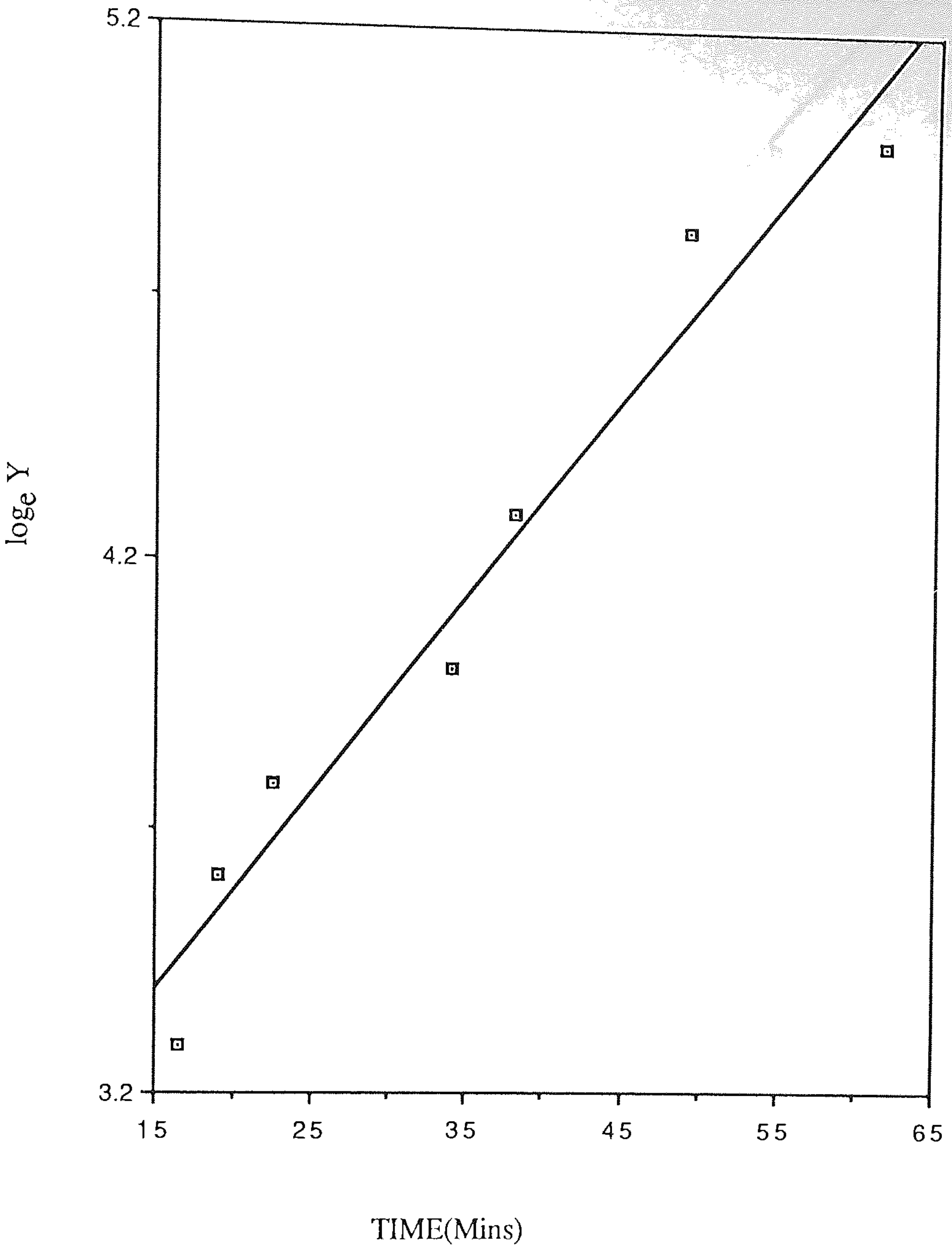


Fig 3-10 Plot of $\log_e$ Y versus time for rate of reaction for the second stage, Te(II) to Te(IV) in aqueous THF.

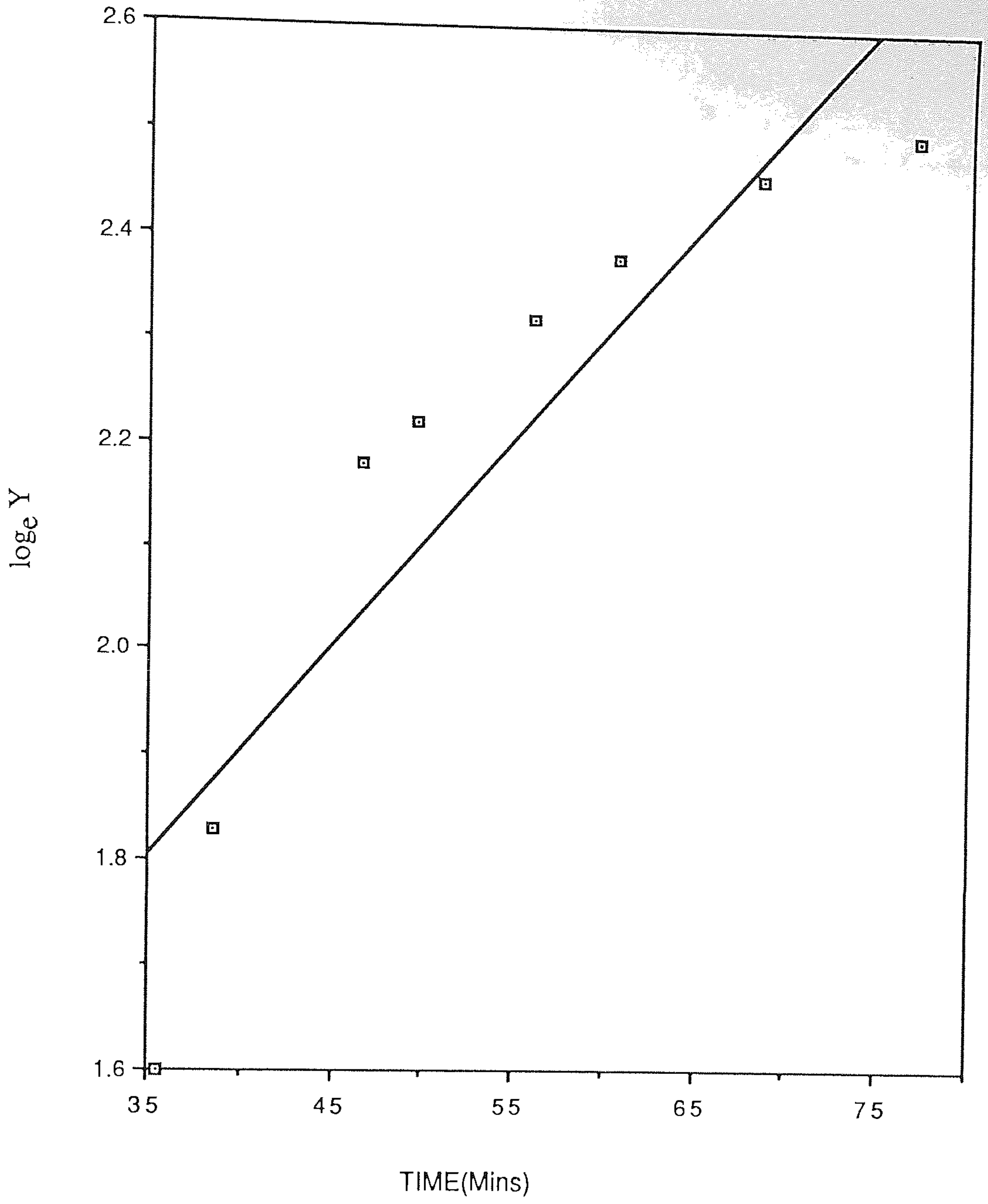


Fig 3-11 Plot of $\log_e$ Y versus time for rate of reaction for the second stage, Te(II) to Te(IV) in aqueous THF.

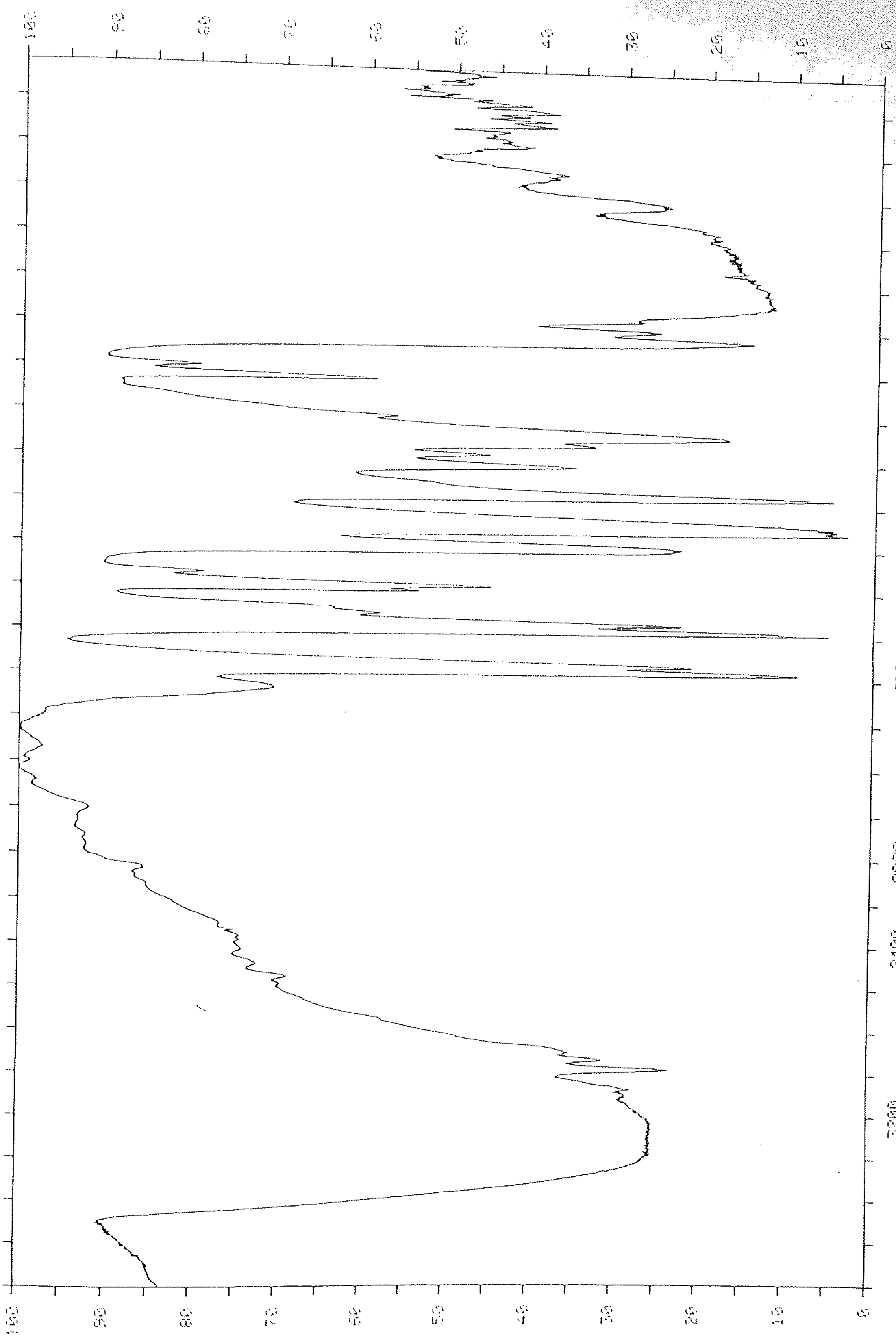


Fig 3-12 IR spectrum of product from reaction between $(p\text{-}EtOPh)_2Te_2$ and H_2O_2 as KBr disc.

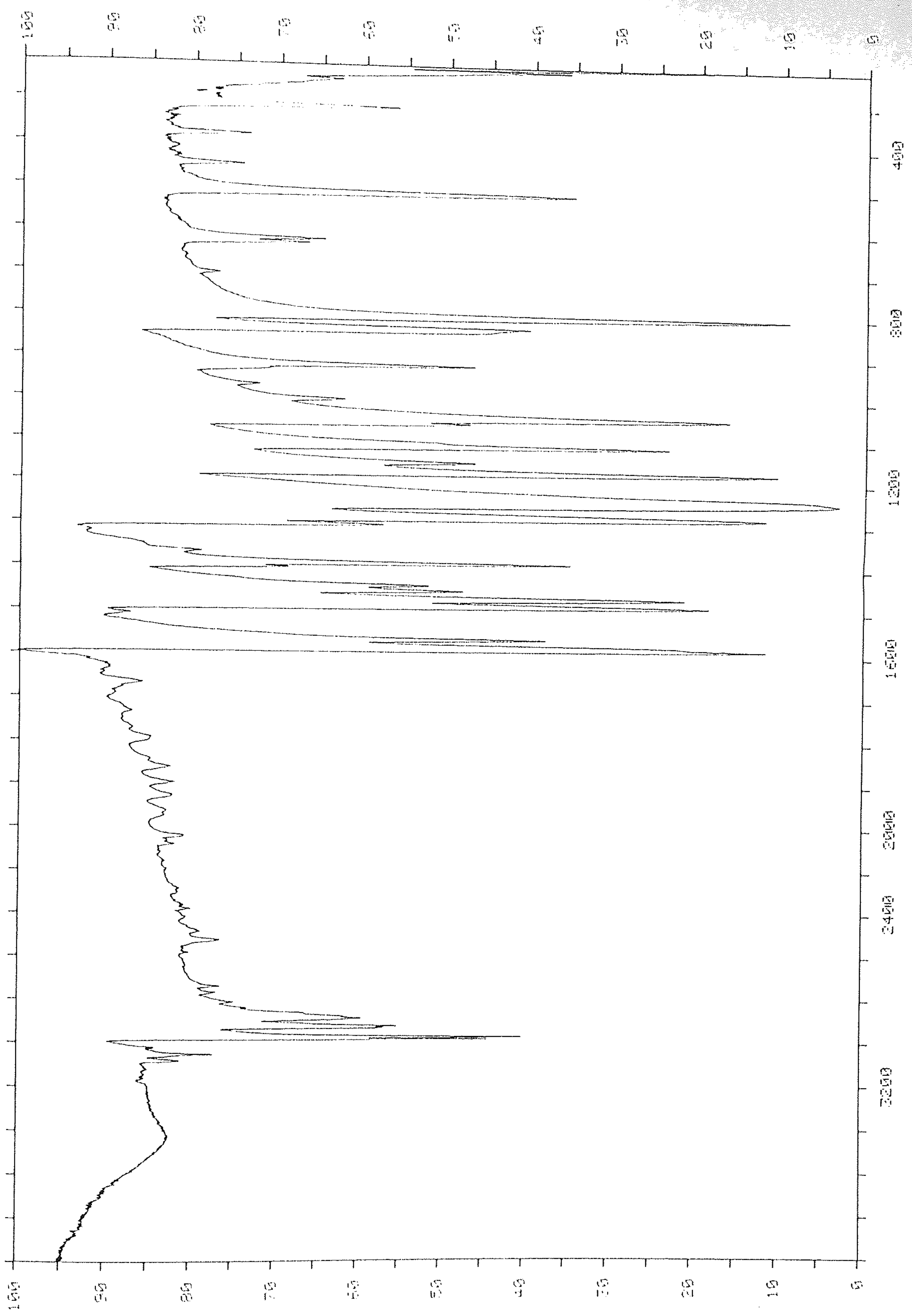


Fig 3-13 IR spectrum of $(p\text{-}EtOPh)_2Te_2$ as KBr disc

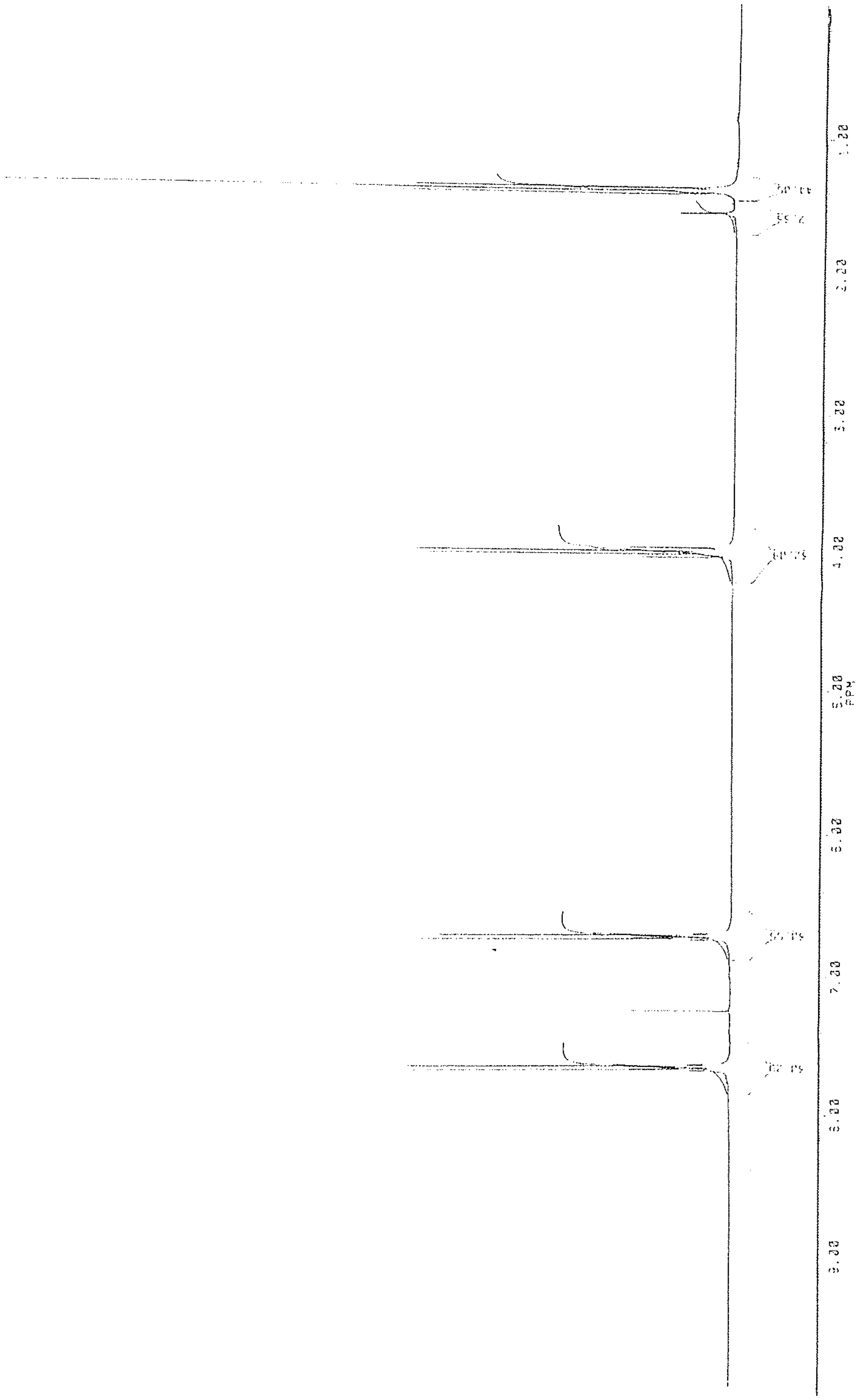


Fig 3-14 ^1H NMR spectrum of (p-EtOPh)$_2$Te$_2$ in CDCl$_3$..

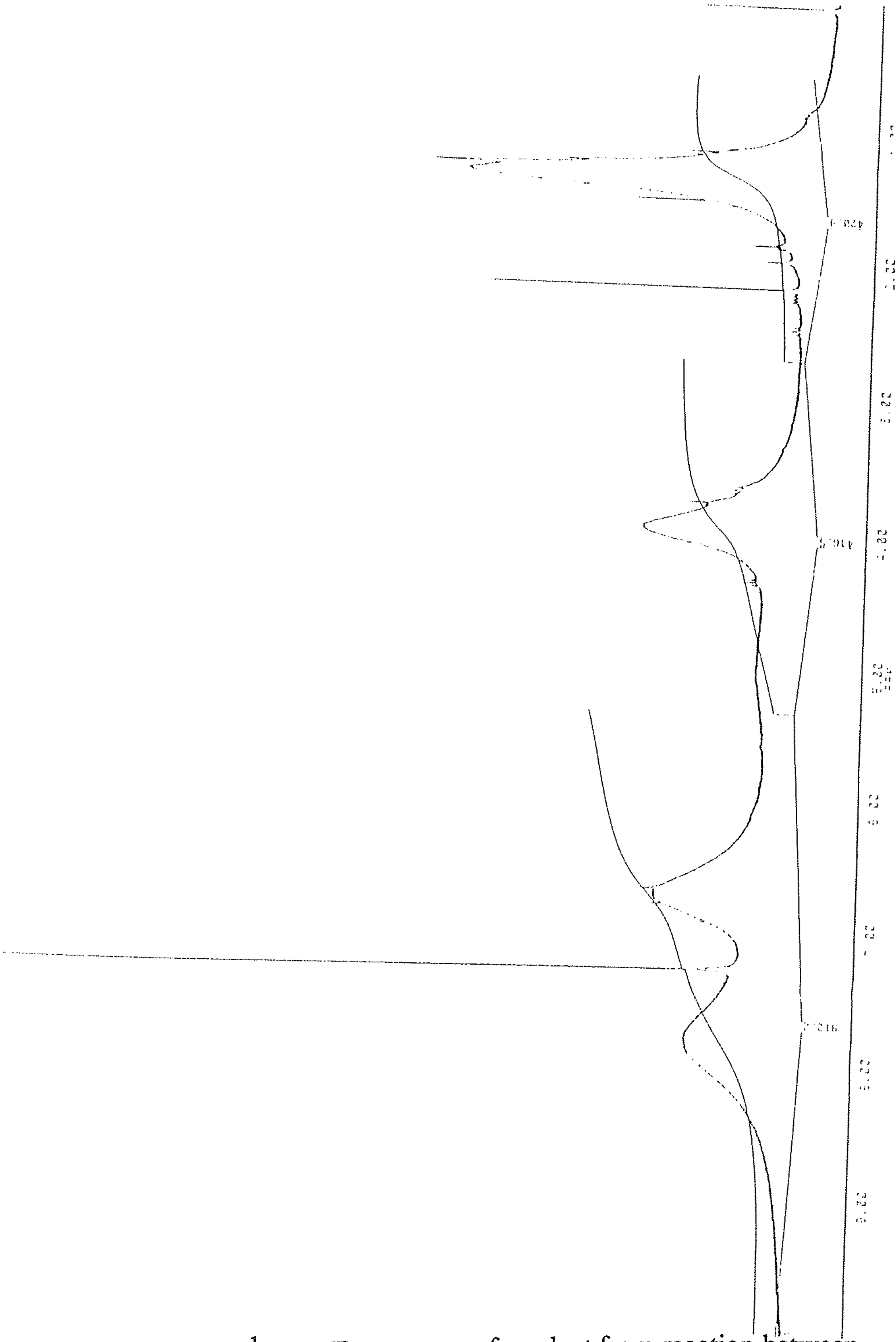


Fig 3-15 ^1H NMR spectrum of product from reaction between $(p\text{-}EtOPh)_2Te_2$ and H_2O_2.

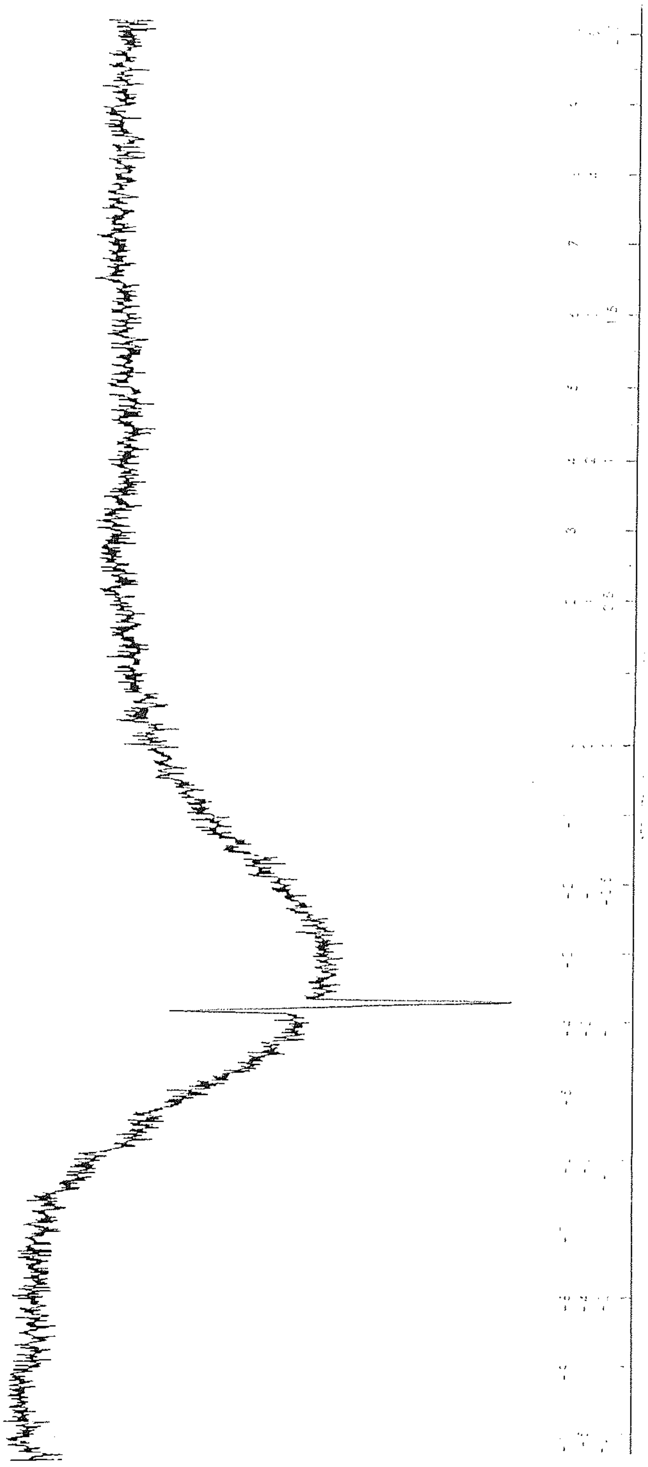


Fig 3-16 E.S.R spectrum of product from reaction between (p-EtOPh)$_2$Te$_2$ and H_2O_2.

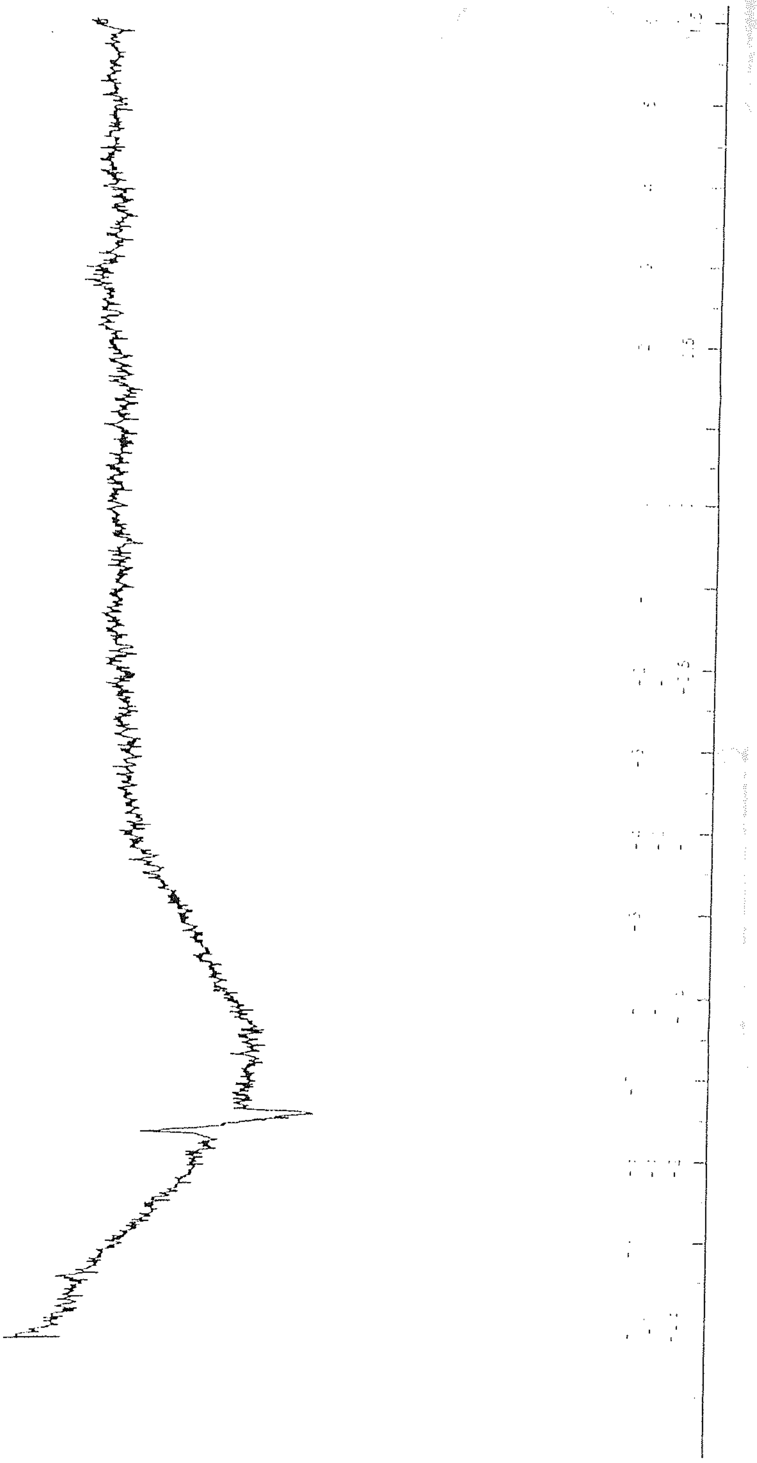


Fig 3-17 E.S.R spectrum of p-ethoxyphenyltellurinic acid (p-EtOPhTe(O)OH).

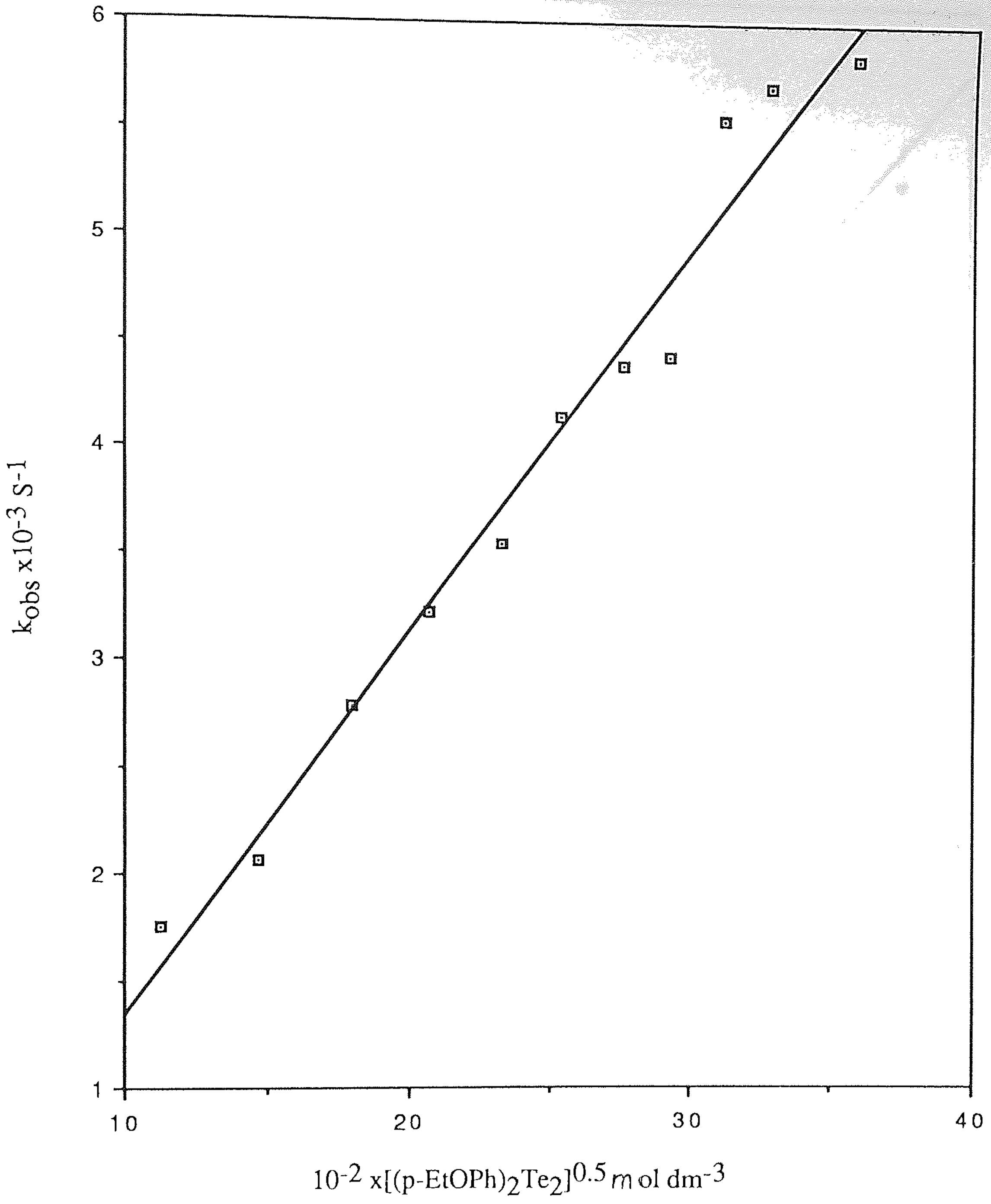


Fig 3-18 Plot of k_{obs} versus square root of the initial $(p\text{-EtOPh})_2Te_2$ concentration for data from the integated rate equation.

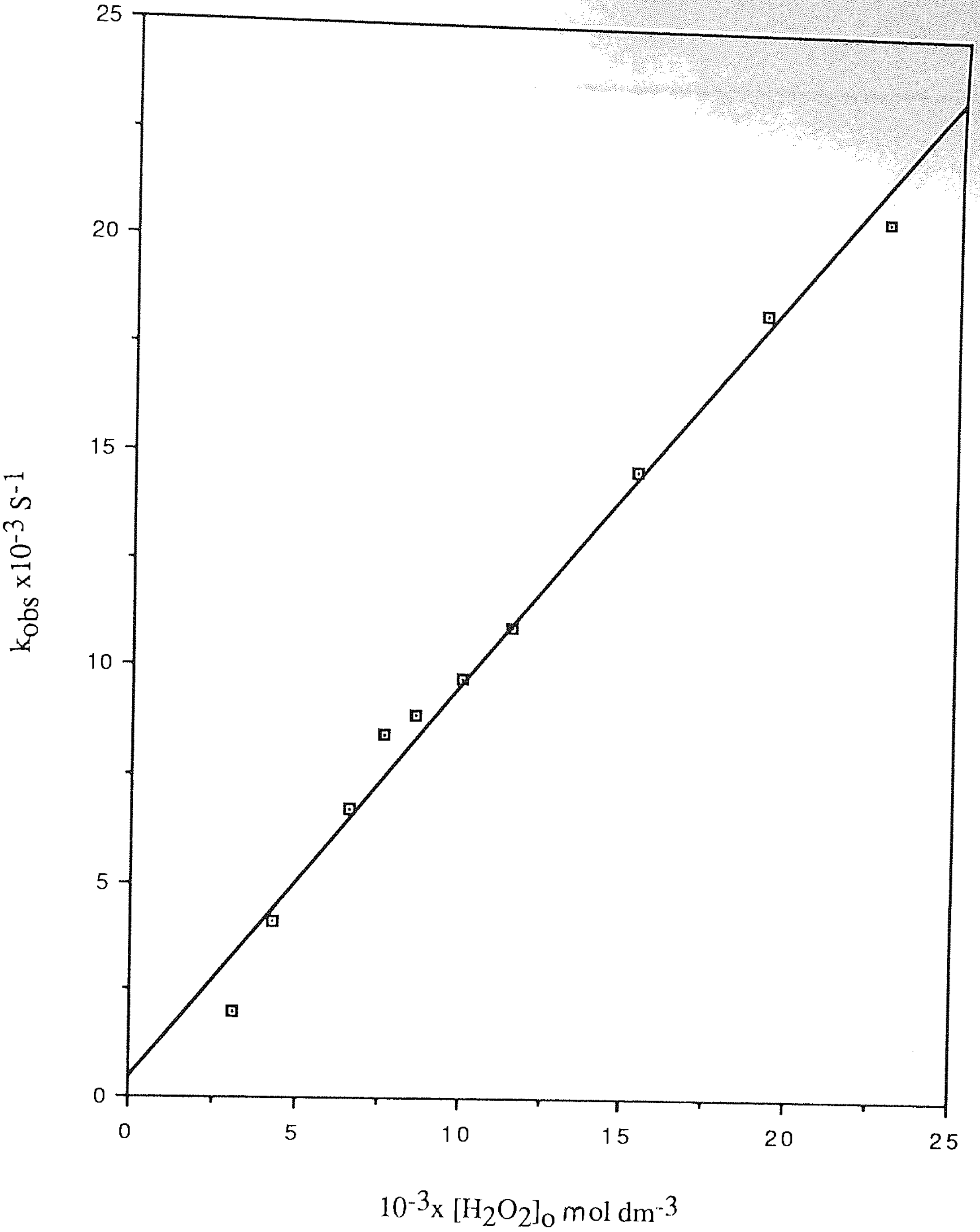


Fig 3-19 Plot of k_{obs} versus initial H_2O_2 concentration for data from the integrated rate equation.

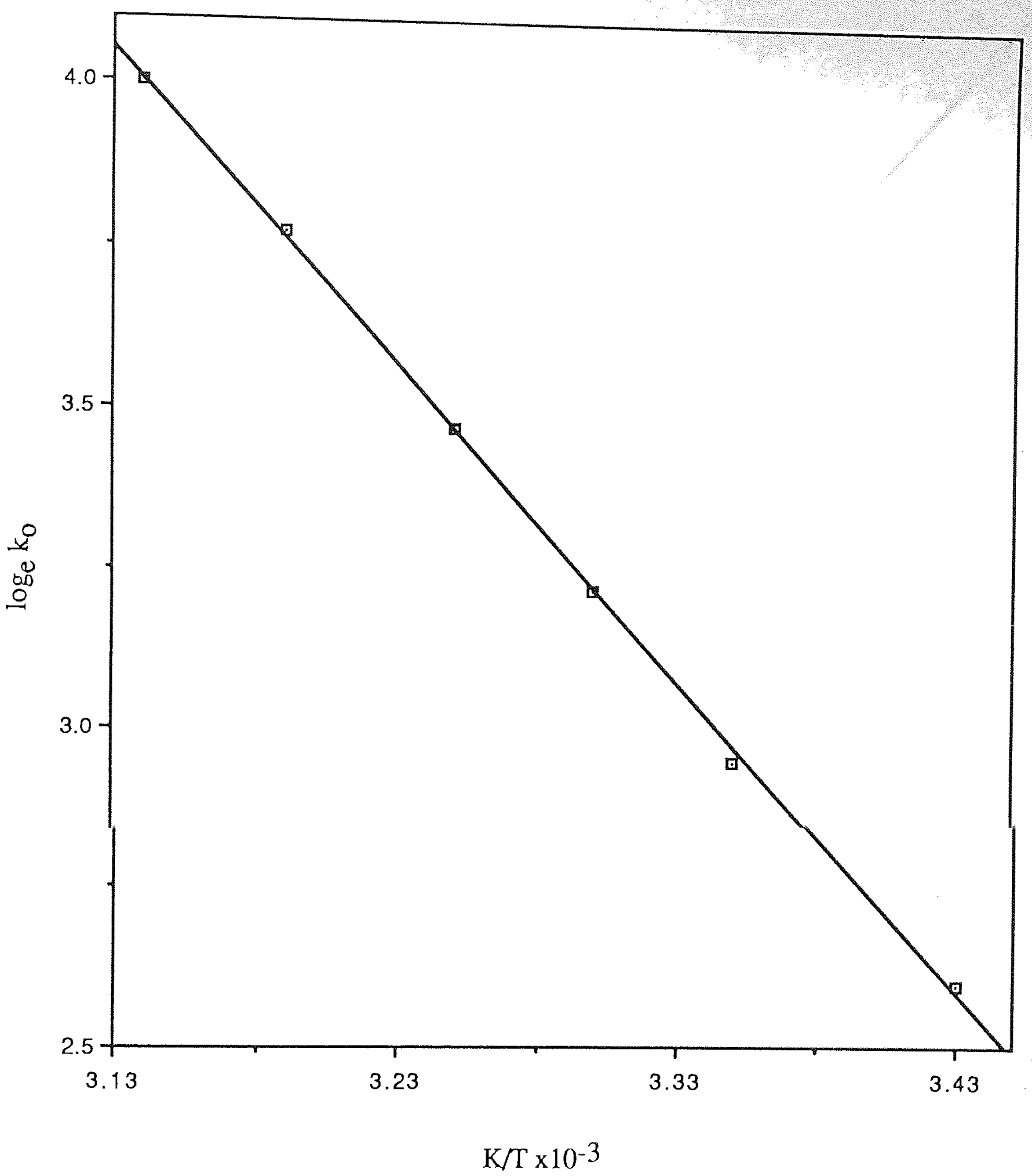


Fig 3-20 Plot of $\log_e k_o$ versus K/T for the reaction of $(p\text{-EtOPh})_2Te_2$ with H_2O_2 in aqueous THF for data from the integrated rate equation.

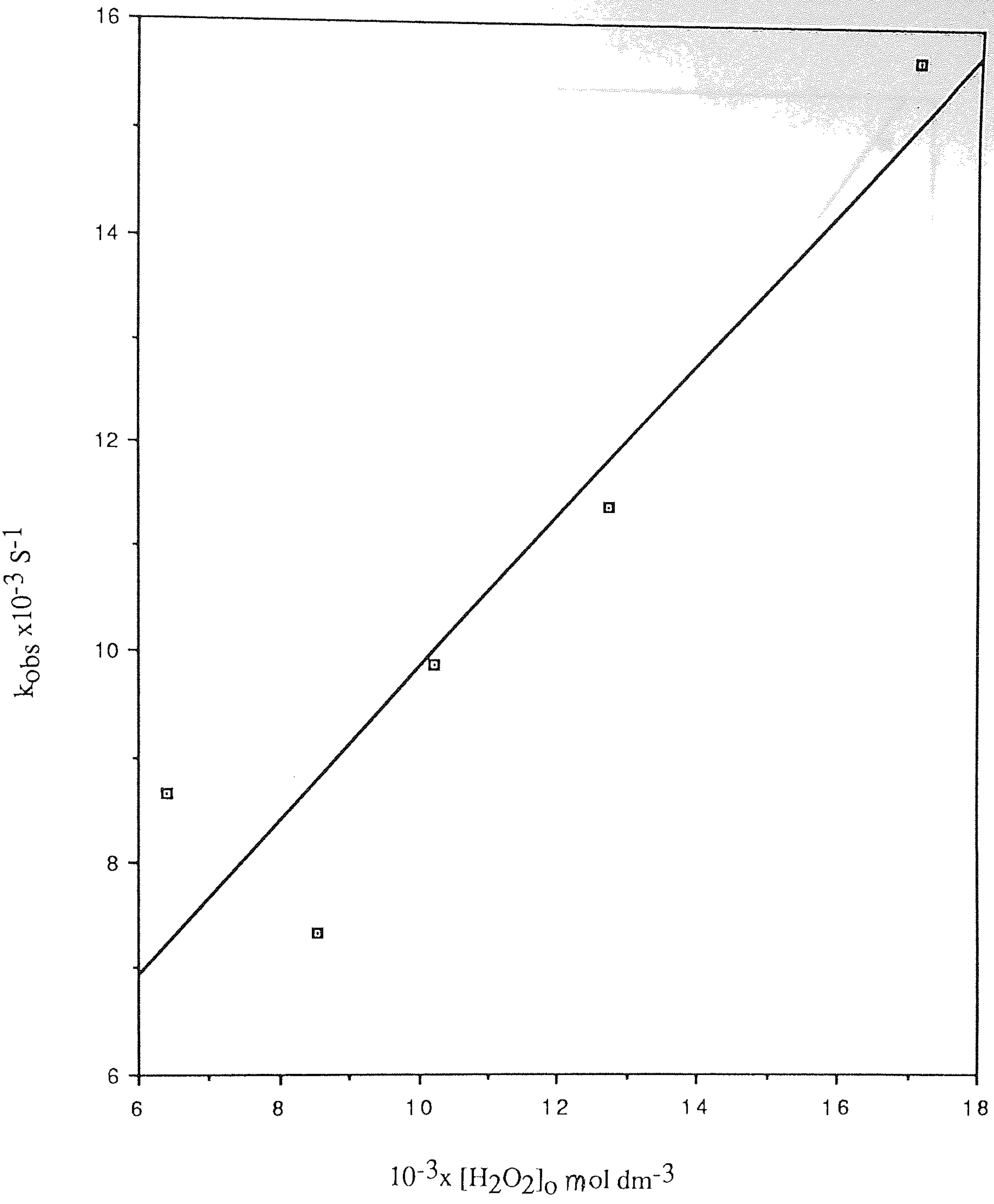


Fig 3-21 Plot of k_{obs} versus initial H_2O_2 concentration at 25°C for data from the integrated rate equation for reaction under a dinitrogen atmosphere.

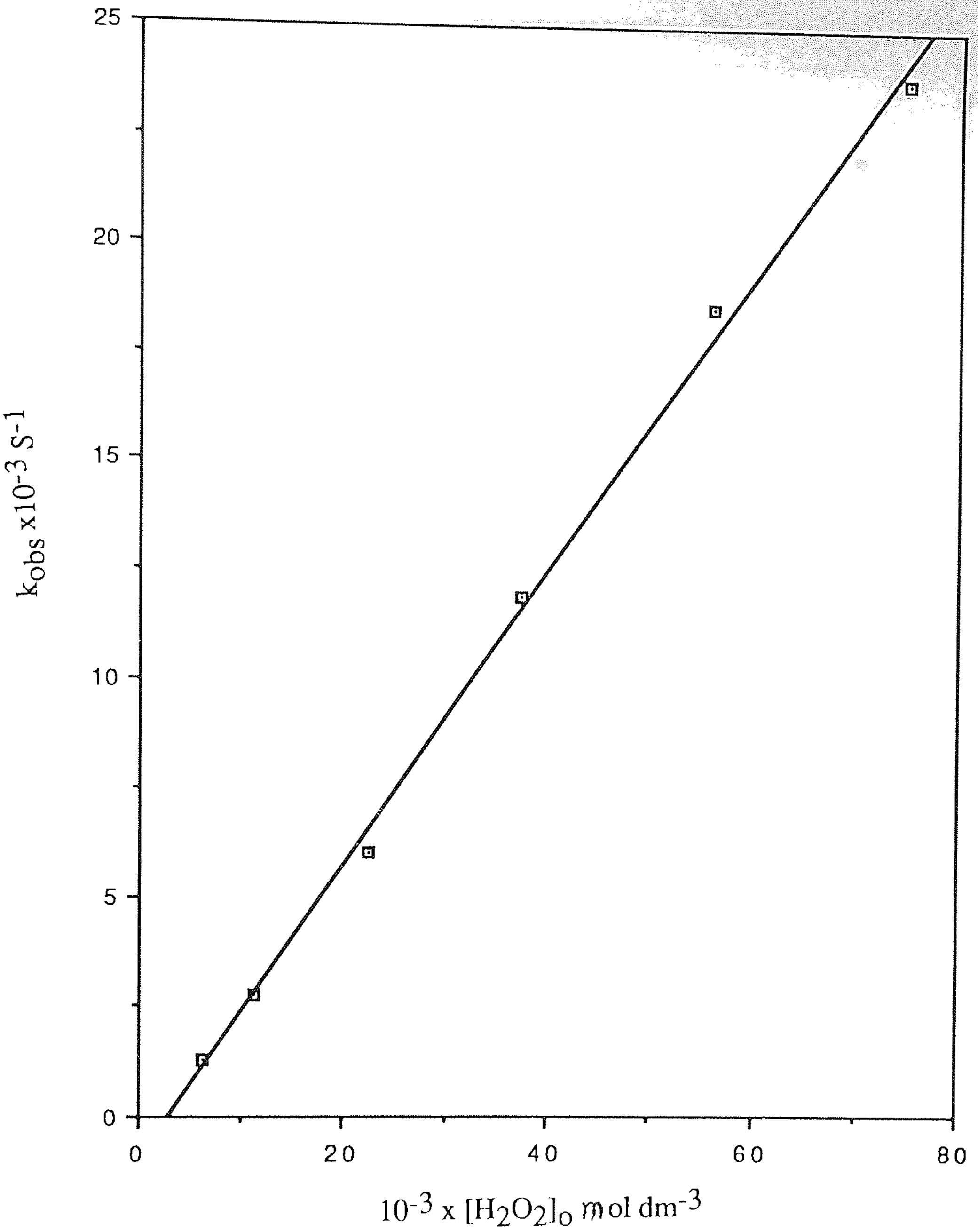


Fig 3-22 Plot of k_{obs} versus initial H_2O_2 concentration at 25°C for data from the integrated rate equation under a dioxygen atmosphere.

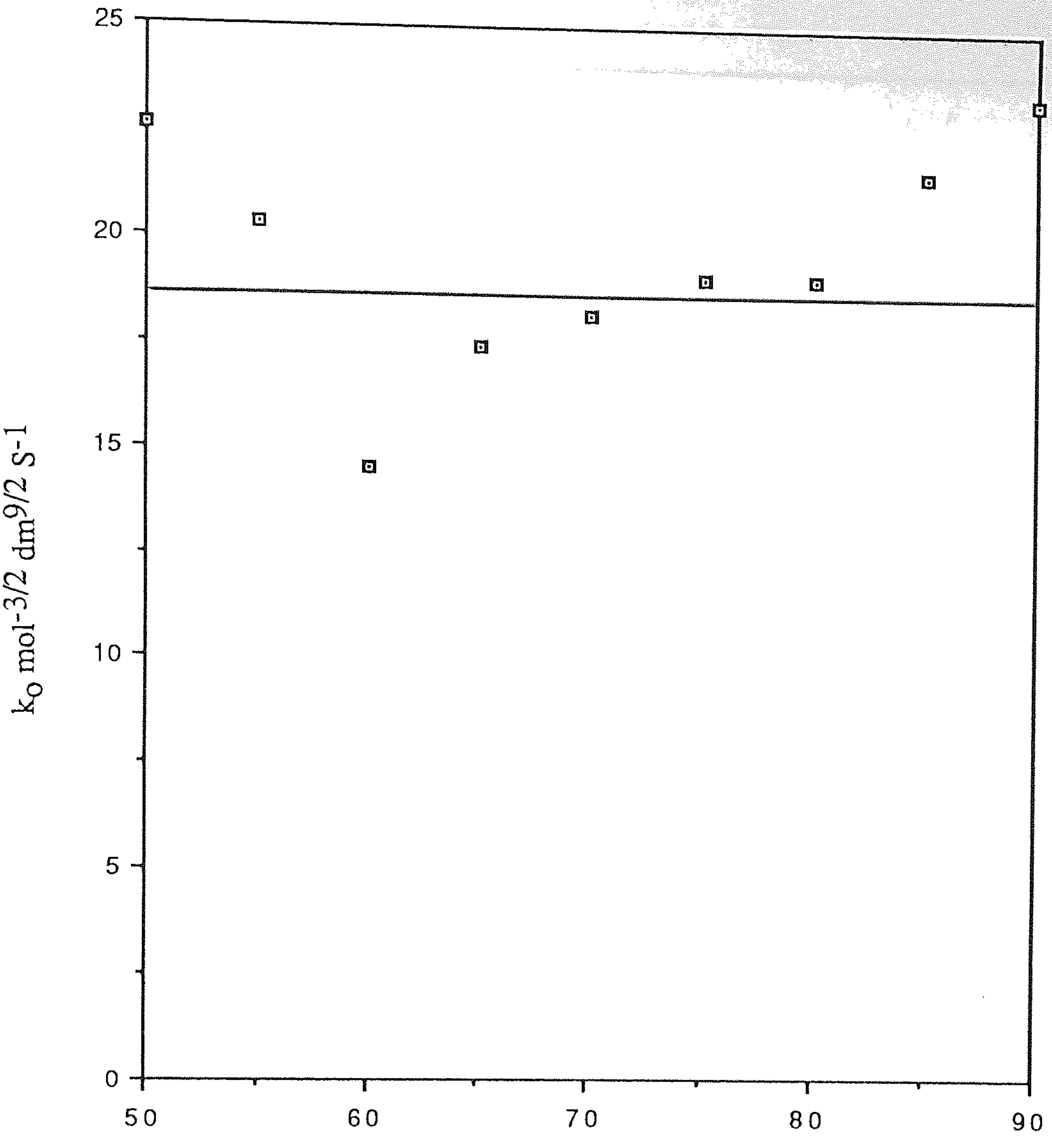


Fig 3-23 Plot of k_o versus percentage THF by volume of mixed solvent for reaction of $(p\text{-EtOPh})_2Te_2$ with H_2O_2 at 25°C for data from the integrated rate equation.

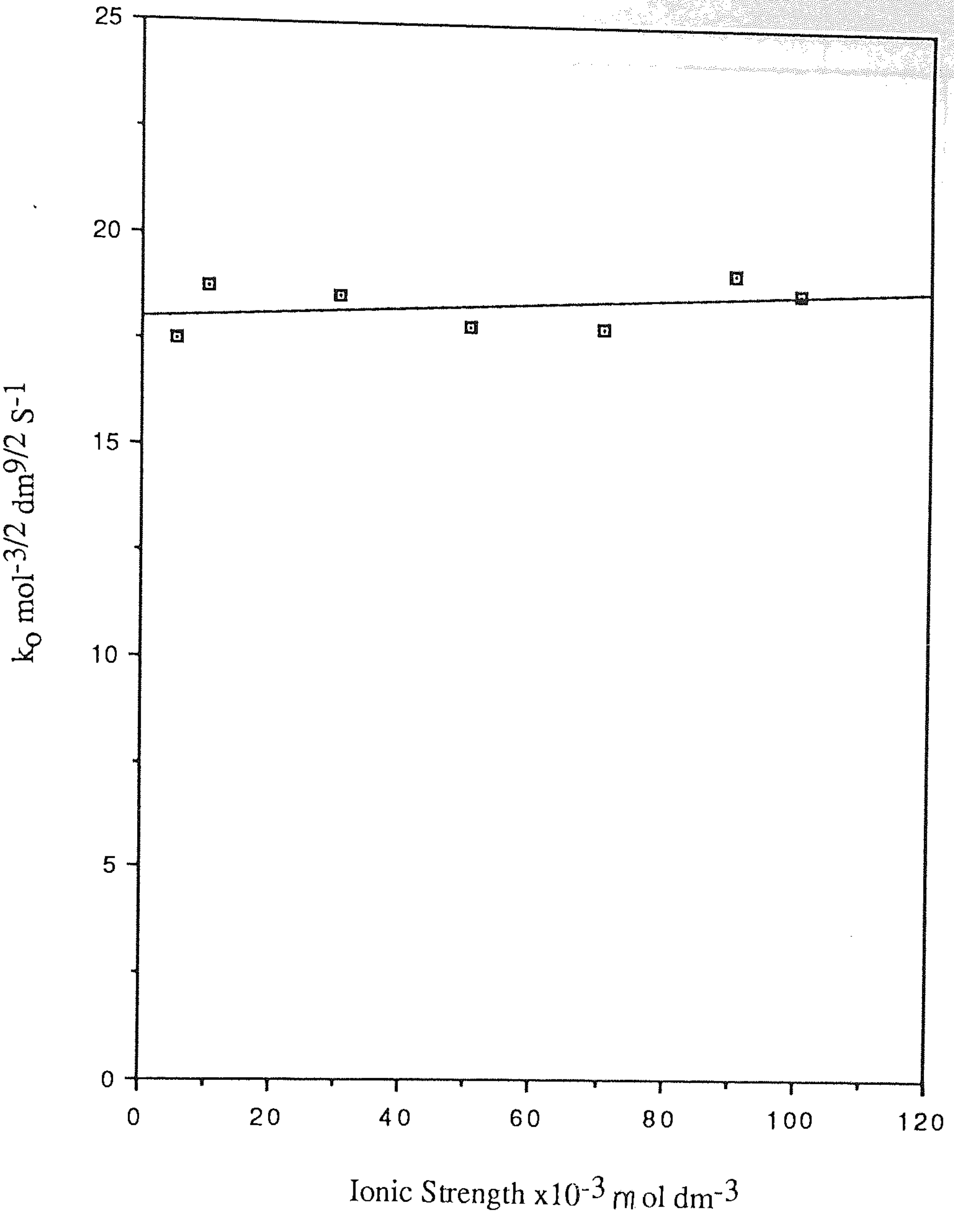


Fig 3-24 Plot of k_o versus ionic strength of reaction solution for reaction of $(p\text{-}EtOPh)_2Te_2$ with H_2O_2 for data from integrated rate equation.

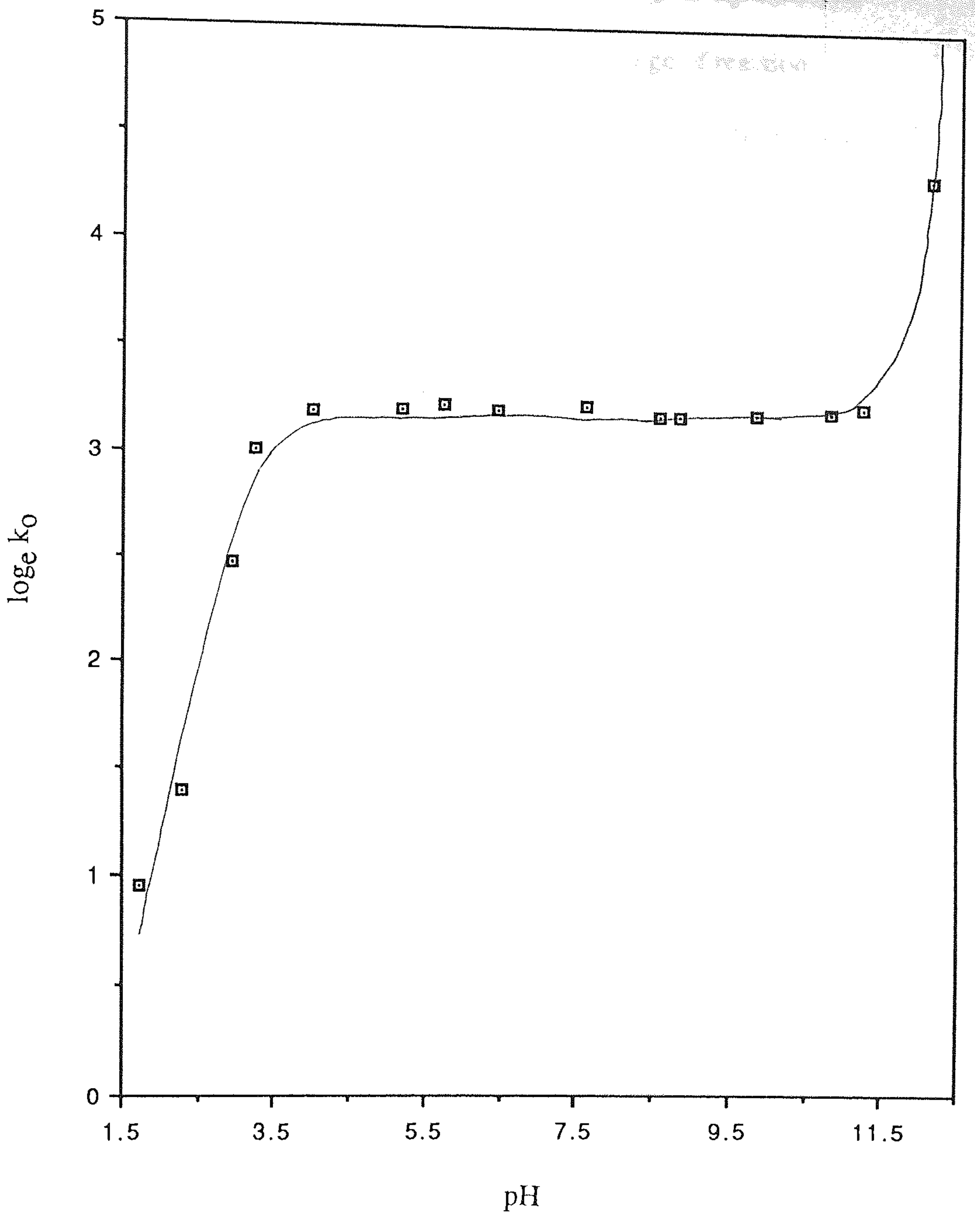


Fig 3-25 plot of $\log_e k_o$ versus pH for the reaction of $(p\text{-EtOPh})_2Te_2$ with H_2O_2 at 25°C and Ionic strength of 0.1mol dm^{-3} in aqueous THF.

3-3 DISCUSSION

The oxidation of bis(p-ethoxyphenyl) ditelluride in THF by an aqueous THF solution of hydrogen peroxide has been studied over a range of reaction conditions. The reaction was followed by monitoring the disappearance of one of the reagents, ditelluride from its absorbance at 400nm. The results obtained were found to be reproducible under all experimental conditions studied.

The reaction profile, fig 3-1, is characterised by two stages. Initially there is an induction period, which may represent the build up of an intermediate. The induction period is then followed by a rate profile which can be fitted closely to the integrated form of a first order rate equation. That is, most of the data for a kinetic experiment from 20-30% completion onwards up to 90% completion can be described by the equation

$$\log_e [A_t - A_{oo}] = k_{obs}\, t + \text{Constant} \qquad \text{--- (3-31)}$$

Even when the hydrogen peroxide concentration is only in a slight excess the rate profile still fits this first order rate equation, even though the observed rate constant is dependent on the initial hydrogen peroxide concentration. It also varies with the initial ditelluride concentration.

The first order data obtained from the kinetic experiments can be summarised in the following way.

In reactions under an air atmosphere the observed pseudo-first order rate constant appears to be proportional to the half power of the initial ditelluride concentration and the first power of the initial hydrogen peroxide concentration (tables 3-2 and 3-3, figs 3-3 and 3-4).

Viz:

$$k_{obs} \ \alpha \ [(p\text{-EtOPh})_2Te_2]^{1/2} \ [H_2O_2]_o$$

When the atmosphere above the reaction is changed the order with respect to the initial hydrogen peroxide concentration for reactions carried out under dinitrogen and dioxygen atmospheres are the same as that obtained under air.

$[N_2] \quad k_{obs} \quad \alpha \quad [H_2O_2]_o$

(table 3-9 and fig 3-9)

$[O_2] \quad k_{obs} \quad \alpha \quad [H_2O_2]_o$

(table 3-8 and fig 3-8)

The appearance of the term in initial ditelluride concentration is surprising, but genuine. Since that reagent is pure, the term is not due to an impurity. Therefore it must appear as a consequence of the steps during the early induction period. A similar argument must hold for the appearance of the hydrogen peroxide concentration in the pseudo-first order rate constant, it is involved in the reaction stoichiometry, but not in determining the form of the rate equation.

In an effort to verify that the reaction studied, the disappearance of the ditelluride, involves oxidation of tellurium(I) only as far as tellurium(II), the reaction stoichiometry at the end of kinetic observations, that is after the ditelluride has disappeared, was determined, table 3-12.

I found that the reaction stoichiometry was lower than that determined in table 3-10 for similar initial concentrations of ditelluride with the hydrogen peroxide concentration being the same. In the last run the stoichiometry was 1.2:1. The stoichiometry of 1.2:1 (in table 3-10) was found using excess ditelluride compared to the experiments described in table 3-12 in which the peroxide is in excess. This clearly demonstrates that in the reaction followed, ditelluride is oxidised in a one-electron step to tellurium(II), but implies that there is always some further oxidation occuring.

No variation in the observed rate constant with varying solvent composition and ionic strength was found (tables 3-5 and 3-6).

Experiments undertaken at different pH values appeared to showed some inverse dependence of the observed rate constant with pH over the range studied (table 3-7 and fig 3-6).

The temperature data, table 3-4 and fig 3-5, gave the following activation parameters:

$$\Delta E^* = 49.1 \pm 2 \ \text{kJ mol}^{-1}$$

$$\Delta H^* = 46.6 \pm 2 \ \text{kJ mol}^{-1}$$

$$\Delta S^* = -137 \pm 5 \ \text{J K}^{-1} \text{mol}^{-1}$$

The product of the reaction is a white powder and no tellurium metal is deposited. In the introduction it has been noted that diaryl diselenides, upon oxidation with hydrogen peroxide, are reported to give aryl seleninic acids as the products. Thus we may hope to find a similar product, p-EtOPhTe(O)OH, here.

The C and H analytical data for the product were lower, C=30.8% and H=4.15%, than those expected for the aryltellurinic acid, p-EtOPhTe(O)OH, C= 34.0% and H=3.5%.Since I could not find any solvent from which to recrystallise the product, any impurities present would lead to lower than expected analytical values. Thin Layer chromatographic analysis using various solvent combination, indicated a single species. The infra-red spectrum, fig 3-12, of the product shows two absorptions of interest. The broad band at 3500-2800cm^{-1} indicates O-H characteristic of an acid (carboxylic acids show similar bands), and a strong band at 750-550cm^{-1} indicating a Te-O bond vibration[25].

The ^{1}H NMR spectrum, fig 3-14, however gives broad signals and thus no splitting structure is observed. However, when it is compared to the ditelluride spectrum, fig 3-15, the signals are in the same region indicating that the p-ethoxyphenyl group grouping is still present. It was initially thought that the broad spectrum was due to an impurity and thus an ESR spectrum was obtained of the product, fig 3-16. The spectrum obtained is the same as that of the p-ethoxyphenyl tellurinic acid, fig 3-17, prepared from base hydrolysis of the corresponding trichloride, indicating that it is not an impurity that is causing the broading of the ^{1}H NMR spectrum but the product itself. I was unable to determine the g-value because of the absence of the Mn(III) standard. I am unable, however, to give an adeqate explanation of the ESR spectrum. Since an ESR signal comes from unpaired electrons it is difficult see them in the postulated reaction product.

Additional experiments were carried out to check if any carbon-tellurium bond cleavage occurs. A solution of hydrogen peroxide and ditelluride was left overnight, then an excess of a reducing agent, hydrazine hydrate, was added after which absorbance measurements were made. The difference in the concentration of ditelluride before and after oxidation by hydrogen peroxide was less than 6%, ie within experiment error the same, suggesting little or no carbon-tellurium cleavage.

The product decomposed without melting at 165-6°C. The tellurinic acid, p-EtOPhTe(O)OH, is reported to decompose at a higher temperature, 235-40°C and the anhydride at 234-38°C. Now the base hydrolysis of aryltellurium trichlorides gives aryltellurinic acids. However, if that product is treated with acid, then the anhydride is formed $(p\text{-EtOPhTeO})_2O$. Since my reaction was carried out in slightly acidic conditions, pH~5-6, it is possible that some of the tellurinic acid formed may be converted to the anhydride. Thus what we may be seeing is a mixture of products. However if this were the case then the elemental analysis for carbon and hydrogen would be expected to be higher that found experimentally. For a tellurium(VI) product on the other hand, the C, H analysis would decrease. Since tellurium(VI) is suggested to be the ultimate reaction product it is probable that a mixture of tellurium(IV) and tellurium(VI) products are present.The following observations, together with the fact that diaryl diselenides give aryl seleninic acids from the reaction with hydrogen peroxide, leads to the conclusion that the product of the reaction between hydrogen peroxide and bis(p-ethoxyphenyl) ditelluride is a mixture of p-ethoxyphenyl tellurinic acid, $[p\text{-}CH_3CH_2OC_6H_4Te(O)OH]$ and a tellurium(VI) compound.

Various experiments to determine the stoichiometry of the reaction were carried out spectrophotometrically. Either the excess ditelluride remaining at the end of a reaction was determined from its absorbance at 400nm, or else any excess hydrogen peroxide from other experiments was determined using the titanium(IV) peroxy complex, which absorbs at 410nm.

The stoichiometry data, tables 3-10 and 3-11, can be summarised as follows. When the relative reagent concentrations are in the range from excess ditelluride to equal molar quantities, the stoichiometry reaches a value slightly greater than $[H_2O_2]/[R_2Te_2] = 1$. This indicates that the major tellurium product is in the oxidation state +2 arising from the reaction of one mole of ditelluride with one mole of peroxide. Since the observed stoichiometry is above 1:1, the implication is that some tellurium(IV) is also present. The possibility of a tellurium(III) product can be eliminated as no tellurium(III) compounds are known.

The likely tellurium(II) product is p-EtOPhTeOH. However this compound has not yet been isolated, probably because it is co-ordinatively unsaturated, as the most common co-ordination number of tellurium is four. One possible explanation for the stoichiometric ratios being between one and two, which can be discounted, is disproportionation

ie

$$3Te^{II} \rightleftharpoons Te_2{}^{I} + Te^{IV}$$

where $Te_2{}^{I}$ is the ditelluride.

To eliminate this possibility, I left a solution of hydrogen peroxide and a three molar excess of ditelluride in aqueous THF, 1:3 by volume, in the dark for two weeks. During this time I monitored the absorbance of the solution and I found that no change in the absorbance had occurred during this time. This implies that no disproportionation occurs under the conditions of experiment or that it is too slow to be observed.

When initially there was up to a three molar excess of peroxide, the resulting reaction stoichiometry was determined to be between two and three, eventually reaching a limiting stoichiometry of three. This implies that the final product is in the form of tellurium(IV).

The last group of stoichiometric experiments are those in which there is more than a three fold excess of hydrogen peroxide . The stoichiometry eventually reaches a value of 4.65 after two weeks standing. This indicates that further reaction occurs to give the ultimate product tellurium(VI). If decomposition is occurring, the other alternative, a final reaction stoichiometry of greater than five to one would be expected, that is above the value for a final product of pure tellurium(VI).

There is supporting evidence from known selenium chemistry, as Reich et al[75] report that arylseleninic acid (ArSe(O)OH) in aqueous THF does not decompose hydrogen peroxide. Thus it is reasonable to suggest that the aryltellurinic acid would not show the same ability to catalyse the decomposition. However, when diaryl diselenides react with hydrogen peroxide, the product is selenium(IV), and no selenium(VI) product is obtained. Therefore we can extrapolate from selenium data only if we can obtain thermodynamic data to justify a different IV to VI behaviour.

To check whether oxidation of tellurium(IV) to tellurium(VI) is possible, electrochemical data were collected for Te(IV)-Te(VI), Se(IV)-Se(VI), H_2O_2-H_2O and H_2O_2-O_2 couples. The potential of the couples are 71

$$H_6TeO_6 + 2H^+ + 2e^- \longrightarrow TeO_2 + 4H_2O \qquad E^o=1.02V \qquad \text{---(3-48)}$$

$$SeO_4^{2-} + 2H^+ + 2e^- \longrightarrow H_2SeO_3 + H_2O \qquad E^o=1.15V \qquad \text{---(3-49)}$$

$$H_2O_2 + 2H^+ + 2e^- \longrightarrow 2H_2O \qquad E^o=1.77V \qquad \text{---(3-50)}$$

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \qquad E^o=0.682V \qquad \text{---(3-51)}$$

From the above values it can be seen that H_2O_2 can act as a reducing agent (3-50) or as an oxidizing agent towards both elements (3-51).

For oxidation by H_2O_2 we have

$$TeO_2 + H_2O_2 + 2H_2O \longrightarrow H_6TeO_6 \qquad E=+0.75V$$

(pH independent) ---(3-52)

$$H_2SeO_3 + H_2O_2 \longrightarrow SeO_4^{2-} + H_2O + 2H^+ \qquad E=+0.62V$$

(pH dependent) ---(3-53)

Using the Nernst equation we can calculate the potential of the selenium couple at pH=6 (reaction conditions)

$$E = E^o + \frac{RT}{ZF} \log_e[H^+]$$

$$= 0.98V$$

Thus, both TeO_2 and H_2SeO_3 could be oxidised by hydrogen peroxide, the latter oxidation is favoured by higher pH.

For the reduction of tellurium(VI) and selenium(VI)

$$H_6TeO_6 + H_2O_2 \longrightarrow TeO_2 + O_2 + 4H_2O \quad E=+0.34V$$

---(3-54)

$$SeO_4^{2-} + H_2O_2 + 2H^+ \longrightarrow H_2SeO_3 + O_2 + H_2O \quad E=+0.47V$$

---(3-55)

At pH=6 the selenium data become

$$\begin{aligned} E &= 0.47 - 0.36V \\ &= 0.11V \end{aligned}$$

ie both couples H_6TeO_6/TeO_2 and SeO_4^{2-}/H_2SeO_3 could catalytically decompose H_2O_2, a view supported by Hughes and Martin for the selenium couple[77].

Mechanistically H_6TeO_6 is already six coordinate and thus it might not be easy to get the necessary seven coordinate transition state needed for the inner-sphere reduction of hydrogen peroxide, which is therefore likely to be very slow; especially as a great deal of atomic movement is necessary. These arguements offer little guidance for RTe containing species except to say that for tellurium the rate of catalytic decomposition would probably be very slow.

To this stage the results discussed were obtained from the pseudo first order fit of data after the induction period is over. Further information was required from the data from the start of the reaction.

Various schemes were tried based on the oxidation of tellurium(I) to tellurium(II) and the experimental data were then fitted to numerically integrated data to determine which schemes could show a reasonable agreement between observed and calculated data. The scheme presented below, equations 3-37 to 3-40, was found to be the best. It was the only scheme that gave consistent computed constants, that is the computed rate constants were reasonably constant from one experiment to another. The numerical integration program is shown in appendix II.

$$H_2O_2 + R_2Te_2 \xrightarrow{k_a} RTe + RTe(OH)_2 \qquad (3\text{-}37)$$

$$R_2Te_2 + RTe(OH)_2 \xrightarrow{k_b} RTe + 2RTeOH \qquad (3\text{-}38)$$

$$RTe + H_2O_2 \xrightarrow{k_c} RTe(OH)_2 \qquad (3\text{-}39)$$

$$RTe + RTe(OH)_2 \xrightarrow{k_d} \text{Inert} \qquad (3\text{-}40)$$

The data, up to 80% completion, could be fitted giving a good characterisation of the reaction profile.

This scheme suggests that the initiation involves production of the RTe radical and the tellurium(III) intermediate $RTe(OH)_2$. The step

$$R_2Te_2 + H_2O_2 \longrightarrow 2RTeOH$$

might be considered as a plausible first and only step. We reason that its non-occurence is because of size factors. X-ray crystallographic studies have led to values of 2.69 to 2.71A for the tellurium-tellurium bond length in ditellurides[27,28,29] whereas the bond length in hydrogen peroxide is 1.49Å[85]. Thus from the bond lengths it is unlikely that the hydrogen peroxide would add across the Te-Te bond in the manner observed in the oxidation of ditelluride by the bigger iodine molecule to RTeI[14], but rather that it would add to one of the tellurium atoms.

The results show that the reaction is sensitive to the mathematical product, $k_a k_b$, rather than to the individual values of k_a and k_b. The computed values of $k_a k_b$ at different temperatures are described well by an Arrhenius plot, implying that the scheme holds over the temperature range studied and is uniformly consistent.

The numerical integration approach was used as it seemed unlikely that a reaction scheme could be found that would fit the experimental data and also be explicitly solved. However, when we had settled on the scheme below, equations 3-41 to 3-43,

$$H_2O_2 + R_2Te_2 \longrightarrow RTe + RTe(OH)_2 \qquad \text{---(3-41)}$$

$$RTe(OH)_2 + R_2Te_2 \longrightarrow 2RTeOH + RTe \qquad \text{---(3-42)}$$

$$RTe + H_2O_2 \longrightarrow RTe(OH)_2 \qquad \text{---(3-43)}$$

as an acceptable description we found that it can be integrated as long as the hydrogen peroxide concentration is regarded as being constant (Appendix IV) giving equations (3-45) to (3-46). We therefore used the method of least squares to find the best fits of the experimental data to equation 3-45 from 0 to 70% completion, or to 10% depletion of H_2O_2 whichever came first.

$$\text{Log}_e \frac{2 - f - 2\sqrt{1 - f}}{f} = \text{Constant} - yt \qquad \text{---(3-45)}$$

where $f = [(p\text{-EtOPh})_2Te_2]_t / [(p\text{-EtOPh})_2Te_2]_o$ ---(3-46)

ie the fraction of the initial concentration of ditelluride remaining at time t, and

where $y = k_{obs}$

$$k_{obs} = \sqrt{4k_o[R_2Te_2]_o\,[H_2O_2]_o^2} \qquad \text{---(3-47)}$$

ie

$$(k_o)^{1/2} = \frac{k_{obs}}{(2[p\text{-EtOPh})_2Te_2]_o^{1/2}\,[H_2O_2]_o} \qquad \text{---(3-56)}$$

Thus the rate constant of the reaction could be determined from the computer program shown in Appendix V. The data obtained from the pseudo-first order and integrated rate equations follow the same pattern, as is found using this approach.

The data obtained for runs at various initial ditelluride concentrations, table 3-17, gave a straight line when the natural logs of the observed rate constant and the initial ditelluride concentration were plotted. The slope is a half implying that k_{obs} is proportional to the half power of the initial ditelluride concentration as equation 3-47 requires.

The data from the variation of the initial hydrogen peroxide concentration runs, table 3-18, also gave a straight line graph when the natural logs of the observed rate constant and initial hydrogen peroxide concentration were plotted together. In this case the slope is one, again in agreement with equation 3-47.

The integrated rate constant (k_o) obtained from the slope of the plot of the observed rate constant versus either the square root of the initial ditelluride concentration, fig 3-18, or the the initial hydrogen peroxide concentration, fig 3-19, using the data in tables 3-16 and 3-17, give $k_o = 19.1\ mol^{-3/2}\ dm^{9/2}\ s^{-1}$.

The experiments carried out to study the effect of solvent composition and ionic strength, tables 3-22 and 3-23, show there is no significant effect upon k_o as shown in figs 3-23 and 3-24. This implies that the reaction does not involve charged species.

However when varying the pH of the solution a small but significant effect on the reaction rate is found. The plot of $\log_e k_o$ versus pH is shown in fig 3-25. There is a region where the rate is independent of the pH, 3.50 to 11.5. However below pH=3.5 and above pH=11.5 there appears to be an inverse hydrogen ion effect which could be attributed to protonation equilibria of the reagents either the ditelluride or the hydrogen peroxide.

As noted in the introduction, general acid catalysis is observed without exception for the oxidation of various nucleophiles by hydrogen peroxide. However, this effect is only observed in strong acid solutions, ie pH < 1 and is due to the $H_3O_2^+$ ion. In my kinetic experiments the concentration of the $H_3O_2^+$ is small and it is therefore unlikely to have any effect on the rate constant. Also the presence of $H_3O_2^+$ would expect to increase the rate which is in contrast to that observed. Next we can consider the possibility that the ditelluride is being protonated. This would require the ditelluride to be a stronger base than hydrogen peroxide, which is not what we would expect. The basicity of elements within a group decreases as the atomic number of that group increases. Thus for group 16 we expect

$$O \gg S > Se > Te$$

to be the order of basicity of the group. Therefore protonation of R_2Te_2 can be discounted.

I observed that the induction period lasted 20 minutes at pH=1.74, compared to 2-3 minutes for the majority of my kinetic experiments, indicating that formation of the reactive species, $RTe(OH)_2$, has been retarded. Thus the protonation of the intermediate might be a distinct possibility, since it is unlikely that either of the two reagents are being protonated. The lack of evidence for data on the strength of ditellurides as bases prevents us from reaching a firm conclusion on this. The alkaline region is more easily explained. The very sharp increase above 11.5 indicates that we are dealing with the equilibrium

$$H_2O_2 + OH^- \rightleftharpoons HO_2^- + H_2O$$

which has a pK_a of 11.81, similar to that indicated by the sharp increase in the kinetic experiments. This implies that HO_2^- is a better oxidizing agent than H_2O_2 in my system.

In Mehdi's photochemical work on the reaction of the same ditelluride with molecular oxygen, the activation energy was found to be zero over the temperature range studied, 20-50^oC.

ie $$R_2Te_2 \xrightarrow{hv} R_2Te_2^* \qquad \text{zero order in } R_2Te_2$$

$$R_2Te_2^* + R_2Te_2 \longrightarrow 2RTe\cdot + R_2Te_2$$

Also the need for dioxygen was demonstrated in which the dependance, however, is neither linear nor very pronounced and the induction period was unobservable under O_2. By contrast under a dinitrogen atmosphere there is a pronounced induction period. The variation in the rate constant was varied in the order

$$O_2 > \text{Air} >> N_2$$

The data table 3-19 for my system under air gave the following activation parameters

$$\Delta E^* = 42.0 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta H^* = 39.5 \pm 2 \text{ kJ mol}^{-1}$$

$$\Delta S^* = -87 \pm 5 \text{ J K}^{-1} \text{ mol}^{-1}$$

So that, while both systems involve dioxygen in some way, the rate determining steps must be very different.

The rate constant, $k_{o,}$ under different gaseous atmospheres was obtained. I found that the rate constant varied in the following order

$$N_2 > \text{Air} >> O_2$$

In my dioxygen experiments problems occurred because of the use of THF. When THF is exposed to air, peroxide formation occurs. This was observed when the THF was saturated with dioxygen, so quinol was added to prevent the formation of peroxide. A solution of ditelluride saturated with dioxygen was left for two days in the dark and no change in the absorbance was noticed. Therefore any reaction between ditelluride and dioxygen can be neglected. The THF used in this study was normally distilled prior to use, although in one experiment the THF (AnalaR grade) was used as commercially supplied. That is THF containing inhibitor, quinol, was used. It gave identical rate data and therefore the presence of quinol would not invalidate any findings described here.

The dioxygen data, table 3-21, gave the following relationship

$$k_{obs} \ \alpha \ [H_2O_2]_o$$

This is similar to the data obtained for experiments carried under an aerial atmosphere. The maximum initial hydrogen peroxide concentration used in the dioxygen atmosphere experiments was three times the maximum concentration used under air, and the induction period was still observed. The rate constant derived from the slope of fig 3-22, k_o = slope/(2[H_2O_2]$_o$) is 7.80 mol$^{-3/2}$ dm$^{9/2}$ s^{-1}. The effect on the rate constant is very pronounced as compared to that of air, k_o =19.1 mol$^{-3/2}$ dm$^{9/2}$ s^{-1}

The data, table 3-20, under a dinitrogen atmosphere gave the same results to those obtained under air and dioxygen atmospheres.

$$k_{obs} \ \alpha \ [H_2O_2]_o$$

The maximum initial hydrogen peroxide concentration used was less than the maximum used under air, leaving the induction period just observable. The rate constant, k_o, derived from fig 3-21 slope = k_o (2 [H_2O_2]$_o$), was found to be 21.5 mol$^{-3/2}$ dm$^{9/2}$ s^{-1}. Again this shows that dioxygen has an effect on the rate as the variation in the rate constant under different atmospheres is

$$N_2 > \text{Air} >> O_2$$

The results so far have discussed the oxidation of tellurium(I) to tellurium(II), although mention has been made of the indication that further oxidation to tellurium(IV) is slow. Using the Ti(IV) peroxy complex, it is possible to follow changes in the peroxide concentration after the tellurium(I) to tellurium(II) stage is essentially complete. Tables 3-13 and 3-14 give the results. These subsequent data were treated using the integrated form of the second order rate equation shown below.

$$k_{obs}\, t = \log_e \, [(A_f - A_t / X)/ (A_f - A_t)] \qquad \text{---(3-35)}$$

Figs 3-10 and 3-11 show the graphs from this treatment to be linear. The reaction rate was slow and consequently only two kinetic experiments were carried out, tables 3-13 and 3-14. The disappearance of the ditelluride was monitored and when essentially complete, the hydrogen peroxide concentration was monitored with time. The observed rate constants derived from equation 3-35 were 6.2 x 10^{-4} s^{-1} and 3.4 x 10^{-4} s^{-1}.These give second order rate constants of 0.11 and 0.18 mol^{-1} dm^3 s^{-1}. The overall stoichiometry achieved at the completion this step was found to be 3.05, clearly indicating tellurium(IV) as the product. However twenty-four hours later the stoichiometry was found to have increased to 3.30, which was attributed to partial tellurium(VI) formation.

The kinetic experiments have shown that there are three distinct reaction stages. Firstly the reaction studied involves oxidation of tellurium(I) to tellurium(II). This is followed by a second slower stage, oxidation of tellurium(II) to tellurium(IV). Finally there appears to be a much slower final stage tellurium(IV) to tellurium(VI) oxidation.

Viz

$$Te_2^{I} \xrightarrow{k_B} 2Te^{II} \qquad \text{---(3-57)}$$

$$Te^{II} \xrightarrow{k_C} Te^{IV} \qquad \text{---(3-58)}$$

$$Te^{IV} \xrightarrow{k_D} Te^{VI} \qquad \text{---(3-59)}$$

$$k_B \quad > \quad k_C \quad >> \quad k_D$$

The numerical integration and integrated rate equation schemes devised on the supposed involvement of the aryltellurium radical, RTe. I therefore ran several ESR spectra on the reaction solution, both under air and dioxygen atmospheres. However, I was unable to detect any signal at all.

Now Mehdi reported that in order to observe the radicals in the photochemical reaction of ditelluride with dioxygen, the presence of dioxygen was required. In fact, an ESR signal was obtained in the absence of ethanol, thus implying that the radical he was observing was $RTeO_2$. That is dioxygen is stabilising the RTe radical. If this is correct then a signal should have been detected in my studies if the RTe radical is formed, as O_2 is normally present. No signal was seen. This implies that the intermediate must be either tellurium(II) or tellurium(III) rather than RTe as was first supposed. This will not have any effect on the mathematical treatment of experimental data.

Two possible intermediates are $RTe(OH)_2$ and RTeOH. The initiation step in the proposed scheme proposed earlier involves $RTe(OH)_2$ and RTe. However, since RTe has been eliminated it would appear that the addition of another hydrogen peroxide molecule to give

$$R_2Te_2.H_2O_2 + H_2O_2 \longrightarrow 2RTe(OH)_2$$

is more likely. Since we have established that tellurium(II) is the initial product prior to further oxidation to the observed tellurium(IV) product, the tellurium(III) intermediate must be reduced to give RTeOH, assumed to be the tellurium(II) product.

The question arising at this stage is what is the dioxygen doing to retard the reaction rate? Firstly, it is not initiating the reaction sequence, since I observed that a solution of ditelluride in THF under a dioxgyen atmosphere remain unbleached in the dark, and it needed light in order to bleach the colour of the ditelluride. If it were initiating the reactions then the rate constant, k_o, would increase with the concentration of dioxygen as opposed to that observed.

Mehdi's photochemical work indicated the possibility of the following equilibrium

$$O_2 + R_2Te_2 \rightleftharpoons R_2Te_2.O_2$$

This equilibrium would reduce the amount of ditelluride available to interact with hydrogen peroxide to form an adduct according to

$$[R_2Te_2]/[R_2Te_2]_{total} = 1/(1 + K_1[O_2])$$

Further evidence to strengthen this hypothesis comes from the rate constant, k_o, which shows that there is a very pronounced change in the rate constant with the variation of the concentration of dioxygen

21.5(N_2) 19.1(Air) 7.80(O_2)

These data must have large associated errors since the design of the experimental procedure cannot exclude all traces of air for the experiments under dioxygen or dinitrogen atmospheres.

The rate constants show that the equilibrium to form the $R_2Te_2.O_2$ adduct appears to lie over to the right . From the rate data I estimate the equilibrium constant to be the order of 10 to 35 $dm^3\ mol^{-1}$, thus the "free" ditelluride available to form the $R_2Te_2.H_2O_2$ adduct is small, and thus the build up of the tellurium(III) intermediate, $RTe(OH)_2$, depends upon the ditelluride-dioxygen equilibrium.

The initiation of the reaction is the formation of the tellurium(III) species. Mehdi's work suggested the radicals were produced photochemically as follows

$$R_2Te_2.O_2 + R_2Te_2 \xrightarrow{k_p} R_2Te_2 + 2RTe + O_2$$

This gave rise to a half order equation in R_2Te_2 which was observed experimentally. My initiation follows similar lines with another hydrogen peroxide molecule interacting with the ditelluride-hydrogen peroxide adduct as such

$$R_2Te_2.H_2O_2 + H_2O_2 \longrightarrow 2RTe(OH)_2$$

One possible step to give RTeOH as the initial product is

$$R_2Te_2.H_2O_2 + RTe(OH)_2 \longrightarrow 2RTe(OH) + RTe(OH)_2$$

where the tellurium(III) is acting as a catalyst. Thus the reaction rate would depend upon the concentration of the $R_2Te_2.H_2O_2$ adduct and we can see that the rate will vary with the dioxygen concentration.

The scheme written in full involves two equilibria, the ditelluride with dioxygen and ditelluride with hydrogen peroxide, where R=p-EtOPh

$$R_2Te_2 + O_2 \overset{K_1}{\rightleftharpoons} R_2Te_2.O_2 \quad \text{---(3-60)}$$

$$R_2Te_2 + H_2O_2 \overset{K_2}{\rightleftharpoons} R_2Te_2.H_2O_2 \quad \text{---(3-61)}$$

$$R_2Te_2.H_2O_2 + H_2O_2 \xrightarrow{k_3} 2RTe(OH)_2 \quad \text{---(3-62)}$$

$$R_2Te_2.H_2O_2 + RTe(OH)_2 \xrightarrow{k_4} 2RTeOH + RTe(OH)_2 \quad \text{---(3-63)}$$

$$2RTe(OH)_2 \xrightarrow{k_5} R_2Te_2 + 2H_2O_2 \quad \text{---(3-64)}$$

$$2RTeOH \xrightarrow{k_6} R_2Te_2 + H_2O_2 \quad \text{---(3-65)}$$

Applying the steady state hypothesis to the tellurium(III) intermediate leads to

$$\frac{-d[R_2Te_2]}{dt} = [R_2Te_2]\sqrt{\frac{4K_2\,k_3\,k_5\,[R_2Te_2]_o\,[H_2O_2]_o^2}{(1 + K_1[O_2])\,(1 + K_2[H_2O_2]_o)}} \qquad \text{---(3-66)}$$

where

$$k_{obs} = \sqrt{\frac{4K_2\,k_3\,k_5}{(1 + K_1[O_2]) + K_2[H_2O_2]_o}}\;[R_2Te_2]_o^{1/2}\,[H_2O_2]_o \qquad \text{---(3-67)}$$

If $1 + K_1[O_2] >> K_2[H_2O_2]_0$ then

$$k_{obs} \;\; \alpha \;\; [R_2Te_2]_0^{1/2}[H_2O_2]_o$$

which is in agreement with that found experimentally.

From the observed rate constant, assuming $1 + K_1[O_2] >> K_2[H_2O_2]_o$, it can be seen that the integrated rate constant, k_o, is

$$\sqrt{\frac{4K_2\,k_3\,k_5}{(1 + K_1[O_2])}}$$

Thus increasing the dioxygen concentration results in a decrease in k_o and the rate constant should vary in the following manner

$$k_o = \sqrt{\frac{1}{(1 + K_1[O_2])}}\;,\;\; \sqrt{4K_2\,k_3\,k_5}$$

However, the experimental method made it impossible to exclude all traces of air, thus it was not possible to control the amount of dioxygen involved precisely enough to test the above relationship.

The possibility of the following steps occuring rather than k_4

$$2RTe(OH)_2 \xrightarrow{k'} RTeOH + RTe(OH)_3 \qquad \text{---(3-69)}$$

was eliminated on the basis of the reaction stoichiometry cited in table 3-10. The above step would give a stoichiometry of >2 as opposed to 1.26 observed in the last run.

The scheme presented involves RTeOH as the tellurium product. However, the final product was found to be mainly aryl tellurinic acid RTeO(OH) and the two steps presented, 3-70 and 3-71 involve oxidation of tellurium(II) to tellurium(IV)

$$RTeOH + H_2O_2 \xrightarrow{k_7} RTe(OH)_3 \qquad \text{---(3-70)}$$

$$RTe(OH)_3 \xrightarrow{k_8} RTe(O)OH + H_2O \qquad \text{---(3-71)}$$

The intermediate, $RTe(OH)_3$, would occur if an adduct $RTeOH.(H_2O_2)$ underwent rearrangement . The final step could also be a one step process rather than these two, Viz:

$$RTeOH + H_2O_2 \xrightarrow{k_z} RTe(O)OH + H_2O \qquad \text{---(3-72)}$$

This stage appears to obey second order kinetics as both suggestions require.

CONCLUSION

The reaction between bis(p-ethoxyphenyl) ditelluride and hydrogen peroxide has been studied. The reaction was found to be retarded by dioxygen, which was attributed to an equilibrium between the ditelluride and dioxygen. The first step is the formation of an adduct, $R_2Te_2.H_2O_2$, followed by attack of another H_2O_2 molecule to give a tellurium(III) intermediate. This intermediate catalyses the destruction of the adduct to give the initial product RTeOH. Further reaction of the tellurium(II) product gives the observed product, aryl tellurinic acid, RTe(O)OH, although tellurium(VI) was believed to be the ultimate product.

CHAPTER FOUR

REDUCTION OF para-ETHOXYPHENYL TELLURIUM TRICHLORIDE BY THE HYDRAZINIUM ION

4-1 INTRODUCTION

In this chapter I describe the reduction of para-ethoxyphenyltellurium trichloride by the hydrazinium ion to yield the ditelluride $(p\text{-EtOPh})_2Te_2$.

The first synthesis of $(p\text{-EtOPh})_2Te_2$ was by Morgan and Drew by reduction of the corresponding trichloride using alkaline metabisulphite[2]. Since then many workers have prepared similar compounds using different reducing agents. Diorganyl ditellurides are important intermediates in organotellurium chemistry leading to a large number of different classes of tellurium compounds.

This study was undertaken in an attempt to gain more information about the redox steps of the intermediates Tellurium(II) to Tellurium(I) in the ditelluride. The step Tellurium(IV) to Tellurium(II) is well based from Tahir's work in the sulphite[16] reduction of the same trichloride. The solvent used in his system was 1,4-dioxane and water (3:1 by volume). Upon mixing the reagents, the trichloride was hydrolysed to give the aryltellurinate($RTeO_2^-$), followed by reduction by sulphite (HSO_3^-) to give $RTeO^-$. This tellurium(II) intermediate was believed to dimerise to R(HO)TeTe(OH)R before being reduced by another mole of HSO_3^-.

$$RTeCl_3 + 2H_2O + H^+ \longrightarrow RTe(O)OH + 3Cl^- + 4H^+$$

$$RTe(O)OH \rightleftharpoons RTeO_2^- + H^+$$

$$RTeO_2^- + HSO_3^- \longrightarrow RTeO^- + SO_4^{2-} + H^+$$

$$RTeO^- + H^+ \longrightarrow RTeOH$$

$$2RTeOH \longrightarrow R(OH)TeTe(OH)R$$

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

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

The redox reaction is believed to be inner-sphere in nature with an oxygen atom as the ligand common to both reductant and oxidant giving a transition state as

$$[\mathrm{RTe(O)OSO_2OH}^{2-}]$$

The absence of dithionate, which would of been be formed by a one-electron transfer process, in the reaction solution also indicated that the reaction was a two-electron transfer process. Tahir also studied the reduction of the trichloride by Vanadium(II) and Chromium(II) ions. The redox reaction was reported to be inner-sphere in nature with a chlorine atom as the bridging ligand.[12]

The reactions between different oxidizing and reducing agents may be interpreted by two types of mechanisms

I) OUTER-SPHERE

In this case the interaction between the oxidant and reductant, at the time of electron transfer, is small and they go through the process with their coordination shells or spheres intact. The redox process must be faster than any substitution process that the oxidant and/or the reductant would undergo[86a]. An example of this mechanism is the oxidation of $\mathrm{Ru(NH_3)_6}^{2+}$ by complex ions of the type $[\mathrm{Co^{III}(NH_3)_5L^{-n}}]^{3-n}$ where $\mathrm{L^{-n}}$ is one of a variety of ligands[87]. Since the interaction of the two reactants is small, the probability of electron transfer is thus small. However the probability of a two electron transfer in the same step is vanishing small and thus as such all known outer-sphere electron transfer reactions, observed without exception, are one-electron equivalents. Also, the Franck-Condon restriction (that is, matching of the energies of the oxidant and the reductant before electron transfer) will be far more serious if two-electrons have to be transferred compared to a one-electron, in a redox step. Since the first coordination spheres of both reactants remain intact during the process of electron transfer, it therefore can be seen that the closest approach of the two reactants would be the second coordination sphere ie in the order of 10A. Despite, however, the large distance of separation of the reactants, compared to the metal-ligand bond lengths which are in the order of 2A, there is sufficient orbital overlap of the reactants to allow electron transfer[86b].

II) INNER-SPHERE

This mechanism is one in which the reductant and oxidant are linked by at least one ligand common to both inner co-ordination spheres with electron(s) being transferred through this bridging group. The best known example of this type of mechanism was provided by Taube and co-workers[88]. The system involved the reduction of Co(III) by Cr(II):-

$$[Co^{III}(NH_3)_5Cl]^{2+} + [Cr^{II}(H_2O)_6]^{2+} \longrightarrow H_2O \; +$$

$$\underset{A}{[(NH_3)_5Co\text{-}Cl\text{-}Cr(H_2O)_5]^{4+}} \longrightarrow [CrCl(H_2O)_5]^{2+} + Co(II) \text{ species} \qquad \text{---(4-1)}$$

which takes place with a binuclear complex(A) with the formation of the reduced Co(II) and oxidised Cr(III). In this case transfer of a chlorine atom from cobalt to chromium is observed. Unlike the outer-sphere mechanism the inner-sphere can be demonstrated by ligand transfer from the oxidant to the reductant and/or by a two-electron equivalent transfer. However ligand transfer does not always accompany inner-sphere electron transfer and therefore is not an essential feature of this mechanism.[89]

4.1.1Mechanistic aspects of Hydrazine Chemistry

Hydrazine is a strong reducing agent and as such reduces many ions to lower oxidation states or even to the bare metal and beyond to the hydride. Hydrazine is a bifunctional base and two series of hydrazinium salts are obtainable. Those of $N_2H_5^+$ are stable in water, whilst those of $N_2H_6^{2+}$ are extensively hydrolysed. In acidic solution hydrazine is almost entirely in the form $N_2H_5^+$ whilst in alkaline solution N_2H_4.

The standard redox potentials of hydrazine

$$N_2H_4 + 4OH^- \longrightarrow N_2 + 4H_2O + 4e^- \qquad E^o=+1.16V \qquad ---(4-2)$$

$$N_2H_5^+ \longrightarrow N_2 + 5H^+ + 4e^- \qquad E^o=+0.23V \qquad ---(4-3)$$

indicate hydrazine is a better reducing agent in alkaline than in acidic solution. Hydrazine can also be oxidizing as well as reducing but there are few examples in the literature of this.

Hydrazine can act as a one or two electron equivalent reductant. Three distinct overall reactions can be identified

$$N_2H_5^+ \longrightarrow 4e^- + N_2 + 5H^+ \qquad ---(4-4)$$

$$N_2H_5^+ \longrightarrow e^- + 0.5N_2 + NH_4^+ + H^+ \qquad ---(4-5)$$

$$N_2H_5^+ \longrightarrow 2e + 0.5HN_3 + 0.5NH_4^+ + 2.5H^+ \qquad ---(4-6)$$

Reaction (4-4) occurs when the oxidizing agent is acidic iodate, neutral iodine or alkaline cyanoferrate, whilst reaction(4-5) is approximated with iron(III) or manganate as the oxidants. However many oxidants give reactions (4-4) and (4-5) simultaneously. Reaction (4-6) occurs predominantly if hydrazine is oxidised in hot, concentrated sulphuric acid with H_2O_2.

Higginson and co-workers[90] grouped the oxidizing agents according to their ability to oxidise hydrazine by one-electron equivalent reactions. They noticed that all simple metals ions fall into one class, whereas oxyacids and their salts, and uncharged oxidizing agents, such as H_2O_2, belonged to the other. They suspected that the ability of the metal ions to absorb hydrazine in their co-ordination sphere determines the path of the reaction. Higginson and Marshall[76] have summarised that oxidation-reduction reactions between simple compounds or ions derived from two non-transition elements, whether metallic or non-metallic, usually occur in two-electron equivalent steps. This is explained by the fact a one-electron equivalent step with two molecules or ions, from p-block elements, would lead to two relatively unstable species, since the difference in stable oxidation states is two for p-block elements, and thus seems unlikely compared with a two-electron equivalent change. The oxidation-reduction reaction between transition elements ions, and compounds or ions derived from non-transition elements may occur in either one or two-electron equivalent steps. The one-electron equivalent mechanism occurs more often and this can be explained by the fact the difference in stable oxidation states for the transition metal ions is unity.

Isotopically labelled hydrazine was used by Higginson and Sutton[91] in an attempt to elucidate the oxidation mechanisms of hydrazine. The isotope analysis showed that in the four electron transfer reaction

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^- \qquad \text{---(4-7)}$$

no N-N fission occurs and no new N-N bonds are formed, whereas the other group of oxidants would cause reactions (4-7) and (4-8) to occur simultaneously

$$N_2H_4 \longrightarrow 0.5N_2 + NH_3 + e^- + H^+ \qquad \text{---(4-8)}$$

In reaction (4-8), half of the evolved dinitrogen molecules were derived from the same N_2H_4 molecule, whilst the other half of the nitrogen atoms came from separate N_2H_4 molecules. Whereas it is possible to study four-electron transfer reactions individually and free from one-electron oxidants, it is not possible to study an isolated one-electron reaction (equation 4-8). There is no oxidizing agent that gives exclusively one-electron oxidation of hydrazine. The fraction of nitrogen formed by one-electron oxidation varies from 0% for acidic iodate to over 80% for cerium(4+) ion as oxidant.

If a one-electron oxidation proceeded through an intermediate tetrazane, $H_2N\text{-}NH\text{-}NH\text{-}NH_2$, which loses one terminal amino group to form triazene which tautomerises prior to loss of the second amine group, the randomisation would be 50% which is in agreement with that found experimentally[92].

$$N_2H_5^+ + Fe^{3+} \longrightarrow Fe^{2+} + N_2H_3^{\cdot} + 2H^+ \qquad \text{---(4-9)}$$

$$2N_2H_3^{\cdot} \longrightarrow H_2N\text{-}NH\text{-}NH\text{-}NH_2 \qquad \text{---(4-10)}$$

$$H_2N\text{-}NH\text{-}NH\text{-}NH_2 \longrightarrow HN{=}N\text{-}NH_2 + NH_3 \qquad \text{---(4-11)}$$

$$HN^*{=}N\text{-}NH_2 \longrightarrow H_2N^*{=}N\text{-}NH \qquad \text{---(4-12)}$$

$$N_3H_3^{\cdot} \longrightarrow NH_3 + N_2 \qquad \text{---(4-13)}$$

The radical intermediate, $N_2H_3^{\cdot}$, may be oxidised further by a one-equivalent reaction to the product expected for a two-equivalent reaction step[93].

$$N_2H_3^{\cdot} + Fe^{3+} \longrightarrow Fe^{2+} + HN{=}NH + H^+ \qquad \text{---(4-14)}$$

$$2N_2H_2 \longrightarrow HN{=}NH + N_2H_4 \qquad \text{---(4-15)}$$

It is assumed that diazene is very rapidly oxidised to nitrogen

$$HN{=}NH + 2Fe^{3+} \longrightarrow N_2 + 2Fe^{2+} + 2H^+ \qquad \text{---(4-16)}$$

Diazene is used in organic synthesis as a very mild reducing agent, which allows selective reduction of double bonds while not reducing other reducible groups in the molecule. It can be detected by the addition of a cyclohexene derivative leading to reduction of the carbon-carbon double bond[94]. Hydrazine, however, does not reduce C=C bonds under the same conditions, apparently because diazene has a higher affinity to the C=C bond than hydrazine itself.

Thus when the products in the oxidation of hydrazine are dinitrogen only, diazene is the only nitrogen intermediate, whereas one-electron oxidisers lead to the hydrazyl radical as an intermediate. If ammonia is found to be one of the products then the oxidation of hydrazine goes via a one-electron step. This means it is possible to determine whether the redox reaction goes via two or one-electron steps at a time by product analysis.

In some redox systems involving hydrazine and one electron oxidants, the reaction stoichiometry varies depending on whether or not an excess of hydrazine is used. Higginson and Brown [93] observed that when the oxidant is in excess the reaction stoichiometry ratio indicated that successive one-equivalent steps occur to give diazene and eventually dinitrogen as the only nitrogen product

$$N_2H_4 \xrightarrow{\text{1-eqv}} N_2H_3^{\cdot} + 2H^+ + e^- \qquad \text{---(4-17)}$$

and

$$N_2H_3^{\cdot} \xrightarrow{\text{1-eqv}} N_2H_2 + H^+ + e^- \qquad \text{---(4-18)}$$

The reduction of the ferric ion by hydrazine goes via a one-electron step. However in an alkaline medium there is quantitative conversion of the hydrazine to dinitrogen, whereas in acidic media the reaction stoichiometry varies showing that the intermediates in acidic solution do not undergo further oxidation and thus dimerise. In alkaline solution, however, dimerisation is suppressed and further oxidation occurs.

The reduction of molybdenum(VI) by hydrazine has been found to have a constant reaction stoichiometry and no ammonia was detected, whatever the ratio of the reagents and pH. This has been attributed to the fact that hydrazine is oxidised by a two-electron equivalent reaction. Thus again showing that if an excess of hydrazine is used, the nitrogen products can differentiate between a one and a two-electron change .

The reaction of the halogeno complexes of iridium(IV) with hydrazine have been studied in perchloric acid media. Higginson and Brown [93] reported that the stoichiometry was 3.5-3.8 moles Ir(IV) per mole of hydrazine depending on pH with excess iridium(IV). Morris and Ritter[95] reported similar results although they did not state the concentration of reagents used, it presumably involved excess iridium(IV) since with excess hydrazine the reaction[92] stoichiometry is reported to be

1:1 (Ir(IV):N_2H_4).

A detailed kinetic investigation of the oxidation by hydrazine by hexachloroiridate(IV) was reported by Sengupta and Sen[96] using excess hydrazine. The reaction was found to be first order in iridium(IV) and fractional order with respect to the hydrazinium ion. The data was consistent with the formation of an intermediate compound between $N_2H_5^+$ and $IrCl_6^{2-}$ followed by decomposition to give the products

$$N_2H_5^+ + IrCl_6^{2-} \rightleftharpoons [N_2H_4IrCl_6]^{2-} + H^+ \qquad \text{---(4-19)}$$

$$[N_2H_4IrCl_6]^{2-} \longrightarrow IrCl_6^{3-} + N_2H_3^{\cdot} + H^+ \qquad \text{---(4-20)}$$

The hydrazyl radical dimerises, then decomposes to give N_2 and NH_4^+. Morris and Ritter[95] extended the study to other halogeno complexes of iridium(IV), $IrCl_6^{2-}$, $[IrCl_5H_2O]^-$, $IrBr_6^{2-}$ and $IrCl_4(H_2O)_2$. The kinetic data suggested that the four different iridium(IV) species react with hydrazine by a similar mechanism. The reaction showed first order dependence on the initial hydrazinium ion and iridium(IV) concentrations suggesting a 1:1 complex formation between the two reagents. The hydrazyl radicals formed undergo further oxidation to dinitrogen. The authors found that their data was consistent with an outer-sphere electron transfer reaction. The overall gibbs free-energy change gave a linear plot against the second order rate constant, for each iridium(IV) species, with a slope of 0.45. This result is consistent with the prediction by Marcus[97] for an outer-sphere reaction which predicts a slope of 0.5. The above reaction is an example where it is possible to indicate whether a reaction is outer-sphere or inner-sphere by reference to the overall Gibbs free-energy for a particular class of compounds, in this case iridium(IV) halogeno complexes.

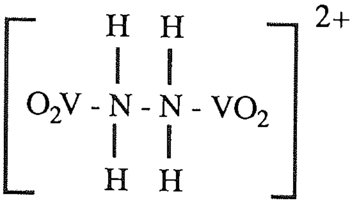
Another one electron oxidant of hydrazine is the ceric(IV) ion. This reaction was first reported by Benrath and Ruland[98] who said that it was a one-electron change with ammonia as the only nitrogen product. Higginson[95] reported that the reaction stoichiometry varied between 1.05 and 1.4 (Ce(IV)/N_2H_4) with dinitrogen and ammonia as the products. The explanation for the variable reaction stoichiometry was due to the fact that one and four-electron changes were occurring simultaneously. Mishra and Gupta[99] made an interesting observation when they attained a limiting reaction stoichiometry of 4. This was obtained with excess ceric(IV) and high acid concentration (10M H_2SO_4). It appears that the dimerisation of the hydrazyl radical is suppressed and successive one-electron changes occur. However with excess hydrazine in the same conditions the effects of a one-electron change are observed.

Morrow and Sheeres[100] reported that the stoichiometry was constant with excess hydrazine. The rate determining step consistent with their data was

$$CeOH^{3+} + N_2H_5^{+} \longrightarrow Ce(III) + N_2H_4^{+} + H_2O \qquad \text{---(4-21)}$$

where $N_2H_4{}^{'+}$ is the protonated form of the hydrazyl radical. The rate expression was identical in form with that found by Davis and Kustin for the Mn(III)-N_2H_4 reaction, although a different mechanism was involved since dinitrogen was evolved, whereas in the Mn(III)-N_2H_4 system no gas was evolved. The study indicated that $Ce(OH)^{3+}$ oxidises $N_2H_5^{+}$ considerably more rapidly than Ce^{4+} does.

The reaction scheme suggested in this chapter for the final stage, ie tellurium(II) to tellurium(I) in the ditelluride, is thought to involve a tellurium dimer . Bengtsson[101] suggested a similar mechanistic step in the reduction of the VO_2^+ ion by hydrazine to V(IV). Analysis of the kinetic data and the finding that dinitrogen was the only nitrogen containing product suggests that the activated state requires two VO_2^+ ions. This indicates that hydrazine is not oxidised in successive steps, but simultaneously by two VO_2^+ coordinated to each nitrogen in hydrazine.



$$\left[O_2V - \underset{H}{\overset{H}{N}} - \underset{H}{\overset{H}{N}} - VO_2 \right]^{2+}$$

This intermediate was suggested to give either 2V(IV) and diimine or 2V(III) and dinitrogen species as the products. The kinetic rate law was consistent with both interpretations, and the author pointed out that no silver metal was precipitated upon the addition of silver sulphate. Evidence, it was claimed, for the absence of V(III) as an intermediate.

My reaction may proceed via a transition state involving a nitrogen-tellurium bound species. In addition to the molybdenium(VI) and VO_2^+ species already discussed, the reduction of chromium(V) and (VI) is also believed to go via an N-Cr bounded intermediate.

Gould[102] reported that reduction of chromium(V) carboxylato-bound complexes by hydrazine goes via a two electron transfer

Viz:

$$(OLig^{2-})Cr^{V}(O)OH + N_2H_5^{+} \rightleftharpoons (OLig^{2-})Cr^{V}(O)N_2H_4(OH) + H^{+} \qquad \text{---(4-22)}$$

The transition state was believed to contain an N-Cr bridge which then decomposes to give the products

$$(OLig^{2-})Cr^{V}(O)(OH)N_2H_4 \xrightarrow{k_3} (HOLig^{-})Cr^{III}(OH)_2 + N_2H_2 \qquad \text{---(4-23)}$$

Haight and Huang[104] reported the reduction of chromium(VI) in high acidities. The reaction was found to be acid catalysed and went via a N-Cr bounded ester.

$$NH_2NH_2^{\pm}CrO_3^{-} \quad \text{or} \quad NH_3^{+}NH\text{-}CrO_3^{-}$$

although neither could be distinguished.

The rate determining step involves acid or base induced dissociation of H^+ from hydrazine to give the transition state

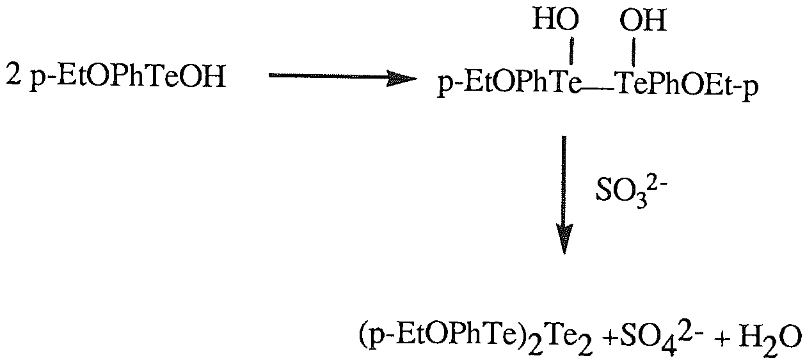
$$H_3N^{+}NH\text{-}CrO_3^{-} \longrightarrow [H_2NNHCrO_3H] + H^{+} \qquad \text{---(4-24)}$$

followed by two electron reduction to give Cr(IV) and N_2H_2. No information was available on the fate of N_2H_2 but the authors suggested that it disproportionates to nitrogen and hydrazine. On the basis of electrode potentials data, they suggested that the Cr(III) product was formed from disproportionation of Cr(IV).

$$2Cr(IV) \rightleftharpoons Cr(III) + Cr(V) \qquad \text{---(4-25)}$$

One may conclude from the literature that oxidation of hydrazine yields two products depending on whether the oxidizing agents favour one or two-equivalent reactions. The reduction by two-equivalent oxidizing agents will yield dinitrogen as the only nitrogen containing product. The production of ammonia, from one-equivalent agents, is favoured at lower pH.

Turning now to the tellurium reagent, Tahir and Miller[16] suggest that dimerisation of the tellurium(II) intermediate occurs prior to reduction to tellurium(I) in the ditelluride, in the reduction of p-EtOPhTeCl$_3$ by sulphite(SO_3^{2-}). Since no dithionate formation was observed, dimerisation followed by reduction would involve a two-electron equivalent as observed. The alternative would be formation of tellurium(I) radical, RTe', which is in contradiction to the clean quantitative conversion of the aryltelluriumtrichloride to ditelluride



$$2\ \text{p-EtOPhTeOH} \longrightarrow \text{p-EtOPh}\overset{\text{HO}}{\text{Te}}\text{—}\overset{\text{OH}}{\text{Te}}\text{PhOEt-p} \xrightarrow{SO_3^{2-}} (\text{p-EtOPhTe})_2\text{Te}_2 + SO_4^{2-} + H_2O$$

---(4-26)

Now turning to my work, a brief summary is given.

The reduction of aryltelluriumtrichloride by the hydrazinium ion results in the production of the diarylditelluride quantitatively. No ammonia was detected, therefore the reaction is believed to proceed via two-electron equivalent steps. The reaction was studied under pseudo-first order conditions, involving excess $N_2H_5^+$ concentrations. The pseudo first order rate constant was aryltelluriumtrichloride independent but hydrazinium ion dependent and varied with the acidity of the solvent medium.

The reaction is believed to go via two stages. Firstly, the rate determining step of the reaction involving reduction of tellurium(IV) to tellurium(II). Secondly, reduction of two tellurium(II) species by the hydrazinium ion gives the ditelluride.

The tellurium(IV) species is believed to be aryltellurinic acid (RTe(O)OH) and the tellurium(II) species RTeOH.

A decrease in the pH is found to retard the reaction rate due to protonation of the tellurium(IV) species. No effect was found on varying the ionic strength, but the rate increased with decreasing dielectric constant of the solvent.

4-2 RESULTS

The reduction of a solution of p-ethoxyphenyltellurium trichloride in THF by a solution of hydrazinium chloride in aqueous THF, 1:1 by volume, has been investigated. The best wavelength to follow the progress of the reaction was found to be 400nm, the absorption maxima of the ditelluride, see section 3-2. No other species in this system has any absorption at this wavelength.

The reaction stoichiometry determination was made by spectrophotometric measurement. The data is listed in table 4-1 and the plot of the molar concentration of $(p\text{-EtOPh})_2Te_2$ produced versus the initial molar ratio of $[N_2H_5Cl]_o/[p\text{-EtOPhTeCl}_3]_o$ is shown in Fig 4-2. The plot shows a reaction stoichiometry of 1.29 ± 0.04. This implies that three moles of N_2H_5Cl react with four moles of $p\text{-EtOPhTeCl}_3$, within experimental error to yield two moles of product. No ammonia was detected as a product the reaction of $p\text{-EtOPhTeCl}_3$ with the hydrazinium ion.

The kinetic studies were monitored by following the increase in the concentration of $(p\text{-EtOPh})_2Te_2$ with time to essentially complete reaction, usually for a period up to 30 minutes using an SP8-100 UV-spectrophotometer . The absorbance-time curves, up to 80 to 90% completion, were used to determine the individual rate constants under different reaction conditions.

The absorbance-time curves show two distinct parts. Initially there is an induction period which lasts around 2-3 minutes. This is followed by an increase in the product, $(p\text{-EtOPh})_2Te_2$, with time to give a rate profile as shown in Fig 4-1. When once the induction period is over, the whole absorbance-time curve can be fitted to an intergrated form of a first order equation . The conditions of study involved using a large excess of hydrazinium chloride leading to pseudo first order conditions for that part of the reaction profile. The derived equation was used to calculate the rate constants as explained in section 3-2.

The effect on the observed rate constant by varying the initial hydrazinium chloride concentration at 30°C was investigated, table 4-2. The range of hydrazinium chloride concentrations used was 0.063 to 6.3 $\times 10^{-3}$mol dm^{-3} , whilst the aryl tellurium trichloride concentration was kept at 1.77 $\times 10^{-3}$mol dm^{-3} . A plot of the initial hydrazinium chloride concentration versus the observed rate constant gives a straight line, fig 4-3, as described by

$$k_{obs} = (0.049 \pm 0.003)\,[N_2H_5{}^+]_o \qquad \text{--- (4-27)}$$

The plot passes through the origin implying that k_{obs} is directly proportional to the initial $N_2H_5{}^+$ concentration. This also indicates that the order in $N_2H_5{}^+$ is one . From this it is possible to calculate the rate constant k_r

Viz:

$$k_r = k_{obs} / [N_2H_5{}^+]_o \qquad \text{--- (4-28)}$$

where k_r is a second order rate constant . The value obtained from these runs is 0.048(2) dm^3 mol^{-1} s^{-1} compared to the slope from fig 4-3 of 0.049(3) dm^3 mol^{-1} s^{-1}.

Thus from the data above, the rate equation can be expressed as

$$\frac{d[(p\text{-EtOPh})_2Te_2]}{dt} = k_{obs}\,[p\text{-EtOPhTeCl}_3] \qquad \text{--- (4-29)}$$

where

$$k_{obs} = k_r\,[N_2H_5^+]_o \qquad \text{--- (4-30)}$$

The effect on the observed rate constant with varying initial aryltellurium trichloride concentration was investigated at 25°C. The range of concentrations of trichloride used were 5.83 to 16.4 $\times 10^{-4}$ mol dm^{-3} and the hydrazinium chloride concentration was kept at 0.0543 mol dm^{-3}. It was found that within experimental error, k_{obs} is virtually constant over the range investigated, thus confirming the order in p-EtOPhTeCl$_3$ is unity. The rate constant k_r was found to be 0.0358 mol^{-1}dm^3 s^{-1}.

Table 4-4 shows the variation in the rate constant, k_r, with temperature over the range 20-45°C for the reaction of $N_2H_5^+$ (23.6 $\times 10^{-3}$ mol dm^{-3}) and p-EtOPhTeCl$_3$ (1.82 $\times 10^{-3}$mol dm^{-3}). An Arrhenius plot of $\log_e k_r$ versus K/T is linear as shown in fig 4-5. The least squares computer program (Appendix II) was used to determine the slope of the plot . Equations 3-33 and 3-34 were used to determine the activation parameters as :

$$\Delta E^* = 61.2 \pm 1.9 \text{ kJ mol}^{-1}$$

$$\Delta H^* = 58.7 \pm 1.9 \text{ kJ mol}^{-1}$$

$$\Delta S^* = -76 \pm 5 \text{ J mol}^{-1}\text{ K}^{-1}$$

The kinetic experiments were repeated using different solvent compositions of THF and water at 30°C . The values of the dielectric constant for the mixed solvent can be found in the work of Critchfield [105] and Triener[106] . The rate constants are listed in

table in table 4-5 . A plot of $\log_e k_r$ versus 1/D presented in fig 4-7 shows a straight line dependence up to high THF percentages , where there is a curvature . A similar observation has been observed in the reduction of p-EtOPhTeCl_3 by sulphite .
I investigated the effect of the ionic strength on the rate constant , k_r , using $NaClO_4$ as the inert salt . The data showing the ionic strength runs are shown in table 4-6 . It was found that a large variation in the ionic strength of the reaction solution gave little change in the rate constant k_r (12% change in k_r). That is, k_r can be regarded as constant throughout the range, within experimental error. Also, the addition of potassium chloride had no effect on the observed rate constant as shown in table 4-7

The variation in the hydrogen ion concentration was investigated by adding $HClO_4$. In these experiments the ionic strength was maintained at 0.0653 mol dm^{-3} by the addition of $NaClO_4$. The rate of reaction was found to be inhibited by the acid . The data listed in table 4-8 , show that there is a slight inverse dependence on the rate constant , k_r, as shown in fig 4-8 .

The effect of the addition of water and acid to the aryltelluriumtrichloride solution on the absorbance-time curve was also investigated. Distilled water(1cm^3) was added to a THF solution (50 cm^3) of p-EtOPhTeCl_3 and left for 30 minutes . A kinetic experiment was undertaken using this trichloride solution and the effect observed shows that the induction period disappears completely . When one cm^3 concentrated perchloric acid was used instead of water , there is a long induction period followed by rest of the rate profile as shown in fig 4-1.

The pseudo first order rate data refer to the profile after the induction period. I decided to attempt a numerical integration on the kinetic data from the start up to 80-90% completion in order to gain a greater understanding of the reaction under study. This obviously includes the induction period and should lead to greater characterisation of the absorbance-time curve. The computer numerical integration which makes chemical sense and gives good results uses the following scheme : R= p-EtOPh

$$RTe(O)OH + N_2H_5^+ \xrightarrow{k_A} RTeOH + N_2H_3^+ + H_2O \qquad \text{--- (4-31)}$$

$$2RTeOH + N_2H_5^+ \xrightarrow{k_B} R_2Te_2 + N_2H_3^+ + 2H_2O \qquad \text{---(4-32)}$$

$$RTe(O)OH + N_2H_3^+ \xrightarrow{k_C} RTeOH + N_2 + H_2O + H^+ \qquad \text{---(4-33)}$$

$$\text{either } 2RTeOH + N_2H_3^+ \xrightarrow{k_{D(a)}} R_2Te_2 + N_2 + 2H_2O + H^+ \qquad \text{--- (4-34)}$$

$$\text{or } RTe(O)OH + RTeOH + N_2H_5^+ \xrightarrow{k_{D(b)}} R_2Te_2 + N_2 + 3H_2O + H^+ \qquad \text{--- (4-35)}$$

The computer program is shown in appendix VI. I found that it is possible to set the value of $k_A[N_2H_4]$ in this scheme at the value of the pseudo first order rate constant(k_{obs}) and obtained excellent data fits by varying the other constants, k_B to k_D. When the individual runs of table 4-9 were all treated in this way I found that the ratio k_C/k_A remained constant from one experiment to another, while the data fit was uniformly excellent. Whether reaction 4-34 or 4-35 was used in the fitting scheme, the k_D term is insignificant and does not make a significant contribution to the overall reaction. Therefore the steps 4-31 to 4-33 probably describe the entire reaction process being observed here.

The results of the numerical integration are summarised in table 4-9. Again good data fits were obtained. The ratio k_C/k_A was constant over the range studied and the rate constants thus derived fit the Arrhenius equation.

N_2H_5Cl/p-EtOPhTeCl$_3$ molar ratio	[(p-EtOPh)$_2$Te$_2$] produced /10^{-5}mol dm^{-3}
1.62	191
1.58	191
1.44	190
1.34	189
1.31	188
1.22	186
1.15	184
1.10	181
1.06	178
0.92	170
0.79	161

Table 4-1 Data for the reaction stoichiometry determination for the reaction between p-EtOPhTeCl$_3$ (4.02×10^{-3}mol dm^{-3}) with different molar concentrations of N_2H_5Cl.

$[N_2H_5Cl]_o$ $/10^{-3}$mol dm^{-3}	Rate Constant k_{obs} $/10^{-4}s^{-1}$	k_r x10^3 /mol^{-1} dm^3 s^{-1}
63	31.3	50
57	28.7	50
47	20.5	44
32	13.7	43
24	10.4	43
16	9.07	57
9.5	4.56	48
8.59	4.33	50
7.88	3.83	49
6.30	3.19	50

Table 4-2 Rate constants for the reaction of p-EtOPhTeCl_3 (1.77 x10^{-3}M) with different molar concentrations of N_2H_5Cl in aqueous THF at 30°C .

$k_r = k_{obs}/[N_2H_5Cl]_o$

$[p\text{-EtOPhTeCl}_3]_o$ $/10^{-4}$ mol dm^{-3}	Rate constant $k_{obs}/10^{-3}s^{-1}$	k_r x10^3 /mol^{-1} dm^3 s^{-1}
16.4	1.64	34.2
13.3	1.72	35.8
11.4	1.66	34.6
8.62	1.66	34.6
7.10	1.86	38.8
5.83	1.77	37.0

Table 4-3 Rate constants for the reaction of N_2H_5Cl (48 x10^{-3}M) with different initial molar concentrations of p-EtOPhTeCl$_3$ in aqueous THF at 25^{o}C .

$k_r = k_{obs}/[N_2H_5Cl]_o$

Temp/^{o}C	K/T x10^3	$k_{obs}/10^{-4}s^{-1}$	k_r x10^3 /mol^{-1} dm^3 s^{-1}	$\log_e k_r$
20	3.41	5.12	22	-3.82
25	3.35	8.51	36	-3.32
30	3.30	11.4	48	-3.03
35	3.24	16.9	72	-2.63
40	3.19	26.4	119	-2.13
45	3.14	38.2	162	-1.82

Table 4-4 Rate constants for the reaction of p-EtOPhTeCl$_3$ (1.82 x10^{-3}M) with N_2H_5Cl (23.6 x10^{-3}M) in aqueous THF at different tempertures .

%THF	D	1/D /10^{-3}	k_{obs} /$10^{-4}s^{-1}$	k_r x10^3 /mol^{-1} dm^3 s^{-1}	$\log_e k_r$
50	38.8	25	3.40	18	-4.02
60	31.1	32.2	4.67	24	-3.73
70	27.3	40.6	7.40	39	-3.24
75	24.1	46.5	10.4	48	-3.04
80	17.8	54.8	13.5	71	-2.65
85	15.6	64.9	14.1	75	-2.59

Table 4-5 Rate constants for the reaction of p-$EtOPhTeCl_3$ (18.4 x 10^{-3}M) with N_2H_5Cl (18.9 x 10^{-3}M) in aqueous THF solutions of different dielectric constant at 30°C .

$[NaClO_4] \times 10^3$ /mol dm^{-3}	Ionic Strength I /10^{-3} mol dm^{-3}	k_{obs} /10^{-4}s^{-1}	$k_r \times 10^3$ /mol^{-1} dm^3 s^{-1}
1.50	11	5.81	61
6.50	16	5.78	61
11.5	21	5.59	59
12.5	22	5.51	58
16.5	26	5.94	63
19.5	29	5.33	56
23.5	33	5.91	62
26.5	36	5.11	54
31.5	41	5.46	58
38.5	48	5.36	60
46.5	56	5.16	54
50.5	60	5.28	56
58.5	68	5.17	54

Table 4-6 Variation of the rate constant with the ionic strength of the solution for the reaction of p-EtOPhTeCl$_3$ (8.95 x 10^{-4}M) with N_2H_5Cl (9.50 x10^{-3}M) in aqueous THF at 30^{o}C.

$[KCl] \times 10^3$ /mol dm^{-3}	Ionic Strength I/10^{-3} mol dm^{-3}	k_{obs} /10^{-3}s^{-1}	$k_r \times 10^3$ /mol^{-1} dm^3 s^{-1}
54.3	77.9	1.04	44
49.0	72.6	1.19	50
43.0	66.6	1.19	50
39.0	62.6	1.19	50
33.0	56.6	1.18	50
30.0	53.6	1.08	46

Table 4-7 Variation in the rate constant with Ionic Strength of the reaction solution for the reaction of p-EtOPhTeCl_3 (1.84 x10^{-3}M) with N_2H_5Cl (23.6 x10^{-3}M) in aqueous THF at 30°C .

10^4x $[HClO_4]$ /mol dm^{-3}	pH	k_{obs} /$10^{-4}s^{-1}$	$k_r x 10^3$ /mol^{-1} dm^3 s^{-1}
—	6.44	17.4	32
2.2	5.88	17.0	31
3.3	4.92	16.9	30
4.4	3.77	16.2	29
6.6	3.26	15.3	28
11	2.89	14.9	27
28	2.41	14.1	26
55	2.08	12.3	23
110	1.77	11.3	21

Table 4-8 Rate constants for the reaction of p-$EtOPhTeCl_3$ (8.65 x10^{-4}M) with N_2H_5Cl (54.4 x10^{-3}M) at different hydrogen ion concentrations in aqueous THF at 25°C at constant ionic strength of 0.0653mol dm^{-3}.

Temperature Data

Temp/^{o}C	$k_1/10^{-4}s^{-1}$	k_2/s^{-1}	$k_3/10^{-3}\ s^{-1}$	k_4/s^{-1}	k_3/k_1
20	5.12	27	25.3	0	49
25	8.51	21	57.0	0	67
30	11.4	70	58.0	0	51
35	16.9	75	110	0	63
40	26.4	83	134	0	51
45	38.2	89	190	0	50

Variable N_2H_5Cl Data

$[N_2H_5Cl]_o$x10^3 /mol dm^{-3}	k_1x10^4 /s^{-1}	k_2 /s^{-1}	k_3x10^{-3} /s^{-1}	k_4 /s^{-1}	k_3/k_1
6.3	3.18	4.30	47	0	148
9.5	3.85	40.0	11	0	28
16	9.07	9.80	28	0	30
24	10.4	42.0	28	0	26
32	13.7	74.0	50	0	36
47	20.4	149	70	0	34
57	28.7	346	120	0	41
63	31.3	436	100	0	32

Table 4-9 Computer Numerical integration data from variable N_2H_5Cl and temperture runs.

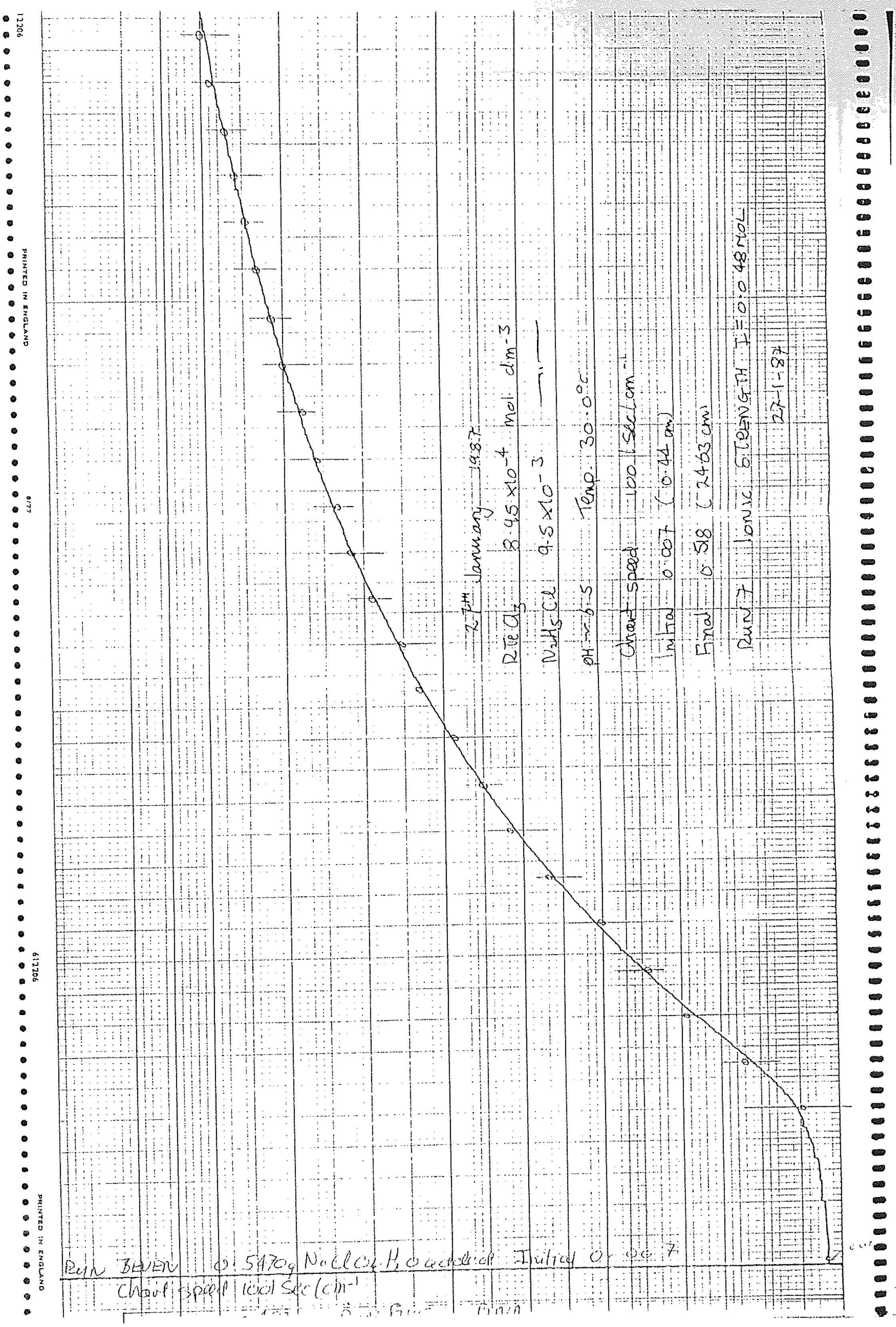


Fig 4-1 Reaction profile of absorbance against time for reaction of $N_2H_5^+$ with p-EtOPhTeCl$_3$.

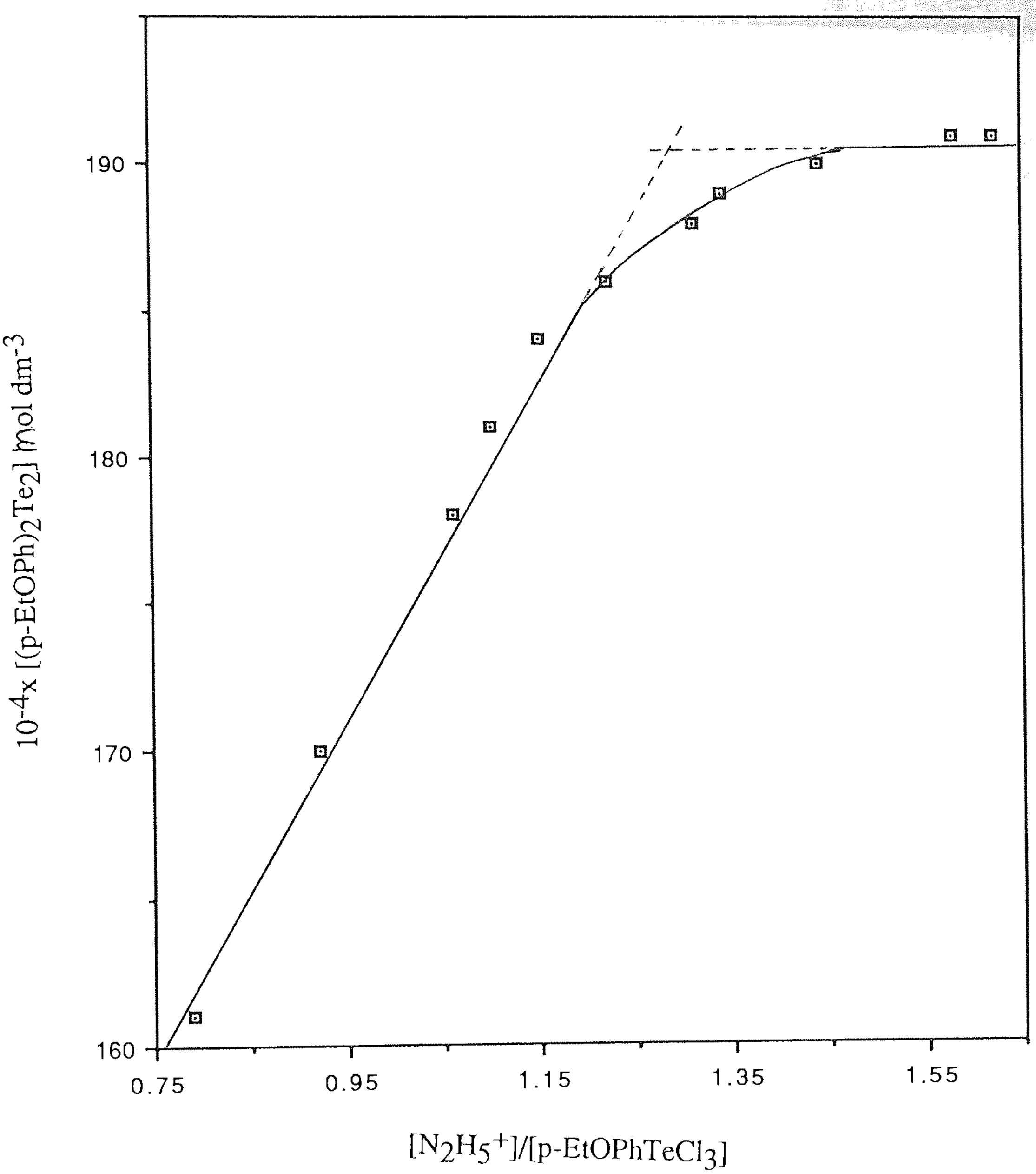


Fig 4-2 Plot of molar (p-EtOPh)$_2$Te$_2$ produced in aqueous THF versus the molar ratio of $N_2H_5^+$/p-EtOPhTeCl$_3$ at 25°C.

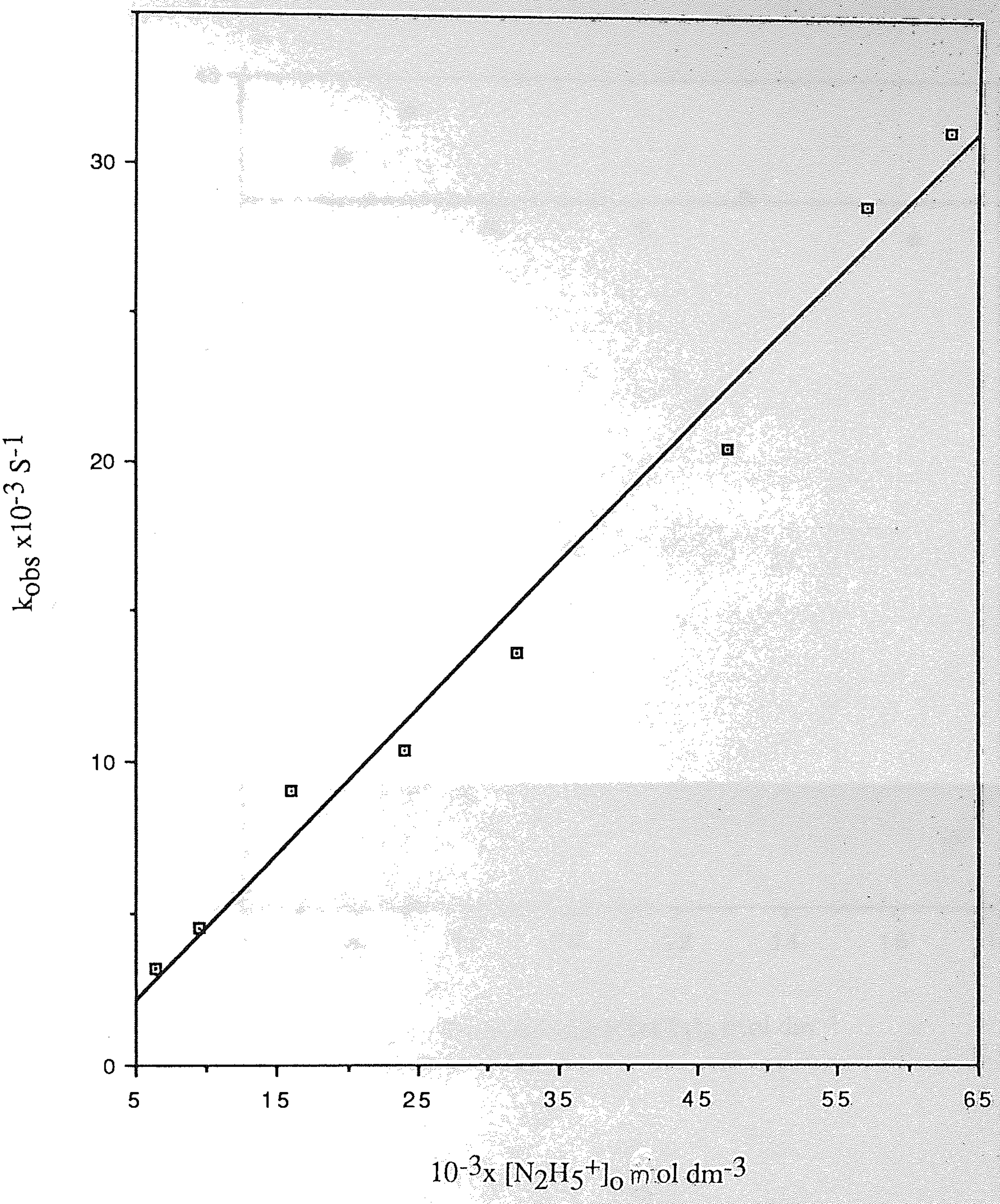


Fig 4-3 Plot of k_{obs} versus initial $N_2H_5^+$ concentration for reaction with p-EtOPhTeCl_3 at 30°C in aqueous THF.

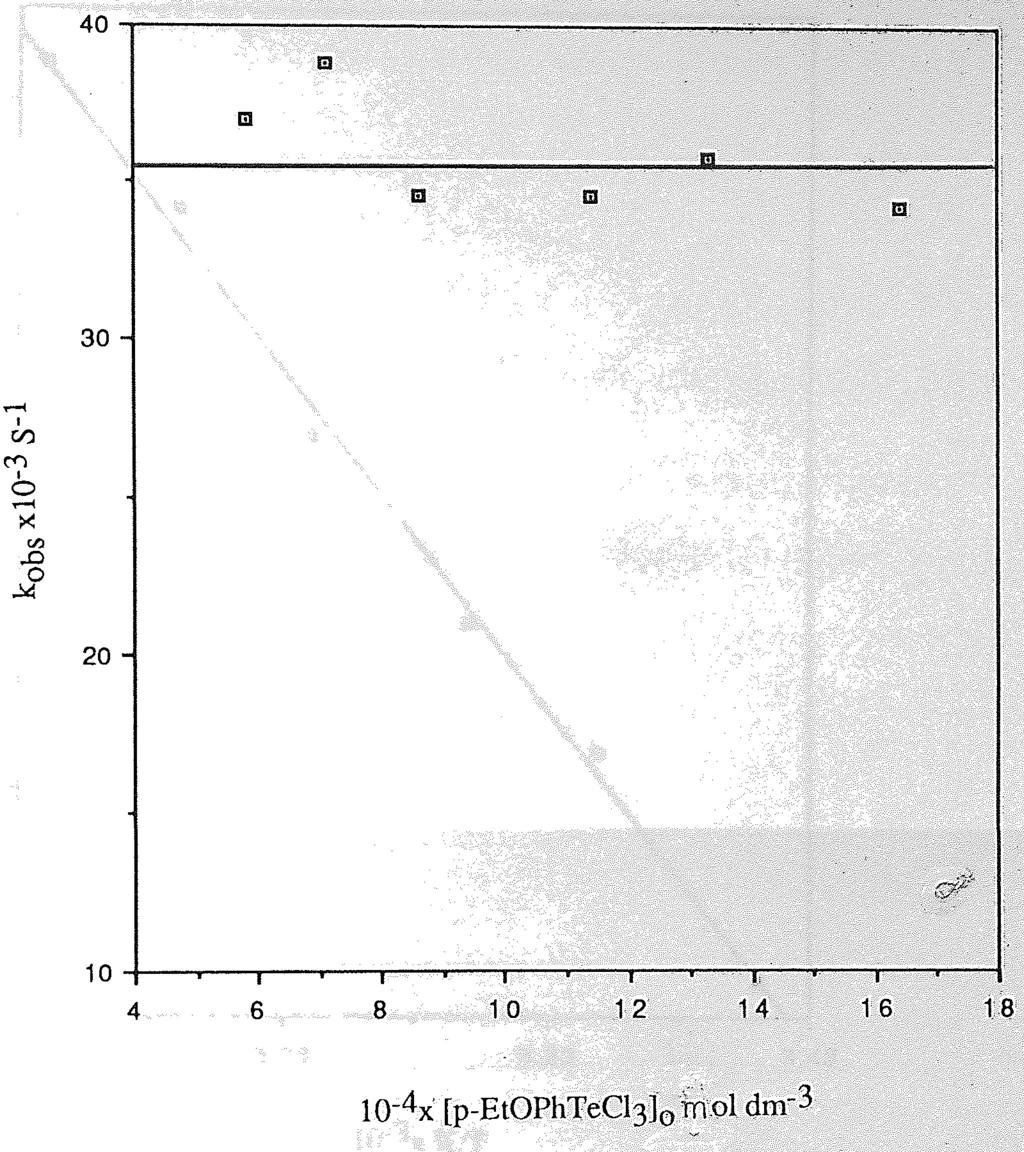


Fig 4-4 Plot of k_{obs} versus initial p-EtOPhTeCl$_3$ concentration for reaction with $N_2H_5^+$ at 25°C in aqueous THF.

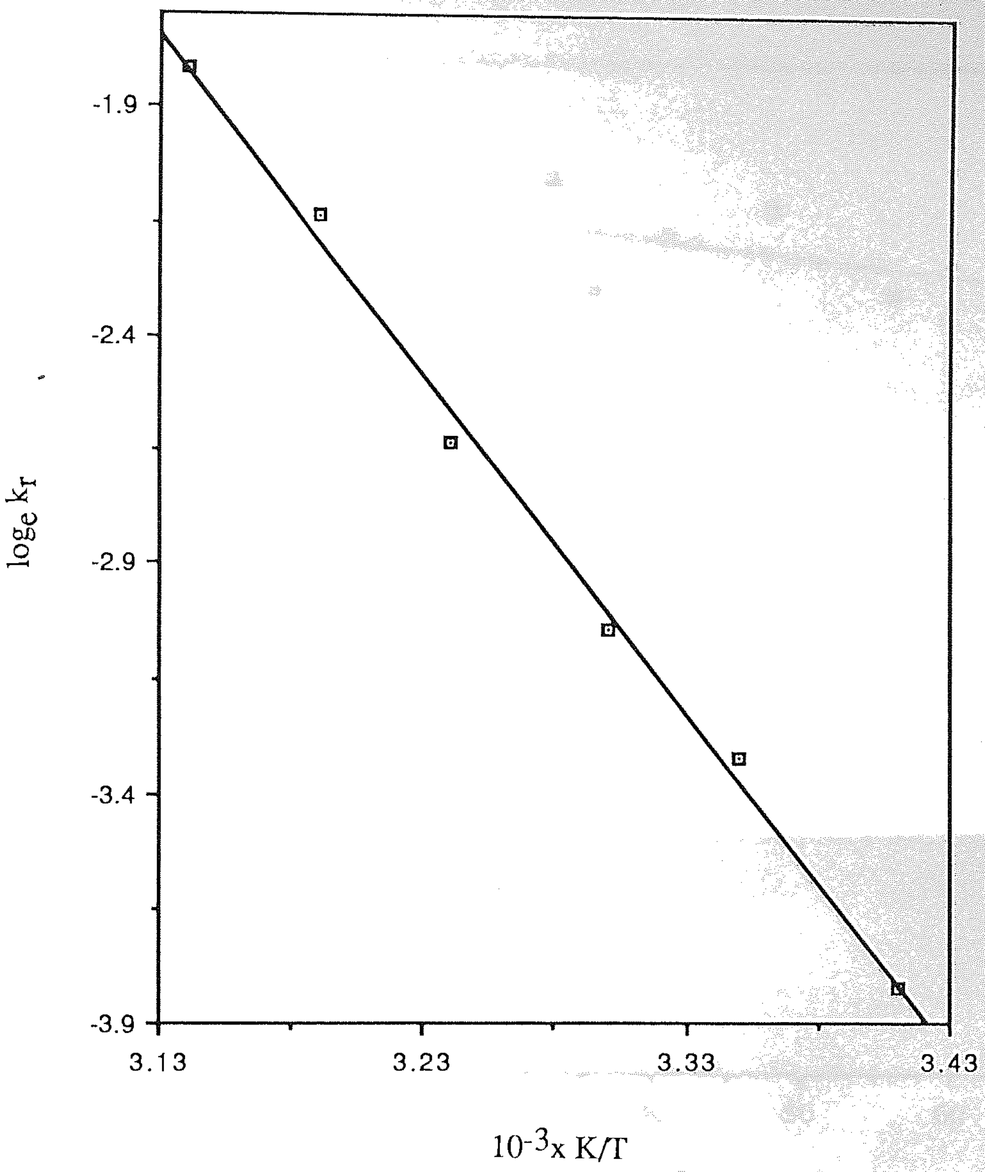


Fig 4-5 Plot of $\log_e k_r$ versus K/T for the reaction of p-EtOPhTeCl_3 with $N_2H_5^+$ in aqueous THF.

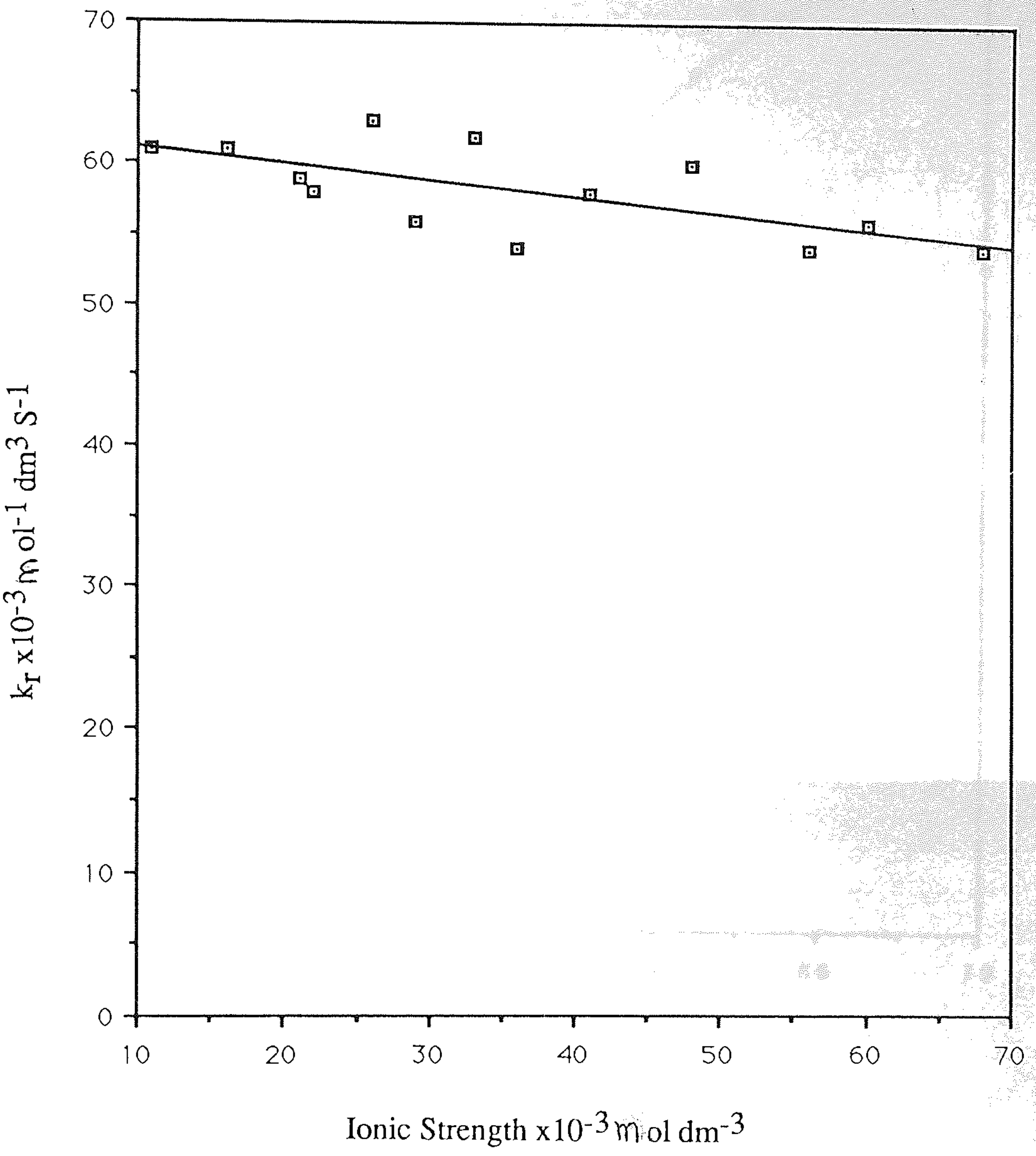


Fig 4-6 Plot of k_r versus ionic strength of reaction solution for reaction of p-EtOPhTeCl$_3$ with $N_2H_5^+$ at 30°C in aqueous THF.

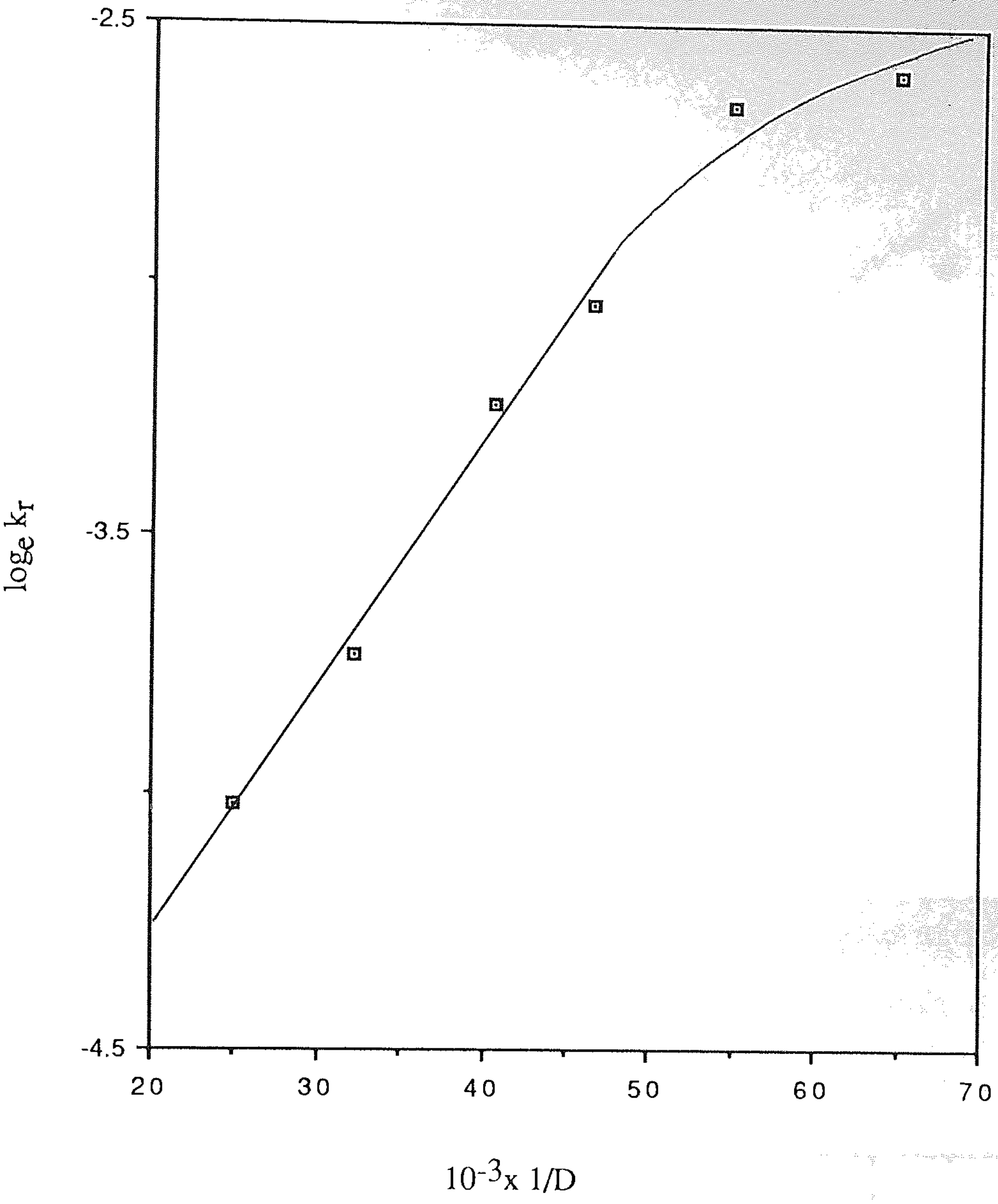


Fig 4-7 Plot of $\log_e k_r$ versus 1/D for reaction of p-$EtOPhTeCl_3$ with $N_2H_5^+$ at 30°C.

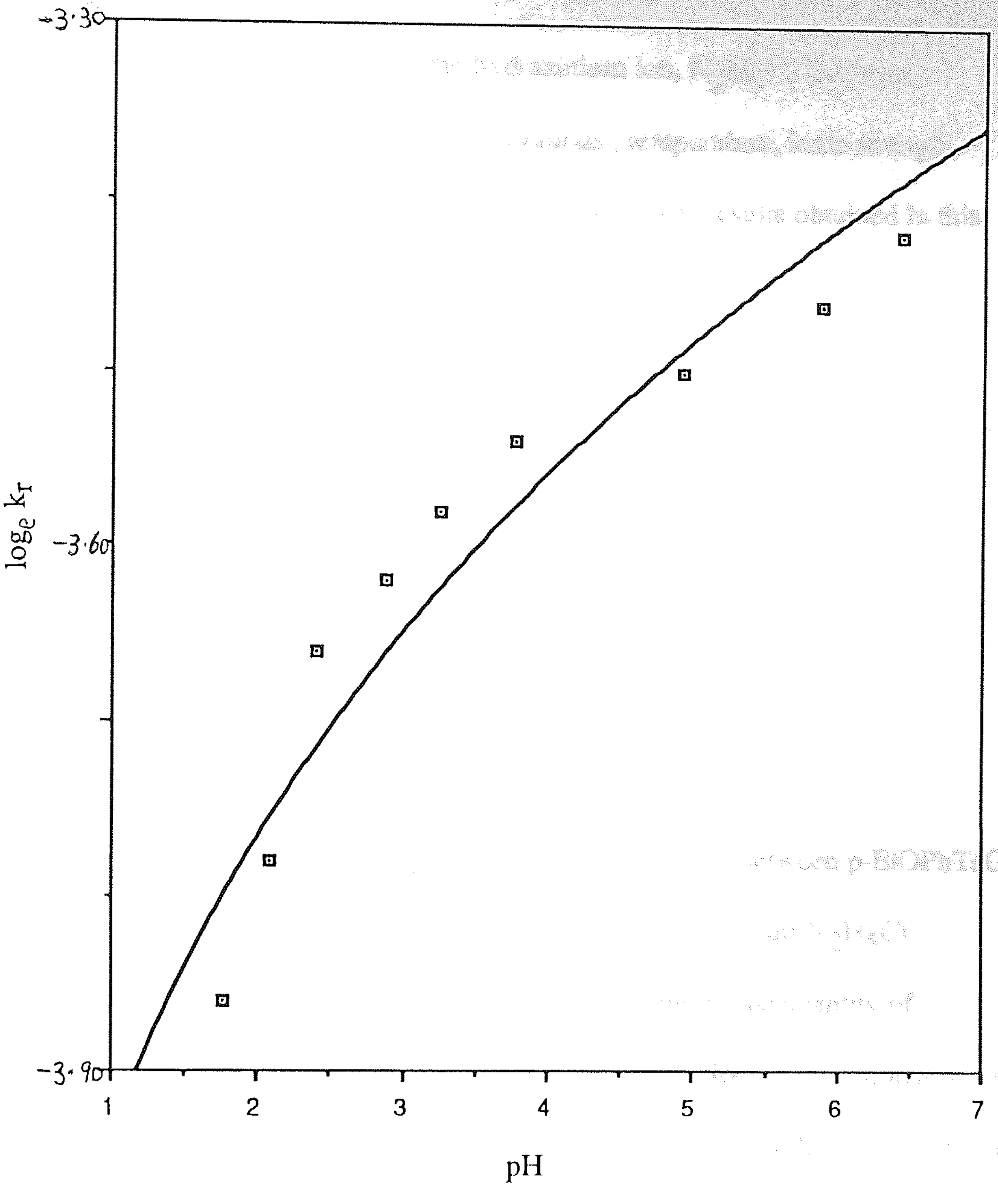


Fig 4-8 Plot of $\log_e k_r$ versus pH for the reaction of p-EtOPhTeCl$_3$ with $N_2H_5^+$ at 30°C and ionic strength of 0.1 mol dm^{-3} in aqueous THF.

4-3 DISCUSSION

The reduction of p-EtOPhTeCl_3 by the hydrazinium ion, $N_2H_5^+$, has been investigated over a range of reagent concentrations , temperature, ionic strength, solvent composition and hydrogen ion concentrations. The results obtained in this study are reproducible .

No absorbance at the monitored wavelength was observed for solutions of hydrazinium chloride in aqueous THF and aryltelluriumtrichloride in THF. Therefore the kinetic studies were carried out by monitoring the increase in the absorbance of the reaction mixture at 400nm, where the product shows a maximum absorbance as explained in section 3-2 .

Stoichiometric measurements were carried out for the reaction between p-EtOPhTeCl_3 and N_2H_5Cl. The stoichiometry was determined by using constant N_2H_5Cl concentrations and varying the p-EtOPhTeCl_3 concentration. The quantity of ditelluride produced was determined from its absorbance at 400nm. The stoichiometric measurements data, table 4-1, show 3 moles of N_2H_5Cl are equivalent to 4 moles of p-EtOPhTeCl_3 . Tests, using Nessler's reagent, indicate that there is no formation of ammonia, which is to be expected from the overall stoichiometry of the reaction .

The measurements indicate that the following overall electron transfer reactions occur quantitatively

$$2\,\mathrm{Te(IV)} + 6e^- \longrightarrow (\mathrm{Te^I})_2$$

$$3\,N_2H_5^+ \longrightarrow 3N_2 + 12\,e^- + 15H^+$$

In more detail the reaction of $N_2H_5^+$ and p–EtOPhTeCl_3 can be written as

$$4\text{p-EtOPhTeCl}_3 + 3N_2H_5^{+} \longrightarrow 2(\text{p-EtOPhTe})_2Te_2 + 12Cl^{-} + 3N_2 + 15H^{+}$$

from the above equation it appears that the reaction proceeds primarily via a preferred sequence of two-electron stages. Otherwise if $N_2H_5^+$ reacts one electron at a time with the tellurium species, the formation of $N_2H_3^+$ radicals would result in the formation of ammonia .

Further studies were carried out in an attempt to verify the stoichiometric measurements. Experiments in which the volumetric titration of excess hydrazine was attempted were unsuccessful. This can be attributed to the small change in hydrazine concentration to be detected. This is inevitable with the hydrazine in a large excess over p-$EtOPhTeCl_3$, leading to large errors (±30%) .

The kinetic studies were carried out by mixing equal volumes of p-$EtOPhTeCl_3$ in THF and N_2H_5Cl in aqueous THF (usually 1:1 by volume) and following the increase in the absorbance with time at 400nm .

The absorbance-time curve had two features. Firstly a short induction period followed by an increase in the absorbance with time as shown fig(4-1). The period after the induction period could be fitted , from 20% to 90% completion of the reaction, to an integrated form of a first order rate equation

Viz:

$$\log_e[A_t - A_{oo}] = k_{obs}\, t + \text{Constant}$$

Where A=absorbance at time t and infinity as indicated by the subscript.

Thus a plot of $\log_e[A_t - A_{oo}]$ versus time was used to provide the individual rate constants for each kinetic experiment.

The conditions in the kinetic experiments involved the use of a large excess of hydrazinium chloride and thus the observed rate constant depends upon the hydrazinium ion concentration. Variation in the aryltelluriumtrichloride concentration produced no change in the observed rate constant (table 4-3 and fig 4-4) , confirming that the order in p-EtOPhTeCl_3 is unity as the form of the rate equation requires .

The data from the pseudo first order rate equation refers to the latter part of the absorbance-time curve trace , ie after the induction period. Characterisation of the trace from time=0 was undertaken by numerical integration and is discussed later.

The data in table 4-2 shows that the rate constant varies with the initial $N_2H_5^+$ concentration. The data is displayed graphically in fig 4-3 . The linear plot passes through the origin which indicates that the observed rate constant is directly proportional to the first power in the initial hydrazinium ion concentration .

The second order rate constant, k_r , derived from table 4-2, is 0.0484mol^{-1} dm^3 s^{-1} at 30^{o}C in agreement with that obtained from the slope of fig 4-2 . The rate constant, k_r, from the variable p-EtOPhTeCl_3 experiments, at the lower temperature of 25^{o}C , was found to be 0.0358 $mol^{-1}dm^3$ s^{-1} . The data used to obtain the activation energy, see table 4-4 , show that the two values are compatible when adjusted to the same temperature .

In the case where the rate was measured as a function of the temperature, a straight line Arrhenius plot was obtained, as shown in fig 4-5 . The activation parameters for the reaction of $N_2H_5^+$ with p-EtOPhTeCl$_3$ are

$$k_r = 0.0358 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ at } 25^{\circ}\text{C}$$

$$0.0484 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1} \text{ at } 30^{\circ}\text{C}$$

$$\Delta E^* = 61.2 \pm 1.9 \text{ kJ mol}^{-1}$$

$$\Delta H^* = 58.7 \pm 1.9 \text{ kJ mol}^{-1}$$

$$\Delta S^* = -76 \pm 5 \text{ J mol}^{-1} \text{ K}^{-1}$$

The effect of the addition of an "inert electrolyte" on the rate of reaction of p-EtOPhTeCl$_3$ with N_2H_5Cl was investigated using sodium perchlorate as the additive. The calculation of the ionic strength was made on the basis that the ions Na^+, $N_2H_5^+$, Cl^- and ClO_4^- are present. p-EtOPhTeCl$_3$ hydrolyses when in contact with water, but since a large excess of hydrazinium chloride was used, the presence of ions derived from the trichloride can be neglected. Also no reliable measurements are possible to allow the direct estimate of the concentration of the hydrolysed tellurium intermediate .

I found that a large change in the ionic strength gave only a small decrease, 12%, in the rate constant (k_r). The small decrease in the rate can be attributed to a change in the pH of the reaction solution, since a large amount of inert salt was used throughout. This is most reasonably interpreted as proof that at least one of the reagents is uncharged .

The variation of the rate on the dielectric constant of the solvent medium was investigated . A solution of p-EtOPhTeCl$_3$ in pure THF gives a very pale yellow colour , which completely disappears upon mixing with an aqueous THF solution of N_2H_5Cl . The hydrolysis of the trichloride becomes slower as the water content of the final mixed solvent decreases . However , I was unable to go above THF percentages of 85% due to the immiscibility of the solutions of N_2H_5Cl and p-EtOPhTeCl$_3$. The induction period throughout decreased with increasing THF percentages, indicating that the hydrolysis of the trichloride is rapid down to a 15% water content. The reaction increases with the decreasing dielectric medium (increasing THF percentages), which again shows that we are dealing with a charged ion and a molecule.

The question now arises as to what the charged reagent is . There are two obvious possibilities, either the hydrazinium ion, $N_2H_5^+$, or the aryltellurate ion , p-EtOPhTeO$_2^-$.

The pK$_a$ of the equilibrium

$$\text{p-EtOPhTeO}_2^- + H^+ \rightleftharpoons \text{p-EtOPhTe(O)OH}$$

was suggested to be in the order of 3 from the reduction[16] of p-EtOPhTeCl$_3$ by sulphite.

Now hydrolysis of the trichloride by water

$$\text{p-EtOPhTeCl}_3 + 2H_2O + H^+ \longrightarrow \text{p-EtOPhTe(O)OH} + 3Cl^- + 4H^+$$

is autocatalytic ie more acid is produced . At the concentration of p-EtOPhTeCl$_3$ used, the pH after mixing the two reagents together would appear to be approximately 3 . If that is so then the aryltellurate would be predominantly in the form of the tellurinic acid, p-EtOPhTe(O)OH .

By contrast, the dissociation constant[96] for

$$N_2H_5^+ \rightleftharpoons N_2H_4 + H^+$$

has been reported as 1.02×10^{-8} at 25°C in water. Unless it changes markedly in the mixed solvent I have used, essentially all the hydrazine will in the form of the hydrazinium ion, $N_2H_5^+$, in the kinetic experiments undertaken . Thus one can argue that the reagents in the rate determining step are $N_2H_5^+$ and p-EtOPhTe(O)OH .

The reaction was also studied at different hydrogen ion concentration, the data are listed in table 4-8. The plot of log k_r against pH , fig 4-8, appears to be linear down to pH = 2.5 where there is a curvature. The overall change in the rate constant , k_r, over the pH range studied is approximately 30%, that is from 0.032 at pH=6.44 to 0.021mol^{-1} dm^3 s^{-1} at pH=1.74. The effect of the added acid could be due to either of two possible equilibria. The tellurium species, the tellurinic acid , could be protonated to give a cationic species

$$\text{p-EtOPhTe(O)OH} + H^+ \rightleftharpoons [\text{p-EtOPhTe(O)OH(H)}]^+$$

with the hydrogen ion attached either to the oxygen or the tellurium atom viz:

$$[\text{p-EtOPhTe(OH)}_2\,]^+ \quad \text{or} \quad [\text{p-EtOPhTe(O)OH(H)}]^+$$

Both tellurium and oxygen have spare electron pairs available but it is not possible to distinguish between these two possible modes of protonation.

The second possibility is further protonation of the hydrazinium ion

$$N_2H_5^+ + H^+ \rightleftharpoons N_2H_6^{2+} \qquad \text{--- (4-17)}$$

The second nitrogen on hydrazine is more difficult to protonate than the first as seen from the pK_2 of protonation of the second nitrogen , $pK_2 = 15.05$. Only strong acids such as perchloric acid are able to protonate the hydrazinium ion and in concentrated aqueous solutions ie $pH < 1$.

Upon addition of $1cm^3$ of concentrated perchloric acid, I observed a considerable induction period, which I attribute to protonation of the tellurium species .
Thus the hydrogen ion concentration data can be attributed to protonation of the tellurium species. The net result may be related to electrostatic force which exists between approaching ions of similarly charge . The deviation at very low pH can be attributed to further protonation of the hydrazinium ion .

In an attempt to check that p-EtOPhTe(O)OH is the tellurium species being reduced, I carried out some additional experiments. After water ($1cm^3$) has been added to a solution of $p\text{-EtOPhTeCl}_3$ in THF($50cm^3$) 30 minutes prior to reduction, the induction period disappears. Tahir suggested that hydrolysis of the aryltelluriumtrichloride is complete prior to reduction in such a case . The effect of adding concentrated acid has been discussed with the pH runs and was attributed to protonation of the tellurium species .

However, when I mixed a benzene solution of hydrazine and $p\text{-EtOPhTeCl}_3$, a rapid appearance of a red colour was observed. The red colour was due to the ditelluride and the implication is that the trichloride can be reduced by neutral hydrazine. The fact the induction period is not observed after water is added indicates that the hydrolysis product rather than the trichloride is reduced .

Up to this point in the text the results obtained from the pseudo first order rate data refer to kinetic data after the induction period is over. Now I turn to a different and more thorough treatment of the experiment data. A numerical integration based on the scheme below, was carried out.

(R = p-EtOPh)

$$RTe(O)OH + N_2H_5^+ \xrightarrow{k_A} RTeOH + N_2H_3^+ + H_2O \quad \text{--- (4-31)}$$

$$2RTeOH + N_2H_5^+ \xrightarrow{k_B} R_2Te_2 + N_2H_3^+ + 2H_2O \quad \text{---(4-32)}$$

$$RTe(O)OH + N_2H_3^+ \xrightarrow{k_C} RTeOH + N_2 + H_2O + H^+ \quad \text{---(4-33)}$$

$$\text{either } 2RTeOH + N_2H_3^+ \xrightarrow{k_{D(a)}} R_2Te_2 + N_2 + 2H_2O + H^+ \quad \text{--- (4-34)}$$

$$\text{or } RTe(O)OH + RTeOH + N_2H_5^+ \xrightarrow{k_{D(b)}} R_2Te_2 + N_2 + 3H_2O + H^+ \quad \text{--- (4-35)}$$

The term $k_A[N_2H_5^+]$ (equation 4-31 in the above scheme) was found to equate to the pseudo first order rate constants listed in tables 4-2 and 4-4. Good fits to experimental data, from mixing onwards, were obtained when $k_{D(a)}$ or $k_{D(b)}$ was small ie effectively zero. If this model is correct, then the first step has the smallest rate constant (k_A) and is rate determining.

On the basis of the effect of pre-mixing the trichloride with water, I have already suggested that the hydrolysed tellurium(IV) species is the species being reduced in the slow step. Thus the trichloride is hydrolysed first to tellurinic acid, then reduced by the hydrazinium ion after the formation of a 1:1 complex between $N_2H_5^+$ and p-EtOPhTe(O)OH which then decomposes in a rate determining step to give the initial products, (R = p-EtOPh)

Viz:

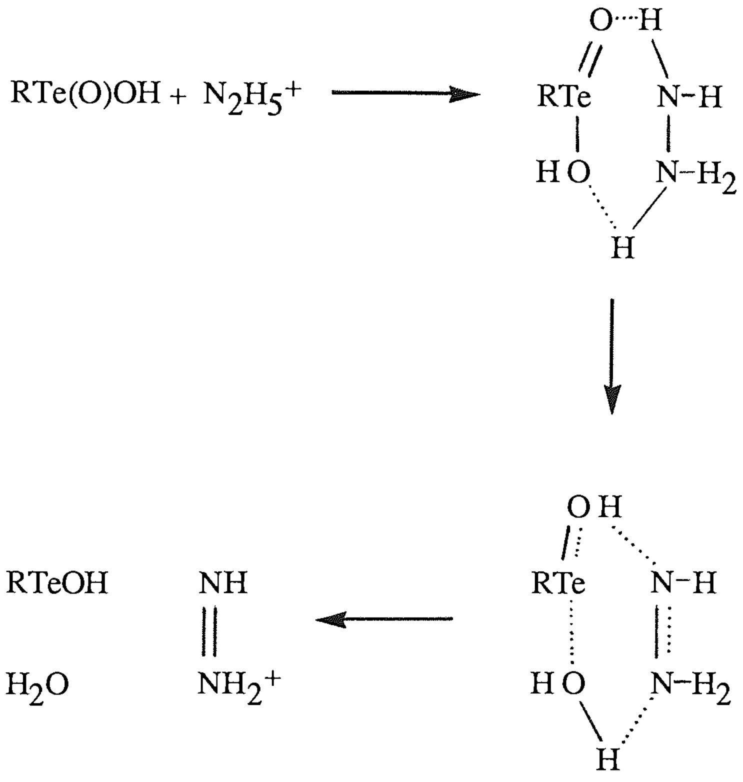
$$RTeCl_3 + 2H_2O + H^+ \xrightarrow{\text{Rapid}} RTe(O)OH + 3Cl^- + 4H^+ \qquad \text{--- (4-36)}$$

$$RTe(O)OH + N_2H_5^+ \underset{\text{FAST}}{\overset{K_1}{\rightleftharpoons}} \underset{\text{1:1 complex}}{[RTe(O)OH.N_2H_5]^+} \qquad \text{--- (4-37)}$$

$$[RTe(O)OH.N_2H_5]^+ \xrightarrow[\text{slow}]{k_2} RTeOH + N_2H_3^+ + H_2O \qquad \text{--- (4-38)}$$

where $N_2H_3^+$ is the protonated form of diimine . Decomposition of the intermediate complex is rate determining in the above scheme. Decomposition to give the products, RTeOH, $N_2H_3^+$ and H_2O, would involve hydrogen transfer as shown below

(R = p-EtOPh)



This involves bond breaking and formation simultaneously with considerable atomic movement, whereas formation of the precursor complex would be straight forward formation of a donor-acceptor complex .

This would also explain why the rate increases with increasing pH, as protonation of the tellurium(IV) species gives rise to two species of similar charge in the rate determining step.

The initial product is RTeOH. This species has been suggested as an intermediate with a short lifetime in the oxidation of the same ditelluride by H_2O_2 and in the reduction of p-EtOPhTeCl_3 by sulphite[16] .

Diimine is the initial nitrogen-containing product, written in the protonated form, $N_2H_3^+$, and has not been isolated , except as diazene complexes such as

$\{N_2H_2[Cr(CO)_5]\}$

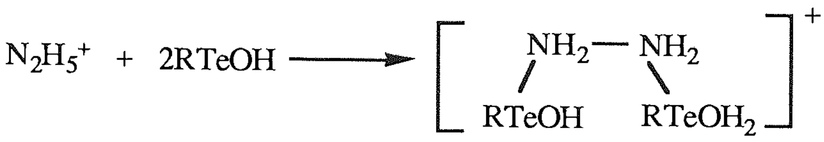
and $\{ m\text{-}N_2H_2[Mo(CO)_5]\}$

which are short lived .

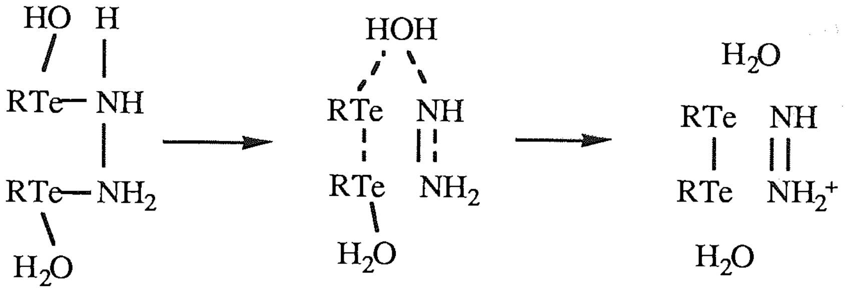
The diimine formed here is likely to be in low concentration relative to $N_2H_5^+$, and thus its reaction with another low concentration intermediate, RTeOH, is insignificant. Hence the $k_{D(a)}$ term can be ignored. Thus it would appear that essentially all $N_2H_3^+$ formed will react by reducing more tellurium(IV) to tellurium(II) .

This work was carried out in an attempt to gain more information on the final stage tellurium(II) to tellurium(I) in the ditelluride. Tahir had earlier suggested that a dimer was formed prior to reduction to give the tellurium(I) species in the sulphite reduction of p-EtOPhTeCl_3 .

This works seems to confirm that no one electron reduction occurs, as no ammonia is formed. Since diimine has been eliminated from the reduction of Te(II) to Te(I)$_2$, it would seem most probable that the hydrazinium ion coordinates with two tellurium(II) species to give a transition state such as :



The formation of a tellurium-tellurium bond takes place after reduction and also involves hydrogen transfer as shown below :



In the Vanadium(V) reduction to V(IV) by $N_2H_5^+$, it was suggested that the hydrazine was coordinated to two V(V) species . Thus there is a precedent for my hypothesis .[101]

This leads to a net reaction of

$$2\ RTeOH + N_2H_5^+ \longrightarrow R_2Te_2 + N_2H_3^+ + 2H_2O \qquad \text{--- (4-39)}$$

An alternative which I cannot disprove, but is less likely, is that RTeOH could react with $N_2H_5^+$ to produce RTeH, the latter being attacked by RTeOH to produce R_2Te_2

Viz:

$$\mathrm{RTeOH} + \mathrm{N_2H_5^+} \longrightarrow \mathrm{RTeH} + \mathrm{N_2H_3^+} + \mathrm{H_2O} \qquad \text{--- (4-40)}$$

$$\mathrm{RTeH} + \mathrm{RTeOH} \longrightarrow \mathrm{R_2Te_2} + \mathrm{H_2O} \qquad \text{--- (4-41)}$$

Organyltellurols are often postulated as reaction intermediates and have been recently isolated under oxygen-free atmospheres.However tellurols are quite acidic and easily oxidised by mild oxidizing agents. My kinetic experiments were carried out under aerial atmosphere so that any tellurol formed might be expected to be oxidised under the conditions of the experiment . Although the results from the kinetic data described do not enable us to decide which of the two above paths is the final reaction pathway, I believe that formation of the two-coordinated tellurium species with $N_2H_5^+$ occurs. If the tellurol were formed, then it would have to react with RTeOH quantitatively . Since RTeOH is in low concentration it seems more likely that at least some of the tellurol will be oxidised by oxygen leading to a variable reaction stoichiometry which is not observed .

Another possible step, $k_{D(b)}$, was eliminated . This involves two tellurium species RTeOH and RTe(O)OH coordinating to $N_2H_5^+$ followed by reduction . The numerical integration only fits the kinetic data well when the $k_{D(b)}$ term is very small indicating that $k_{D(b)}$ is insignificant .

The reaction scheme can be presented as follows where R=p-EtOPh

R.D.S = Rate Determining Step

$$RTeCl_3 + 2H_2O + H^+ \xrightarrow{\text{FAST}} RTe(O)OH + 4H^+ + 3Cl^- \qquad \text{---(4-36)}$$

$$RTe(O)OH + N_2H_5^+ \underset{\text{FAST}}{\overset{K_1}{\rightleftharpoons}} [RTe(O)OH.N_2H_5]^+ \qquad \text{---(4-37)}$$

$$[RTe(O)OH.N_2H_5]^+ \xrightarrow[\text{R.D.S}]{\text{slow}} RTeOH + N_2H_3^+ + H_2O \qquad \text{---(4-38)}$$

$$N_2H_5^+ + 2RTeOH \rightleftharpoons \{ N_2H_5[RTeOH]_2 \}^+ \qquad \text{--- (4-42)}$$

$$\{N_2H_5\ [RTeOH]_2\}^+ \longrightarrow R_2Te_2 + N_2H_3^+ + 2H_2O \qquad \text{---(4-43)}$$

$$N_2H_3^+ + RTe(O)OH \rightleftharpoons [RTe(O)OH.N_2H_3]^+ \qquad \text{---(4-44)}$$

$$[RTe(O)OH.N_2H_3]^+ \longrightarrow RTeOH + N_2 + H_2O + H^+ \qquad \text{---(4-45)}$$

The results of the redox steps presented here involve pre-equilibria , equations 4-37, 4-42, 4-44, prior to electron transfer and decomposition of the successor complex, equations 4-38, 4-43, 4-45.

The work from this investigation shows that no one electron change occurs. This clearly implies that reduction of tellurium(II) to tellurium(I) goes via an intermediate containing two tellurium(II) species co-ordinated to the the hydrazine.

The electron transfer process must be inner-sphere in nature since a two electron equivalent is occurring, whereas an outer-sphere mechanism would require a one-electron equivalent reaction . Thus this work indicates that the tellurium in p-EtOPhTeCl$_3$ prefers an inner-sphere redox reaction, and the final stage is a two electron equivalent reaction .

CHAPTER FIVE

SOLVOLYSIS OF para-ETHOXYPHENYL TELLURIUM TRICHLORIDE IN NON-AQUEOUS MEDIA

5-1 INTRODUCTION

In this chapter I describe the solvolysis of aryltellurium trihalides in non-aqueous media. The solovolysis was studied under different conditions of solvent composition, temperature, p-EtOPhTeX_3 (X=Cl, Br, I), acid and salt concentrations.

The work was prompted during the study by Tahir of the reduction of the aryltellurium trichlorides to the corresponding diaryl ditelluride[16]. He found that the hydrolysis of the aryltellurium trichloride to give the aryltellurate ($RTeO_2^-$) was the initial step, preceding reduction. When the water content of the mixed solvent is low this hydrolytic step becomes rate determining. Thus, since the pathway of the reduction of aryltellurium trihalides to diaryl ditellurides starts with the hydrolysis of the trihalides, the aim of this chapter is to gain a better understanding of that early stage of the mechanism of the reduction.

Tahir[12] undertook a preliminary investigation of the solvolysis of p-EtOPhTeX_3 using mixtures of methanol/benzene and methanol/1,4-dioxane as the non-aqueous solvent. He suggested that the reaction is a reversible acid catalysed reaction which was agreed to be associative. Methanol was used as the active solvolytic component in the binary solvent mixture. That choice was made because of its miscibility with benzene and because it retains some close structural and chemical similarities to water. Two other features helped to make it an appropriate choice. Firstly, the rate of methanolysis in non-aqueous media is slower than that of hydrolysis in aqueous media. Secondly, both p-EtOPhTeCl_3 and its solvolysis products are more soluble in non-aqueous media than in aqueous media.

Several investigations have been made of the hydrolysis of aryltellurium trihalides in moist air, neutral, acidic and basic aqueous media[6, 10, 51]. A mechanism of the hydrolysis of aryltellurium trihalides with water under different conditions has been suggested[51]. The argument is based solely upon the structure of the isolated product of the hydrolysis, and is therefore not reliable. It was considered that the first stage involves the formation of a monomeric species, compound (A), arising from nucleophilic attack of water on the tellurium atom in $RTeCl_3$, and the resultant breaking of the halogen bridge bonds. R = p-EtOPh

$$\begin{tikzcd}
RTeX_3 \arrow[r, "H_2O"] & \underset{A}{[RTeX_3.H_2O]} \arrow[r, "-HCl"] & \underset{B}{[RTeX_2(OH)]} \arrow[d] \\
& RTe(O)X & \underset{C}{[(RTeX_2)_2O]} \arrow[l, "H_2O/-HX"']
\end{tikzcd}$$

---(5-1)

Attempts to isolate the compounds corresponding to B and C failed. Only mixtures of $RTeX_3$ and RTe(O)X could be obtained even though samples were taken at various reaction times and under a range of conditions. Thus, if stages (B) and (C) are involved, the intermediates must be short lived.

The hydrolysis of $RTeX_3$ under alkaline conditions leads to the formation of RTe(O)OH and $(RTeO)_2O$. However, earlier workers treated the alkaline hydrolysis products with dilute acid prior to analysis. It is generally accepted that the anhydride is the correct formulation for the product and that RTe(O)OH is the hydrolysis product[51]. The reactions are suggested to follow a similar pattern to that of acid hydrolysis. R = p-EtOPh

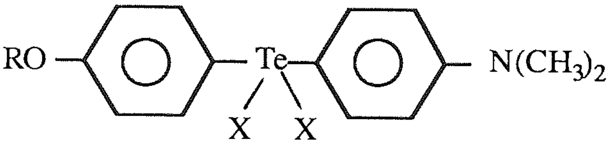
$$\mathrm{RTeX_3} \xrightarrow[\mathrm{H_2O}]{\mathrm{OH^-}} \mathrm{RTe(OH)_3} \xrightarrow{\mathrm{H_2O}} \mathrm{RTe(O)OH}$$

$$\mathrm{RTe(O)OH} \xrightarrow{\mathrm{H^+}} \mathrm{[(RTeO)_2O]} + \mathrm{H_2O} \qquad \text{---(5-2)}$$

The products of hydrolysis depend on the conditions employed. Thus, hydrolysis in acid media yields RTe(O)X, whereas in alkaline media the hydrolysis product is mainly RTe(O)OH or $(RTeO)_2O$.

The difference in the behaviour of $RTeCl_3$ (R = aryl) in acidic and basic media may be attributed to its donor and acceptor properties[106]. In the solid state $RTeX_3$ molecules are known to have one Te-X bond longer than the other two Te-X bonds[30,31]. The presence of a Lewis acid in the medium might then induce an increase in the electron density at the X atom of the longer Te-X bond by interacting with that atom. Such an interaction would weaken the Te-X bond further and increase its tendency to cleave. In the presence of a Lewis base, the tellurium atom has the ability to accept a pair of electrons into one of its vacant orbitals and therefore behave as a Lewis acid. Thus the hydrolysis of aryltellurium trihalides may be ascribed to the increase in the polarity of a Te-X bond in the presence of a lewis acid or the ability of the tellurium atom to accept and share a pair of oxygen electrons into a vacant orbital. Thus there are easy hydrolysis routes under both sets of conditions, although they may be routes with different mechanisms.

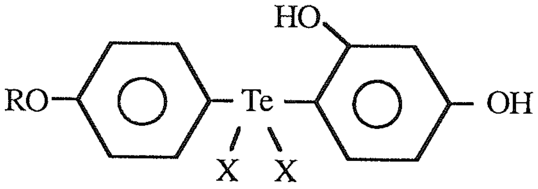
It was reported by Petragnani[107] that only one of the halide atoms of an aryltellurium trihalide is replaced when it undergoes condensation reactions with acetone (E), acetophenone (G), N-dimethylaniline (D), or resorcinol (F) to produce diorganyl tellurium dihalides, Ar = ROC_6H_4, where R = CH_3, C_2H_5, C_6H_5.



D

$ArTeX_2(CH_2COCH_3)$

E



F

$ArTeX_2(CH_2COC_6H_5)$

G

However, the triiodides are unreactive, and with the tribromides no reaction was observed with acetone or acetophenone. Petragnani suggested the easy solvolysis of $RTeCl_3$ as compared with that of the tribromides and triiodides was due to a decrease in the electrophilic character of the positive fragment $RTeX_2^+$ on passing from X=Cl to X=I. However, Raina and Khandelwal[32] reported conductance and molecular weight studies on p-EtOPhTeCl_3 and p-MeOPhTeCl_3 in organic solvents. They concluded that they are present in their molecular form in organic solvents such as benzene, CCl_4, $CHCl_3$ and 1,4-dioxane.

Hydrolysis of arylselenium trihalides using water[68], aqueous alkaline[108-111] and silver hydroxide[112], gives the arylseleninic acids as the products. Foster[108] reported that arylselenium tribromides and trichlorides could be recovered unchanged from an aqueous solution of the trihalide. Both the chlorine and bromine from the trihalides could be precipitated by the addition silver nitrate. Foster suggested that the tribromides and trichlorides do not hydrolyse since the expected product phenyl seleninic acid was not observed. However, the trihalide could be prepared from the arylseleninic acid in an aqueous solution containing HCl.

$$\mathrm{PhSe(O)OH} + 3\mathrm{HCl} \longrightarrow \mathrm{PhSeCl_3} + 2\mathrm{H_2O} \qquad \text{---(5-3)}$$

Thus indicating that if hydrolysis does occur, it must be reversible.

5.1.1 Mechanistic Aspects of Ligand Substitution Reactions

In the replacement of ligands, three distinct mechanistic types can be discussed according to the classification proposed by Langford and Gray[113].

1) The dissociative (D) mechanism: involving an intermediate of reduced coordination number

$$\mathrm{MX_6} \longrightarrow \mathrm{MX_5} + \mathrm{X} \xrightarrow{\mathrm{L}} \mathrm{MX_5L}$$

2) The associative (A) mechanism : in this extreme a fully formed intermediate complex of increased coordination number is formed, MX_6L, which then dissociates.

$$\mathrm{MX_6} + \mathrm{L} \longrightarrow \mathrm{MX_6L} \longrightarrow \mathrm{MX_5L} + \mathrm{X}$$

3) A concerted process, or interchange mechanism, involving the exchange of a ligand in the coordination sphere. The associative(A) and dissociative(D) mechanisms can be regarded as the extremes of the substitution process, while the interchange mechanisms involve different levels of interactions in the transition state. The associative interchange(I_a) mechanism can be considered to involve some degree of bonding between the entering and leaving groups which falls short of a fully formed intermediate, MX_6L. By contrast the dissociative interchange(I_d) involves different

degree of bond breaking in the transition state up to an intermediate ML_5 in the fully dissociative mechanism. At the mid-point of the range an I mechanism would occur.

The solvolysis reaction studied in this chapter was found to be both acid catalysed and an associative process. A review of the literature shows that associative acid catalysed solvolysis reactions are rare. One such example is the solvolysis of silanes by various alcohols which have have been reported to be both acid and base catalysed, and to be an associative process. Since the solvolysis of p-EtOPhTeCl$_3$ was found to be acid catalysed comparison with the silicon work will indicate features to look for. The base catalysed reaction is not relevant here. The acid and base catalysed cleavage of benzylosilanes in absolute ethanol containing chloroacetic acid and sodium ethoxide was reported by Boe[114]. The rate was found to be independent of the acid concentration at fixed buffer ratios and thus is an example of specific acid catalysis. The mechanism suggested involves a rapidly maintained pre-equilibrium followed by a rate determining attack by ethanol to form a pentacoordinate transition state which breaks down to yield the products.

$$\mathrm{R'_2R\text{-}Si\text{-}O\text{-}CH_2R'' + EtOH \longrightarrow R'_2R\text{-}Si\text{-}(OH)^+\text{-}CH_2R'' + EtO^-}$$

$$\mathrm{R'_2R\text{-}Si\text{-}(OH)^+\text{-}CH_2R'' + EtOH \longrightarrow R'_2R\text{-}Si\text{-}OEt + HOCH_2R''} \quad \text{---(5-4)}$$

R' = CH_3

R = XC_6H_4 where X = p-CH_3O, p-CH_3, m-CH_3, p-F, p-Cl, m-Cl

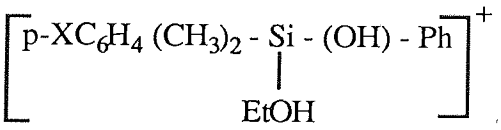
R" = C_6H_4Y where Y = p-CH_3O, p-CH_3, m-CH_3, p-Cl,m-Cl, p-NO_2

The proton was considered to be attached to the oxygen atom by analogy with the behaviour of alkoxysilanes in strongly acidic solutions. The activation parameters for the acid catalysed reaction given were found to be $\Delta H^* = 38$ kJ mol^{-1} and $\Delta S^* = -196$ J K^{-1} mol^{-1}. The entropy of activation I find for the solvolysis of p-$EtOPhTeCl_3$ is similar, at -222 J K^{-1} mol^{-1}, to that above.

The solvolysis of aryldimethylphenoxysilanes, $[(p\text{-}XC_6H_4)(CH_3)_2SiOPh)]$ in absolute ethanol indicated that an intermediate complex was formed[115]. The reaction was found to be first order with respect to the hydrogen ion concentration over the range studied, 3 x10^{-3} to 60 x10^{-3} mol dm^{-3} sulphuric acid. The author indicated that the rate of solvolysis was increased by electron-donation from substituents in the para position of aryl group, $-C_6H_4X$. It was considered that attack by ethanol on the protonated complex(H) to form a pentacoordinate complex(J) is rate determining.

$$EtOH_2^+ + (p\text{-}XC_6H_4)(CH_3)_2Si\text{-}O\text{-}Ph \longrightarrow EtOH + [(p\text{-}XC_6H_4)(CH_3)_2Si\text{-}(OH)\text{-}Ph]^+$$

$$[(p\text{-}XC_6H_4)(CH_3)_2Si\text{-}(OH)\text{-}Ph]^+ + EtOH$$



$$\longrightarrow \left[p\text{-}XC_6H_4\,(CH_3)_2 - \underset{\substack{|\\ EtOH}}{Si} - (OH) - Ph \right]^+ \quad J$$

$$(p\text{-}XC_6H_4)(CH_3)_2\text{-}Si\text{-}OEt + HOPh \longleftarrow$$

---(5-5)

No data at different temperatures were given for this solvolysis reaction.

The methanolysis of N-(trialkylsilyl)amines was also reported[116] to be acid catalysed. Although no temperature data were given, the rate of solvolysis using different solvents was reported. The rate of solvolysis was found to vary in the following order

$$H_2O > CH_3OH > CH_3CH_2OH > (CH_3)_2CHOH$$

and the results were consistent with the following mechanism

i-Pr = $(CH_3)_2CH$- , Ar = XC_6H_4 where X = H, m-CH_3

$$ArNH\text{-}Si(i\text{-}Pr)_3 + MeOH_2^+ \longrightarrow Ar(NH_2^+)\text{-}Si(i\text{-}Pr)_3 + MeOH$$

$$Ar(NH_2^+)\text{-}Si(i\text{-}Pr)_3 + MeOH \longrightarrow ArNH_2 + [(i\text{-}Pr)_3Si\text{-}(HOMe)]^+$$

$$[(i\text{-}Pr)_3Si(HOMe)]^+ + MeOH \longrightarrow (i\text{-}Pr)_3SiOMe + MeOH_2^+$$

---(5-6)

The effect of the change of the solvent on the rate of solvolysis was considered to be due to the acidity of the alcohol and also to an increase in steric hindrance.

The silicon work that I have reviewed involves an associative process which is acid catalysed as also does my solvolysis work. The entropy of activation for the solvolysis of benzylosilanes is large and negative, and similar in magnitude to that for the solvolysis of p-$EtOPhTeCl_3$. Also the fact that the rate of alcoholysis varies in the order of increasing number of carbons present in the alcohol is similar to my observation for the solvolysis of p-$EtOPhTeCl_3$. It can be explained in terms of the pK_a of the alcohols. The order of pK_a of the alcohols is

$$H_2O < CH_3OH < CH_3CH_2OH < (CH_3)_2CHOH$$

Examples of acid catalysed dissociative processes are required so that comparisons between dissociative and associative processes can be made. The hydrolysis of nitritochromium(III) complexes is reported to be acid catalysed[117,118]. The complexes studied were

$[Cr^{III}(NH_3)_5ONO]$, and cis and trans-$[Cr^{III}(en)_2(ONO)X]$

where en = ethylenediamine and X = ONO, H_2O, Cl, Br, DMF and DMSO

The pseudo-first order rate constant was found to vary as

$$\text{Rate} = k_H[H^+]$$

In all the examples studied the oxygen-nitrogen bond is broken in the rate determining step. The mechanism of aquation is believed to involve rapid protonation followed by the breaking of the O-N bond to give the products.

$$\begin{array}{llllll}
[Cr\text{-}ONO]^{2+} & + \; H^+ & \longrightarrow & [Cr\text{-}OHNO]^{3+} & & \text{Rapid} \\
[Cr\text{-}OHNO]^{3+} & & \longrightarrow & [Cr\text{-}OH]^{2+} & + \; NO^+ & \text{Slow} \\
[Cr\text{-}OH]^{2+} & + \; H^+ & \longrightarrow & [Cr\,H_2O]^{3+} & & \text{Rapid}
\end{array}$$

The activation parameters of the system were determined and the entropies of activation lie in the range +13 to +75 J mol^{-1} K^{-1}.

Tobe and Dasgupta[119] reported the aquation of cis and trans-diacetato bis(ethylenediamine) cobalt(III) to be acid catalysed, while the order in hydrogen ion concentration changed from 1 at low H^+ concentrations to zero at higher acid concentrations. This is consistent with a limiting rate law involving a protonation equilibrium. The observed rate law could be accounted for by either of the two mechanisms,

Either rapid reversible protonation of the substrate occurs followed by a slow dissociation of the protonated species,

$$\begin{tikzcd}
{[Co(en)_2(OAc)_2]^+ + H_3O^+} \arrow[r, shift left, "K_1"] & {[Co(en)_2(OAc)(HOAc)]^{2+} + H_2O} \arrow[l, shift left] \arrow[d, "k_1"] \\
 & {[Co(en)_2(OAc)H_2O]^+ + CH_3CO_2H}
\end{tikzcd}$$

---(5-7)

Or a slow bimolecular attack of H_3O^+ on the protonated species must occur

$$[Co(en)_2(OAc)_2]^+ + H_3O^+ \xrightarrow{k_2} [Co(en)_2(OAc)(H_2O)]^{2+} + CH_3CO_2H$$

Stereochemical changes in the trans-isomer indicated that acetic acid, CH_3CO_2H, was the leaving group. However, no change was observed in the cis isomer and the authors assigned a dissociative mechanism to both. The bimolecular mechanism was eliminated on the grounds that no evidence of a trans effect of the acetate group in trans-$[Co(en)_2(OAc)Cl]^+$ had been observed. The entropies of activation for the cis- and trans- isomers are -52 and +4 J K^{-1} mol^{-1} respectively.

It can be seen that the acid catalysed associative solvolysis reactions seem to be characterised by a large negative entropy of activation values, whereas the largely dissociative solvolysis reactions have positive or slightly negative values.

Other examples of known associative mechanisms are the substitution reactions of platinium(II) planar complexes. The activation parameters for the hydrolysis of $[Pt(dien)X]^+$ X= Cl^-, I^-, N_3^-, SCN^- or NO_2^- and dien = diethylenetriamine, were reported[120]. High rates of substitution of the X ligand by water parallel low enthalpies of activation of activation and all have appreciably negative entropies of activation. The values range from -75 J K^{-1} mol^{-1} for X = Cl and Br, up to -130 J K^{-1} mol^{-1} for the other ligands.

Turning to my work a brief summary is given. The solvolysis of p-$EtOPhTeCl_3$ in methanol/benzene media has been studied. The reaction was monitored by following the changes in the readings of a pH meter. The replacement of the chloride ligands by methanol is acid catalysed and the replacement of the first chloride is deduced to be rate determining.

A large negative entropy of activation was found and an associative mechanism was therefore assigned. The product isolated still contains one chloride per tellurium atom. This is probably an artifact of the separation technique. The addition of glacial acetic acid and formic acid to the reaction solution had little effect on the rate of solvolysis. However, sodium acetate retarded the rate. This is attributed to the fact that it removes as undissociated acetic acid some of the H^+ produced.

When different alcohols were used, the rate of solvolysis was found to fastest in methanol and slowest in 2-methylpropan-1-ol. This was attributed to the pK_a of the alcohol and the initial hydrogen ion concentration.

5-2 RESULTS

The solvolysis of p-$EtOPhTeCl_3$ has been studied under various reaction conditions. It was established that all results obtained in this investigation are reproducible. The solvolysis reactions were followed by taking pH-meter readings of the reaction solution over a period of time. The decrease in the pH-meter reading with time is due to the production of HCl and typically continues for an overall time of ten minutes.

The values of the observed rate constant, k_{obs}, were obtained by fitting the experimental data to the integrated equation appropriate to the following scheme

$$RTeCl_3 \quad + \quad H^+ \quad \overset{K_1}{\rightleftharpoons} \quad Int \qquad \text{---(5-8)}$$

$$Int \quad \xrightarrow{k_2} \quad Prod. \quad + \quad (n+1)H^+ \qquad \text{---(5-9)}$$

$$RTeCl_3 \quad \xrightarrow{k_3} \quad Prod. \quad + \quad nH^+ \qquad \text{---(5-10)}$$

where R = p-EtOPh, Int represents an intermediate and Prod. is the final solvolysis product. Accordingly the hydrogen ion concentration can be expressed as

$$\frac{d[H^+]}{dt} = n(k_3[RTeCl_3] \quad + \quad k_2[Int]) \qquad \text{---(5-11)}$$

and $[Int] = K_1[RTeCl_3][H^+]$

If [Int] is small compared to $[RTeCl_3]$ then integration of equation (5-11) leads to the final form of:

$$k_3(1 + [H^+]_o X)\, t \; = \; \ln \frac{(1/X \; + \; [H^+]_t\,([H^+]_{oo} \; - \; [H^+]_o))}{(1/X \; + \; [H^+]_o\,([H^+]_{oo} \; - \; [H^+]_t))} \qquad \text{---(5-12)}$$

where $[H^+]_o$, $[H^+]_t$ and $[H^+]_\infty$ are the hydrogen ion concentrations at time=0, t and infinity and

$$1/X = k_3/(K_1 k_2)$$

(The full integration is show in Appendix VII)

Tahir indicated that the values of 1/X that fitted the above equation were in the range 10^{-8} to 10^{-6}. This indicated that the value of k_3 is relatively very small and thus its contribution to the overall scheme is negligible. The scheme can therefore be simplied leading to an overall rate equation of

$$k_{obs}\, t = \ln \frac{([H^+]_t ([H^+]_{oo} - [H^+]_o))}{([H^+]_o ([H^+]_{oo} - [H^+]_t))} \qquad \text{---(5-13)}$$

where $k_{obs} = K_1 k_2 [H^+]_{oo}$ ---(5-14)

Plots of pH-meter readings against time for 70-80% completion of the reaction can be fitted to equation 5-13 which was used in a BASIC program (Appendix VIII) to calculate the values of k_{obs} under different solvolysis conditions.

The observed rate of solvolysis (k_{obs}) of p-EtOPhTeCl$_3$ in a mixed solvent of benzene/methanol, (5:1 by volume), using different initial concentrations of p-EtOPhTeCl$_3$ was studied at 25°C. The range of initial p-EtOPhTeCl$_3$ concentrations used was (9.34 to 1.33) $\times 10^{-5}$ mol dm^{-3} and the results are presented in table 5-1. A plot of k_{obs} versus (3[p-EtOPhTeCl$_3$]$_o$) is linear as shown in fig 5-1. The final pH-meter reading of the solution was observed to increase with the decreasing initial trichloride concentration used. This indicates that k_{obs} is proportional to 3[p-EtOPhTeCl$_3$]$_o$ and since the intercept is zero we have

$$k_{obs} = 3\,k_s\,[\text{p-EtOPhTeCl}_3]_o \qquad \text{---(5-15)}$$

where k_s is the rate constant for the solvolysis of p-EtOPhTeCl_3. The gradient of figure 5-1 is the rate constant, k_s, and gives a value of $k_s = 2150$ mol^{-1} dm^3 s^{-1}.

The effect on the observed rate constant over the temperature range 5-30°C was investigated at a constant p-EtOPhTeCl_3 concentration (6.65×10^{-5} mol dm^{-3}) with the runs carried out at 5°C intervals. The results are presented in table 5-2 and an Arrhenius plot of $\log_e k_s$ versus K/T is linear, fig 5-2. The slope was determined by the least squares program(Appendix II) and equations 3-33 and 3-34 were used to determine the values of the activation parameters as:

$$\Delta E^* = 14.8 \pm 1 \ \text{kJ mol}^{-1}$$

$$\Delta H^* = 12.3 \pm 1 \ \text{kJ mol}^{-1}$$

$$\Delta S^* = -222 \pm 11 \ \text{J mol}^{-1}\,\text{K}^{-1}$$

Also I found that at the same benzene/methanol ratio (5:1) the observed rate of disappearance of the trihalide colour varied in the following order

$$\text{Cl} > \text{Br} > \text{I}$$

The effect on the rate constant of varying the solvent composition from 91.8% to 1.6% by volume benzene was investigated.The trichloride concentration was kept constant at 2.87×10^{-5} mol dm^{-3}. The results are shown in table 5-3. The plot of the rate constant versus the percentage benzene (by volume) is shown in fig 5-3. The plot shows that k_s increases with the percentage methanol in the mixed solvent at percentages above 80%.

The addition of lithium chloride has no effect on the rate constant. Lithium chloride was used since it was soluble in methanol and the p-EtOPhTeCl$_3$ concentration was kept at 2.57 x10^{-5} mol dm^{-3}. The results are given in table 5-4 and show that within experimental error the rate is virtually constant over the range studied, fig 5-4.

The effect of the addition of sodium acetate was investigated. The p-EtOPhTeCl$_3$ concentration used throughout was 8.83 x10^{-5} mol dm^{-3}. The results are shown in table 5-5 and show that the observed rate constant increases upon decreasing sodium acetate concentration. A plot of the reciprocal of k_{obs} versus sodium acetate concentration is linear as shown in fig 5-5. I also found that the overall change in the pH-meter reading decreases with increasing sodium acetate concentration used. A plot of $\log_e k_{obs}$ versus the overall pH-meter reading change is linear as shown in fig 5-6.

Table 5-6 shows the effect of the addition of acid on the rate constant, k_s. The acid used was glacial acetic acid and within experimental error k_s is constant throughout the range studied. However, the pK$_a$ of acetic acid in aqueous solution is 4.75, so it would appear that the hydrogen ion concentration is low, ~10^{-6} mol dm^{-3}, and thus its contribution to the reaction negligible. So another organic acid was used, formic acid. Formic acid is a stronger acid than acetic acid (pK$_a$ = 3.75), and the results obtained are presented in table 5-7. The p-EtOPhTeCl$_3$ concentration used throughout was 2.1 x10^{-5} mol dm^{-3}. I observed that the rate constant appears to decrease slightly upon increasing acid concentration.

The effect of using different alcohols in place of methanol was investigated. The alcohols used were ethanol, propan-1-ol, propan-2-ol, butan-1-ol and 2-methylpropan-1-ol. The concentration of p-EtOPhTeCl_3 was 6.7×10^{-5} mol dm^{-3}. I observed that the rate varied in the order of increasing carbon chain length.

The attempts to obtain the methanolysis product were the most difficult part of this study. Addition of pure methanol to the trichloride resulted in the formation of a white precipitate. However, upon evaporation of the methanol in a dry box, I observed that a yellow solid appeared (Tahir made the same observation). I repeated the procedure and drew off the liquor and added more methanol until drying gave a white product. An IR spectrum of the product is shown in fig 5-7. Elemental analysis gave the following results C=32.2%,H=2.87%, Cl=11.5% and the product decomposed without melting at 234°C.

$[p\text{-EtOPhTeCl}_3]_o$ /10^{-5} mol dm^{-3}	Observed rate constant k_{obs} /s^{-1}	k_s /$mol^{-1}dm^3 s^{-1}$	Final meter reading
9.34	0.613	2188	0.45
6.96	0.461	2208	0.60
4.91	0.311	2111	0.63
3.03	0.194	2134	0.82
1.33	0.148	3709	1.15

Table 5-1 Variation in the observed rate constant for the solvolysis of different initial concentrations of p-EtOPhTeCl$_3$ in benzene/methanol solvent (5:1by volume) at 25°C.

Temp ^oC	$1/T / 10^{-3}$	k_{obs} / s^{-1}	k_s $/mol^{-1} dm^3 \, s^{-1}$	$\log_e k_s$
5	3.60	0.150	1409	7.25
10	3.53	0.166	1559	7.35
15	3.47	0.194	1822	7.51
20	3.41	0.205	1925	7.56
25	3.36	0.234	2197	7.69
30	3.30	0.253	2376	7.77

Table 5-2 Variation in the rate constant for the solvolysis of p-$EtOPhTeCl_3$ (3.55 x10^{-5} mol dm^{-3}) in benzene/methanol solvent (5:1 by volume) at different temperatures.

%Benzene by volume	Mole fraction Methanol	Observed rate constant k_{obs} /s^{-1}	k_s /$mol^{-1}dm^3 s^{-1}$
1.60	0.993	0.422	4902
4.90	0.977	0.334	3879
9.80	0.953	0.273	3171
16.7	0.917	0.265	3078
26.2	0.861	0.209	2437
34.4	0.808	0.200	2323
42.6	0.748	0.194	2253
51.0	0.679	0.213	2473
67.0	0.520	0.209	2427
75.0	0.423	0.228	2648
83.3	0.306	0.210	2439
91.8	0.164	0.213	2474

Table 5-3 Variation of the rate constant with different solvent (benzene/methanol) compositions for the solvolysis of p-EtOPhTeCl_3 (2.87 x10^{-5} mol dm^{-3}) at 25°C.

$[LiCl]_o$ /10^{-4} mol dm^{-3}	Observed rate constant k_{obs} /s^{-1}	k_s /$mol^{-1}dm^3$ s^{-1}
51.4	0.200	2594
23.6	0.210	2724
11.1	0.256	3320
7.73	0.220	2853
2.87	0.214	2776

Table 5-4 Effect on the observed rate constant with the addition of Lithium Chloride for the solvolysis of p-$EtOPhTeCl_3$ (2.57×10^{-5} mol dm^{-3}) in benzene/methanol solvent (5:1 by volume) at 25°C.

$[CH_3CO_2Na]_o$ /10^{-4} mol dm^{-3}	Observed rate constant k_{obs} /s^{-1}	k_s /mol^{-1}dm^3 s^{-1}	pH-meter Difference
6.14	0.080	302	1.45
5.03	0.088	332	1.55
4.44	0.096	362	1.73
2.96	0.106	400	2.11
2.07	0.120	453	2.42
1.48	0.242	914	4.04
0	0.570	2152	~8

Table 5-5 Variation of the observed rate constant with the addition of different molar concentrations of sodium acetate (CH_3CO_2Na) for the solvolysis of p-EtOPhTeCl$_3$ (8.83 x10^{-5} mol dm^{-3}) in benzene/methanol solvent (5:1 by volume) at 25^oC.

$[\text{Acetic acid}]_o$ $/10^{-4}$ mol dm^{-3}	Observed rate constant k_{obs} /s^{-1}	k_s /mol^{-1}dm^3 s^{-1}
114	0.250	2137
57.0	0.234	2000
11.4	0.247	2111
8.55	0.267	2282
5.70	0.264	2256

Table 5-6 Effect on the observed rate constant with the addition of glacial acetic acid for the solvolysis p-EtOPhTeCl$_3$ (3.90×10^{-5} mol dm^{-3}) in benzene/methanol solvent (5:1 by volume) at 25°C.

$[\text{Formic acid}]_o$ $/10^{-3}$ mol dm^{-3}	Observed rate constant k_{obs} $/s^{-1}$	k_s $/mol^{-1}dm^3\ s^{-1}$
64.7	0.126	2000
49.0	0.116	1841
33.0	0.147	2333
17.0	0.183	2905
8.58	0.192	3048
4.29	0.183	2905

Table 5-7 Effect on the rate constant with the addition of formic acid for the solvolysis of p-EtOPhTeCl$_3$ (2.10×10^{-5} mol dm^{-3}) in benzene/methanol solvent (5:1 by volume) at 25^{o}C.

Alcohol	Observed rate constant k_{obs} /s^{-1}	k_s /$mol^{-1}dm^3\ s^{-1}$
Methanol	0.446	2219
Ethanol	0.334	1661
Propan-1-ol	0.131	652
Propan-2-ol	0.129	642
Butan-1-ol	0.061	303
2-Methyl-propan-1-ol	0.070	348

Table 5-8 Variation in the rate constant for the solvolysis of p-$EtOPhTeCl_3$ (6.7×10^{-5} mol dm^{-3}) in benzene/alcohol solvent (5:1 by volume) with different alcohols at 25°C.

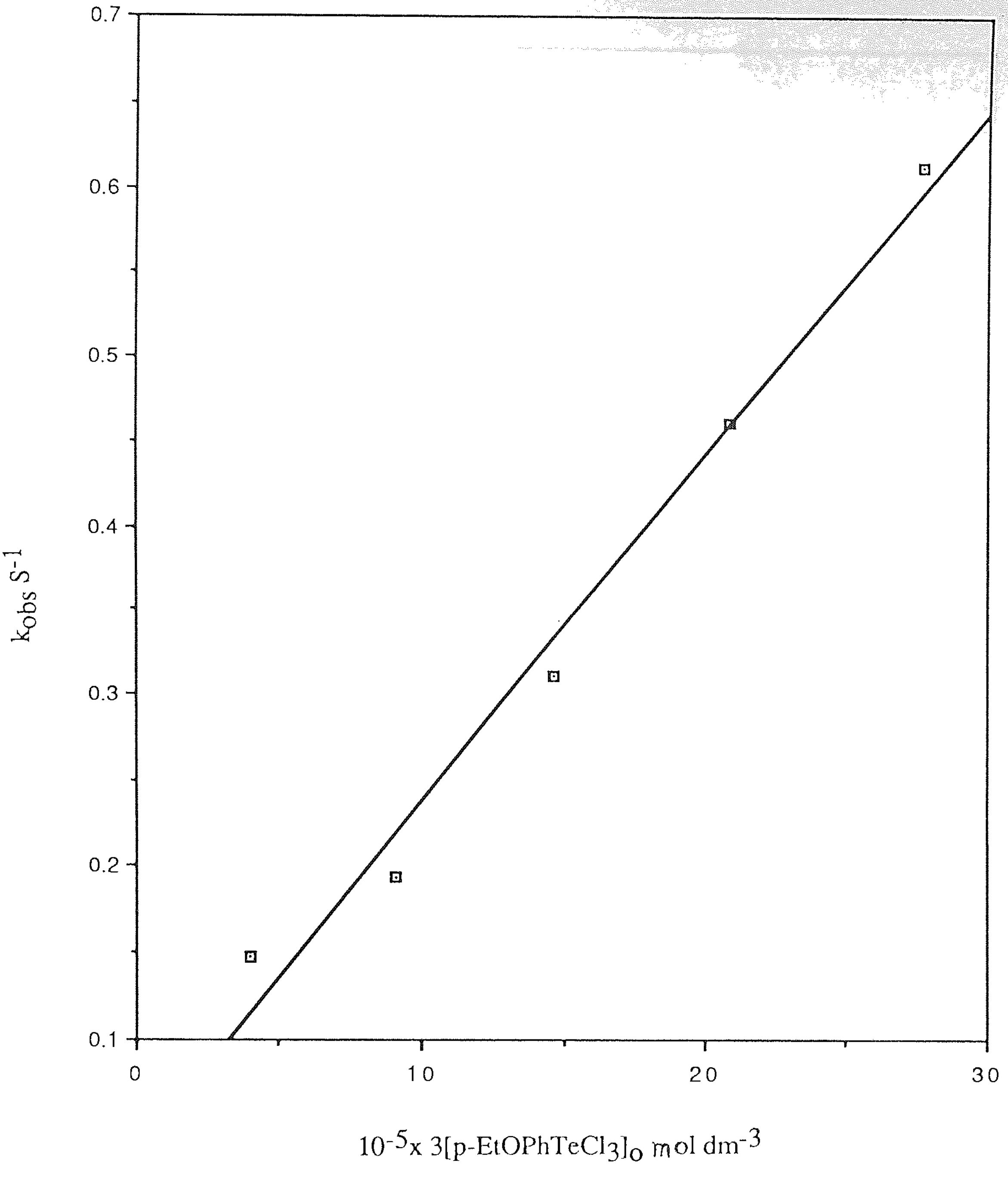


Fig 5-1 Plot of k_{obs} versus 3[p-EtOPhTeCl$_3$]$_o$ concentration for the solvolysis of p-EtOPhTeCl$_3$ at 25°C in a mixed solvent of methanol/benzene.

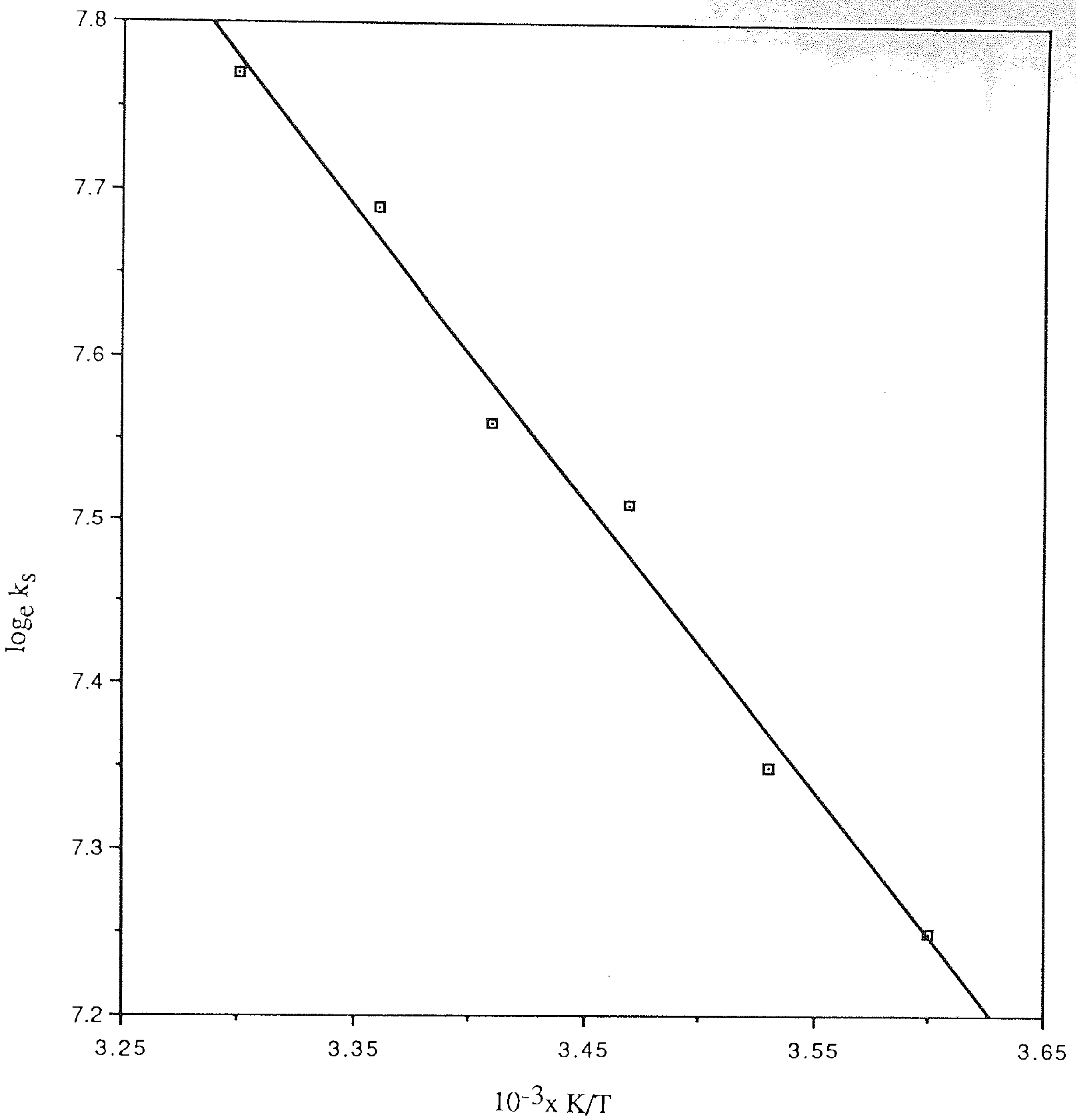


Fig 5-2 Plot of $\log_e k_s$ versus K/T for the solvolysis of p-EtOPhTeCl$_3$ in a mixed solvent of methanol/benzene at 25^{o}C.

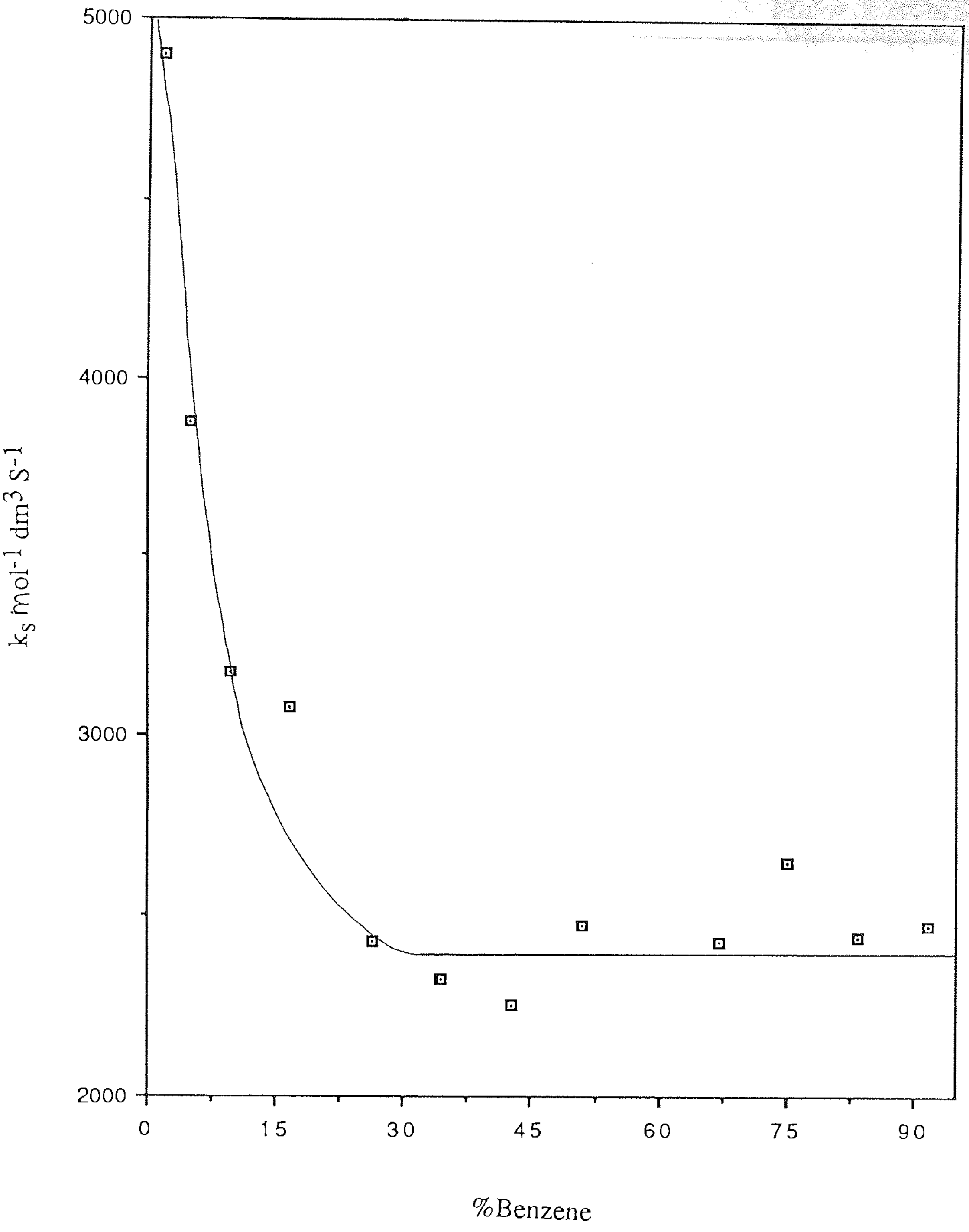


Fig 5-3 Plot of k_s versus percentage benzene by volume in the mixed solvent methanol/benzene for the solvolysis of p-EtOPhTeCl$_3$ at 25°C.

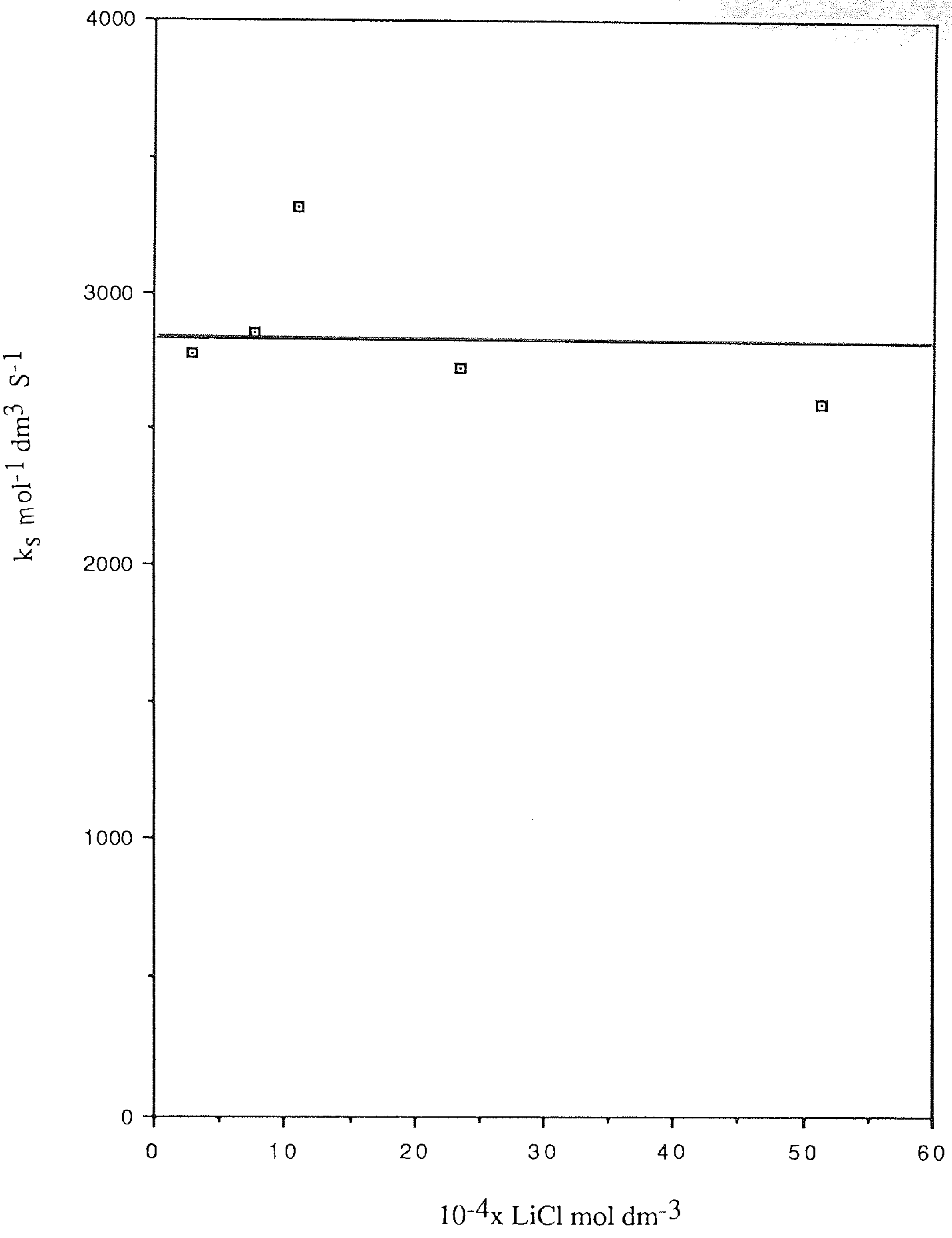


Fig 5-4 Plot of k_S versus molar concentration lithium chloride added for the solvolysis of p-EtOPhTeCl$_3$ in a mixed solvent of methanol/benzene.

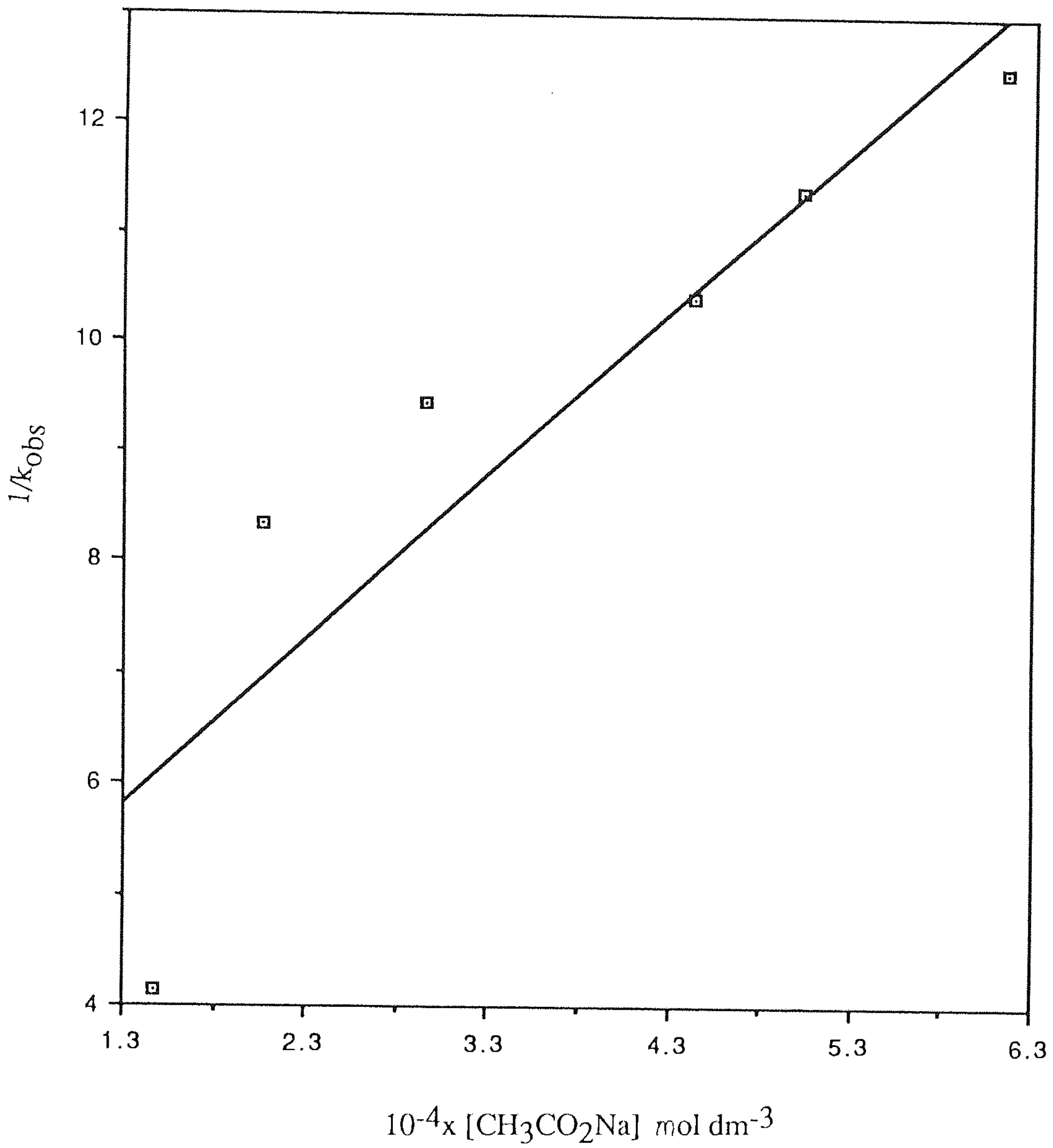


Fig 5-5 Plot of $1/k_{obs}$ versus molar concentration sodium acetate added for the solvolysis of p-EtOPhTeCl_3 in a mixed solvent of methanol/benzene at 25°C.

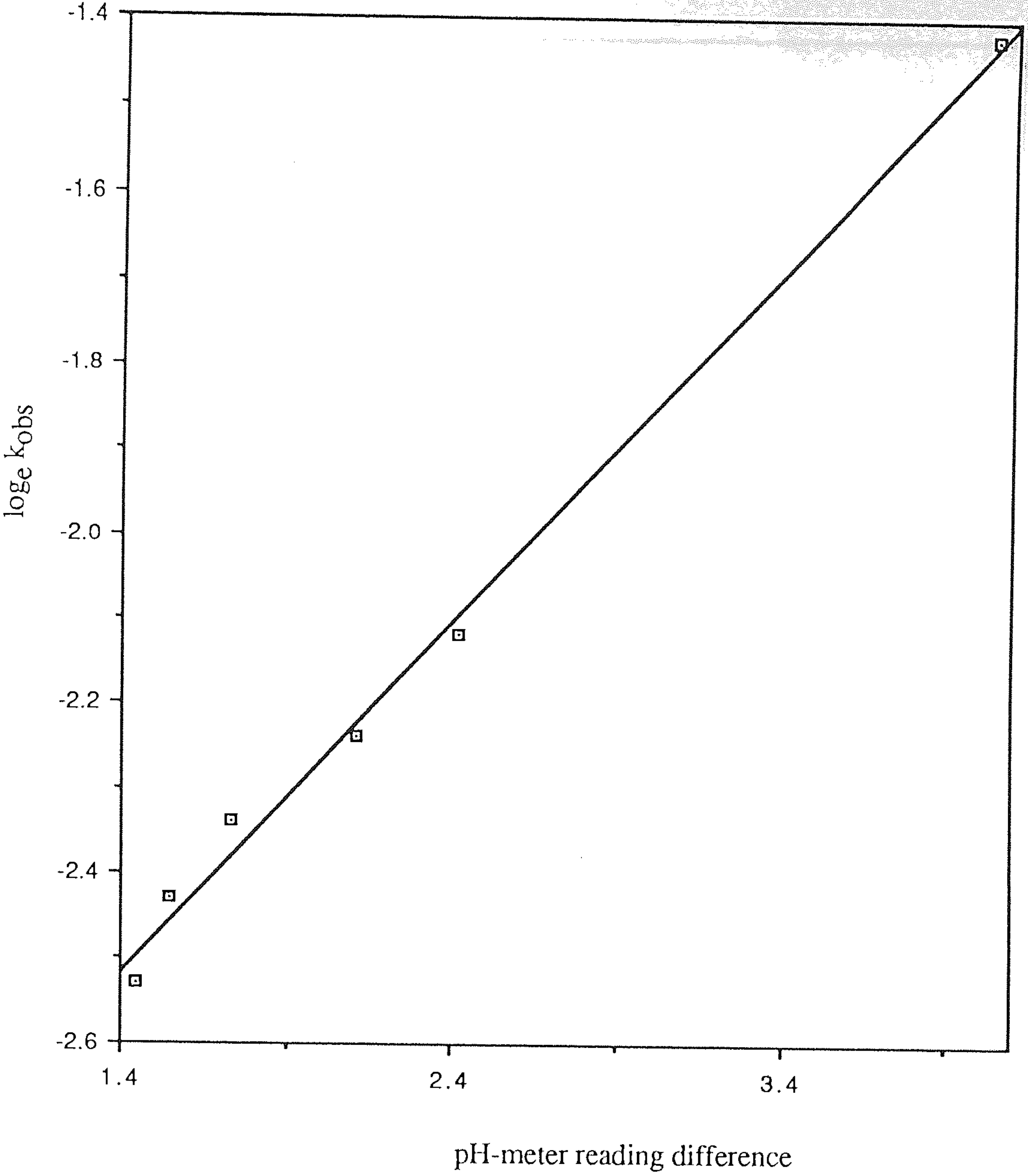


Fig 5-6 Plot of loge k_{obs} versus the difference in pH-meter readings for the added sodium acetate experiments.

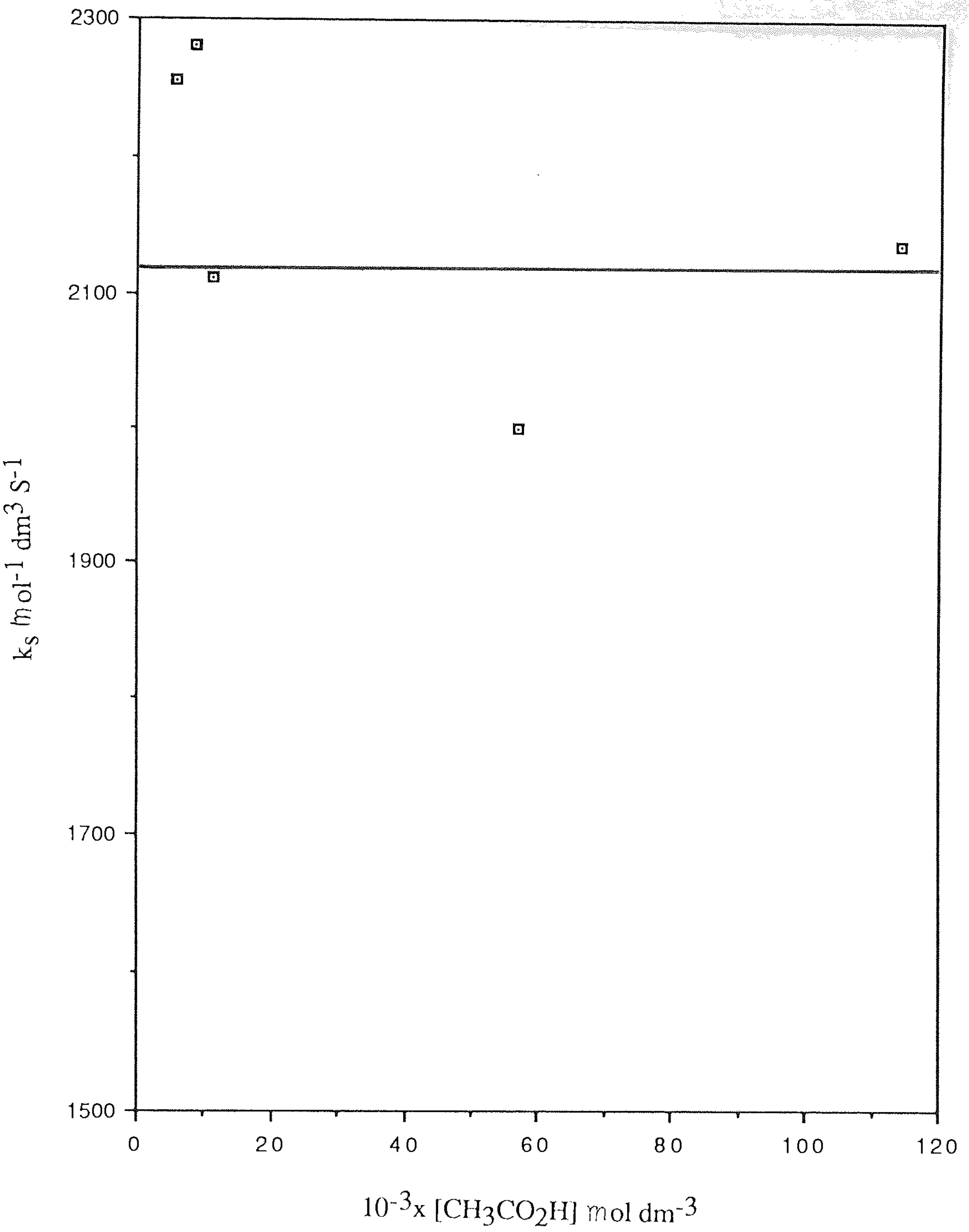


Fig 5-7 Plot of k_s versus acetic acid concentration for the solvolysis of p-EtOPhTeCl$_3$ in a mixed solvent of methanol/benzene at 25°C.

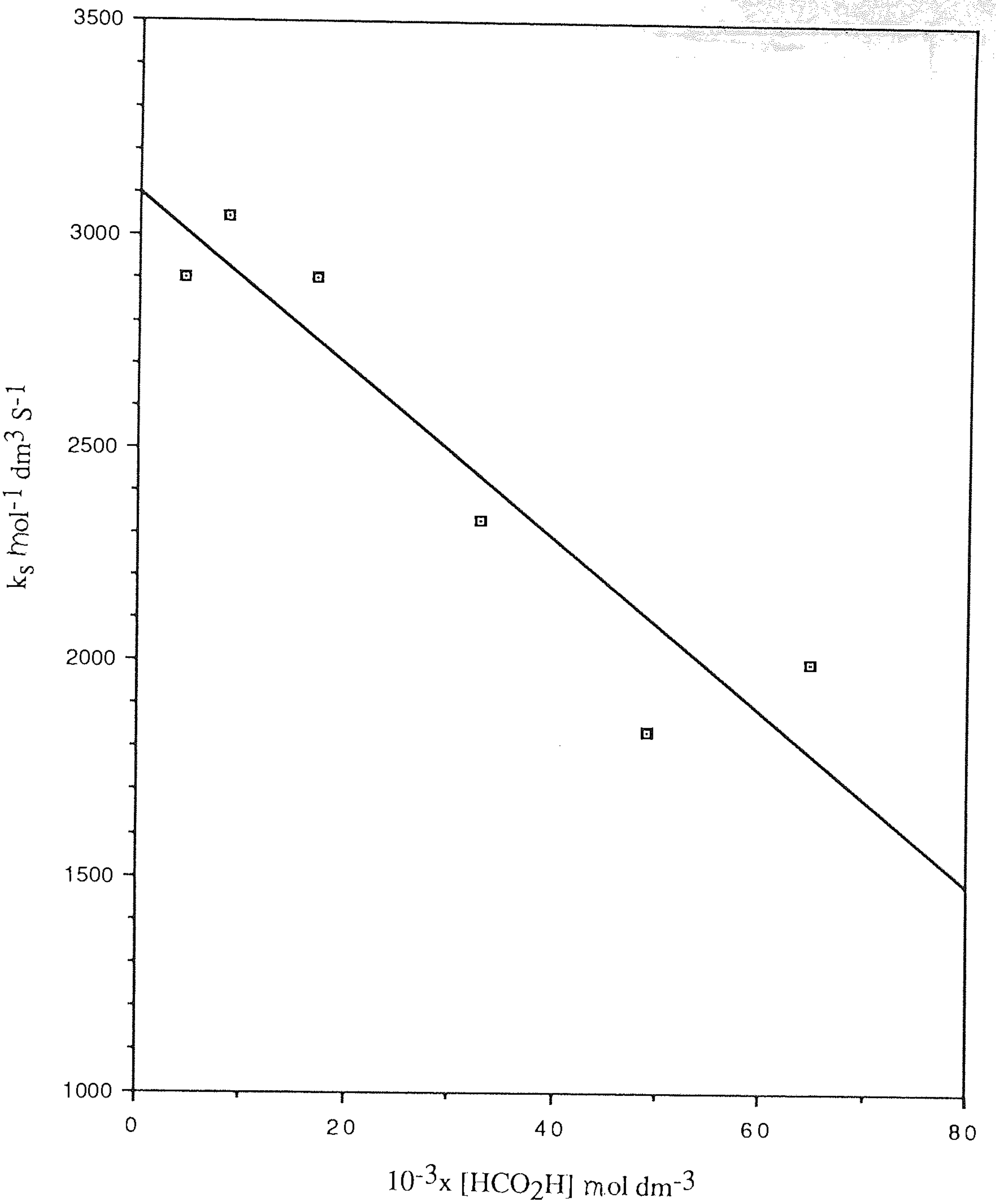


Fig 5-8 Plot of k_s versus formic acid concentration for the solvolysis of p-EtOPhTeCl_3 in a mixed solvent of methanol/benzene at 25^{o}C.

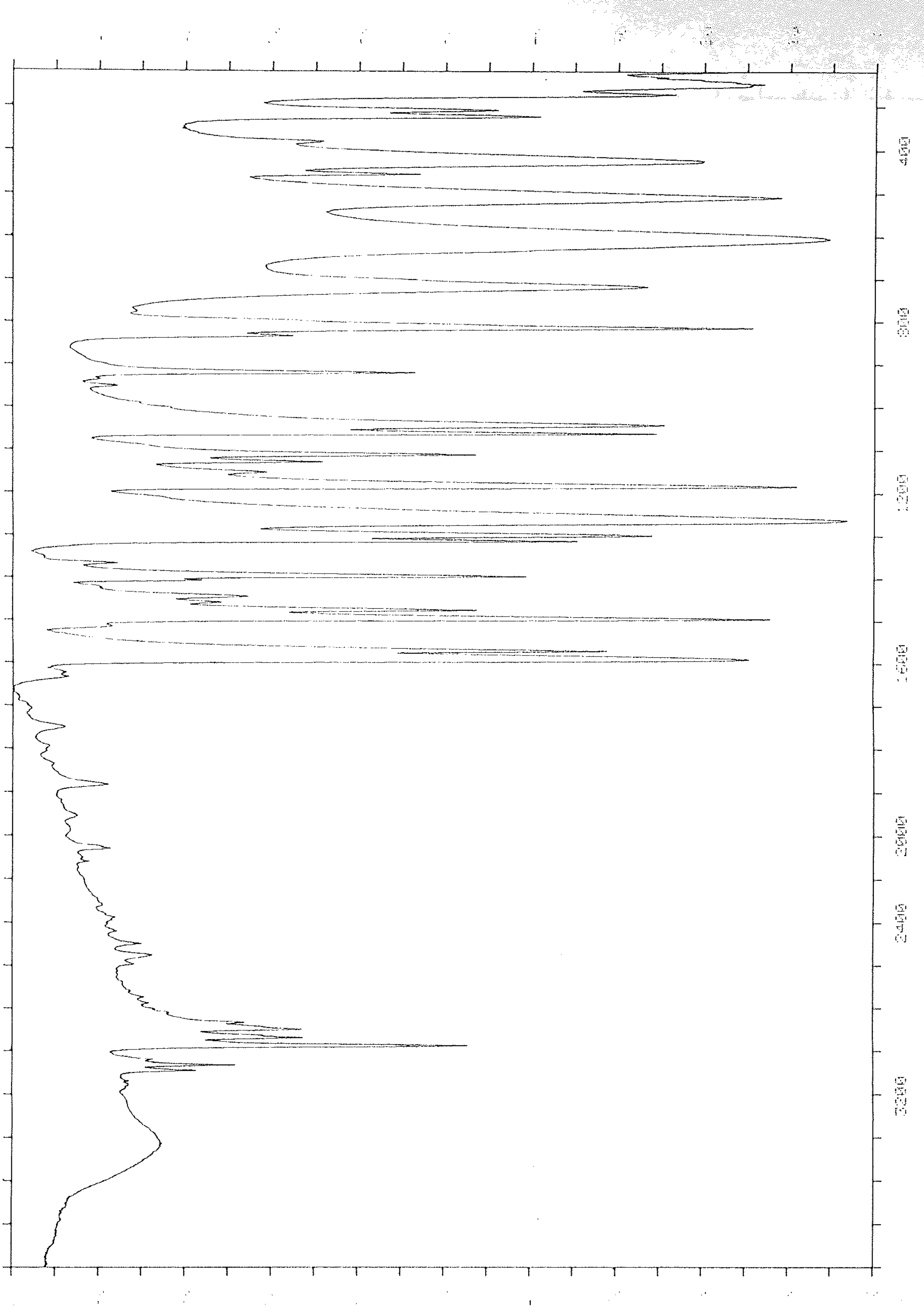


Fig 5-9 IR spectrum of the methanolysis product as a KBr disc.

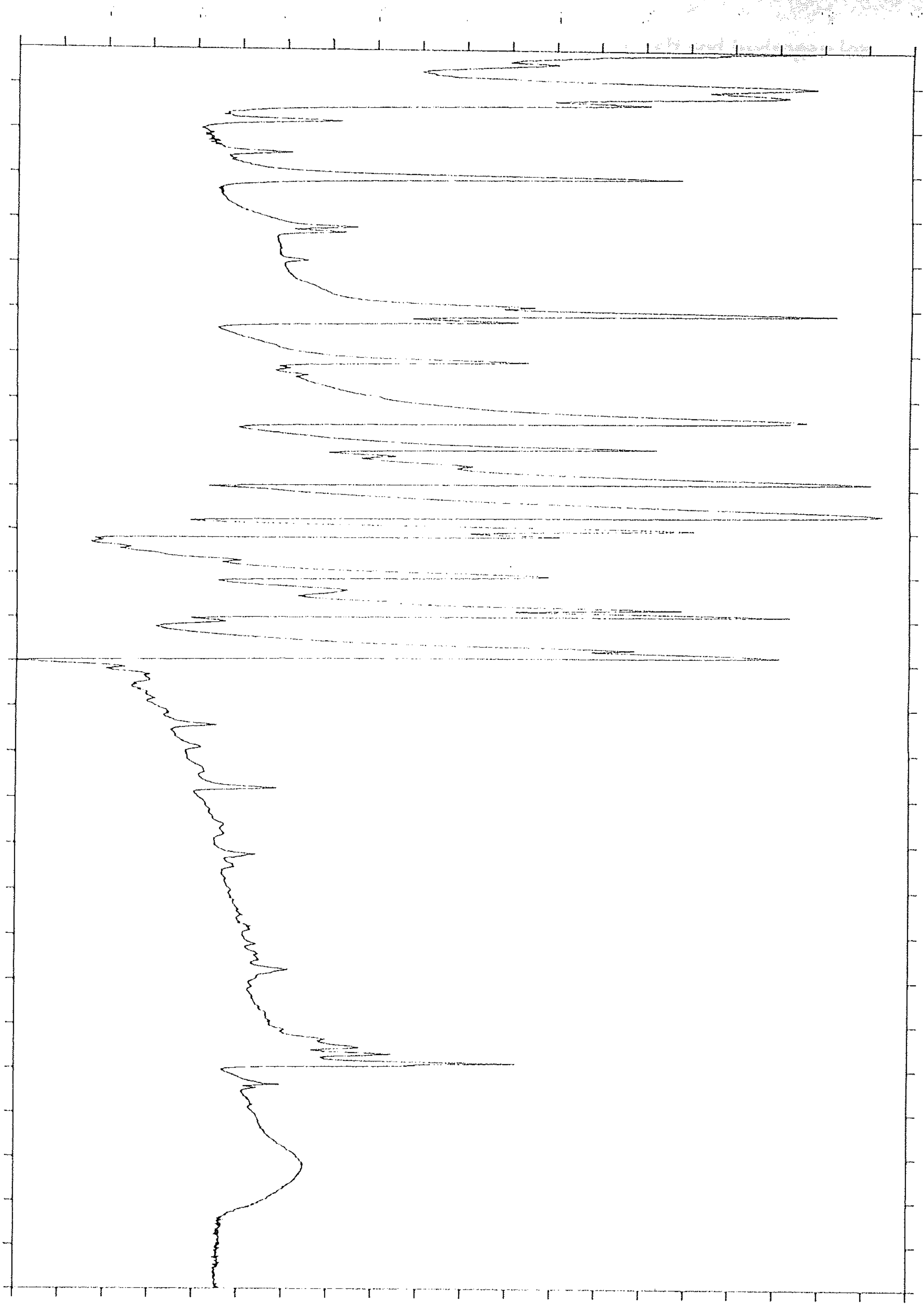


Fig 5-10 IR spectrum of the p-EtOPhTeCl$_3$ as a KBr disc.

5-3 DISCUSSION

The solvolysis of p-EtOPhTeCl_3 under different reagent, salt and hydrogen ion concentrations, solvent compositions, and temperatures has been studied in methanol/benzene mixtures. The kinetic studies were carried out by measuring the decrease in the pH-meter reading of the reaction solution over the period of time (up to 10 minutes) taken to reach completion.

The solvent composition, methanol/benzene, was found to affect the performance of the glass electrode. Robinson[121] found that the response of a glass electrode is substantially unimpaired in solvent compositions of alcohol/water below 90% by weight alcohol. However, the solvent used in this investigation ranged from 98.4% to 8% methanol which is different from mixtures with more than 10% water in alcohol. The performance of the electrodes can therefore be expected to be altered. That is found to be the case. Nevertheless the glass electrode responds adequately and shows a good quantitative comparisons of the acidities for the different experiments undertaken.

Acidity functions in different aqueous and non-aqueous organic solvents have been reported and discussed[122,123]. The main conclusion is that acidity function (Q) varies linearly with acid concentration and can be represented by the equation

$$Q = m - n \log_{10}[H^+] \qquad \text{---(5-15)}$$

Thus the pH-meter readings are in fact acidity function measurements. They behave similarly to the true pH of the solution, and are governed by the constants m and n.

The final pH-meter readings for the solvolysis reactions, listed in table 5-1, vary with the final acid concentration indicating that equation 5-15 is valid. The difference between the calculated pH and the final pH-meter reading may be influenced by several parameters. These include liquid junction potentials of the electrodes, the affinity of the solvent(s) for the hydrogen ion, and any equilibrium involving the overall reaction producing the acid.

Although the difference between the acidity function (pH-meter reading) and the true pH of the medium under the same conditions might vary from one experiment to another, it will not have any effect on the calculated rate constants discussed in this section. That is because the rate equation (5-13) uses the ratios of differences between readings. This eliminates the differences between the pH-meter readings and the real pH of the solution due to the constants m and n. So the overall change in the acidity function (pH-meter reading) in the solvolysis reaction can be used to follow the progress of the reaction.

The results obtained from the solvolysis of aryltellurium trichlorides are reproducible under all conditions studied. The kinetic studies were initiated by adding a concentrated solution of aryltellurium trichloride to a rapidly stirred benzene/methanol mixture and the reaction profile was recorded on a chart recorder. The reaction is followed by measuring the decrease in the reading over a period of time. The decrease in the pH-meter reading is due to the production of HCl and typically continues for ten minutes.

None of the experiments undertaken gave any indication of a rapid initial generation of acid, but rather a smooth increase over a period of time. Although there was a sharp drop in the pH-meter reading (up to 1 pH scale unit) during the addition of the concentrated aryltellurium trichloride solution, this was attributed to the mixing of the solutions. The drop can be reproduced by adding pure benzene. Thus when mixing is complete and a homogeneous solution is formed, the equilibrium between the electrodes and the solution has been re-established, the pH-meter readings versus time can be recorded for the solvolysis reaction.

The data from the kinetic experiments can be fitted to equation (5-13) from the start up to 70-80% completion

$$k_{obs}\, t = \ln \frac{([H^+]_t\,([H^+]_{oo} - [H^+]_o))}{([H^+]_o\,([H^+]_{oo} - [H^+]_t))} \qquad \text{---(5-13)}$$

The subscripts $[H^+]_t$, $[H^+]_o$ and $[H^+]_{oo}$ are calculated from the pH-meter readings at time t, initially and at infinity.

The variation in the observed rate constant (k_{obs}) with the aryltellurium trichloride concentration is given in table 5-1. The final pH-meter reading for each experiment is also shown and is seen to decrease with increasing aryltellurium trichloride concentration. This clearly demonstrates that more acid, HCl, is produced as more p-$EtOPhTeCl_3$ is used. A plot of the initial p-$EtOPhTeCl_3$ concentration versus the observed rate constant is linear, fig 5-1. The observed rate constant is related to the final acid concentration by equation (5-14)

$$k_{obs} = K_1 k_2 [H^+]_{oo} \qquad \text{---(5-14)}$$

Now, assuming that under the experimental conditions all the chlorides are replaced by the solvent

Viz:

$$p\text{-EtOPhTeCl}_3 + 3\text{MeOH} \longrightarrow p\text{-EtOPhTe(OMe)}_3 + 3\text{HCl}$$

Then the observed rate constant is related to the initial p-$EtOPhTeCl_3$ concentration by

$$k_{obs} = 3\ k_s\ [p\text{-EtOPhTeCl}_3] \qquad \text{---(5-15)}$$

Thus the slope from fig 5-1 represents the rate constant, k_s, for the solvolysis of aryltelluriumtrichloride. The value obtained from fig 5-1 is $k_s = 2150\ mol^{-1}\ dm^3\ s^{-1}$.

Using similar concentrations of p-$EtOPhTeCl_3$, p-$EtOPhTeBr_3$ and p-$EtOPhTeI_3$, I found that the rate of disappearance of the aryltellurium trihalide varies in the following order (same solvent composition)

$$Cl > Br > I$$

This order in the rate of solvolysis is in agreement with Tahir's results.

The effect on the rate constant of changing the temperature was studied. The data are shown in table 5-2 and they fit an Arrhenius plot, fig 5-2. A least squares program was used to determine the slope and the activation energy. Equations 3-33 and 3-34 were used to calculate the entropy and enthaply of activation for the solvolysis of p-$EtOPhTeCl_3$. The activation parameters determined are:

$$k_s = 2150\ mol^{-1}\ dm^3\ s^{-1} \text{ at } 25^oC$$

$$\Delta E^* = 14.8 \pm 1\ kJ\ mol^{-1}$$

$$\Delta H^* = 12.3 \pm 1\ kJ\ mol^{-1}$$

$$\Delta S^* = -222\ J\ mol^{-1}\ K^{-1}$$

The large negative entropy of activation ($-222\ J\ mol^{-1}\ K^{-1}$) indicates that the reaction is associative. In the introduction it was noted that the alcoholysis of silanes is associative with a reported value of $\Delta S^* = -196 \text{ J mol}^{-1} \text{ K}^{-1}$. Dissociative processes in general tend to have positive values or small negative values.

The variation of the rate constant, k_s, with different solvent compositions was investigated. The range of methanol concentrations used in the methanol/benzene mixture was from 98.4% to 8% by volume. The results are shown in table 5-3 and a plot of the rate versus percentage methanol is shown in fig 5-3. The plot shows that the rate is independent of the solvent composition up to 80% by volume methanol. Above these percentages there is a steep rise in the rate constant. The rate constant in pure methanol can be estimated by extrapolation of the data above 80 % methanol. This gives an approximate value of ~5000 $\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. Only close to pure methanol does the rate of solvolysis increase, showing that addition of methanol is not involved in the rate determining step. Now some phenomenon must be occuring which causes this increase in k_s, but I am unable to offer an adequate explanation due to the lack of information. As the mole fraction of methanol increases the solvent changes from predominately benzene to pure methanol. Thus the phenomenon may be associated with the solvation sphere around the tellurium species. However, further information is required about that sphere, which might be derived from NMR. Low temperatures would be required to slow the rate so that studies could be undertaken. Perhaps the nuclei ^1H, ^{13}C and ^{125}Te would be used. Unfortunately this would involve a major research project. At present I do not have enough experimental information to explain with any certainly the increase in k_s.

The effect of the addition of lithium chloride was investigated. The range of lithium chloride concentrations used extended up to 400 times the p-EtOPhTeCl$_3$

concentration used. The results, table 5-4, show that within experimental error the chloride ion has no effect on the rate, fig 5-4. Therefore we can eliminate the chloride as an active reagent.

The solvolysis reaction was reported by Tahir to be acid catalysed. Thus experiments were undertaken to investigate the effect of added acid. The acid chosen was glacial acetic acid. The effect on the rate by adding sodium acetate was also investigated.

The results presented in table 5-5 show the effect on the rate of the addition of sodium acetate. The results show that the rate decreases with increasing sodium acetate concentration. Note also that the difference between the initial and final pH-meter readings decreases as more sodium acetate is added. This demonstrates that the acid produced as the solvolysis reaction proceeds is removed as undissociated acetic acid. Viz:

$$CH_3CO_2Na \quad + \quad HCl \quad \longrightarrow \quad CH_3CO_2H \quad + \quad NaCl \qquad \text{---(5-17)}$$

The solvolysis reaction can be represented by

$$\text{Reagent} \quad + \quad H^+ \quad \longrightarrow \quad \text{Products} \quad + \quad (n+1)H^+ \qquad \text{---(5-18)}$$

If this is correct then combining equations (5-17) and (5-18) we can see that a plot of $\log_e k_{obs}$ should vary linearly with the change in the pH-meter reading from start to finish. The plot is linear as shown in fig 5-6. Therefore acid catalysis is occurring in my system.

The acetic acid experiments, table 5-6, show that the rate is constant within experimental error over the range of acetic acid concentrations used even at 400:1 ratio (CH_3CO_2H:p-EtOPhTeCl_3), fig 5-7. However, the pK_a of acetic acid in aqueous solution for

$$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$$

is 4.75. The hydrogen ion concentration, even in in water, is small at the concentration used in my experiments. Therefore no effect is to expected in a non-aqueous solvent as the hydrogen ion concentration is insignificant. I therefore decided to use a stronger acid, formic acid, to study the effect of acid on the rate. However, I found that upon increasing formic acid concentration the rate decreased slightly.

Formic acid is a stronger acid than acetic acid and in the experiments undertaken the hydrogen ion concentration must be greater than without acid. Since the reaction is acid catalysed the retarding effect on the rate must be due to the formate ion. One possibility is coordination of the formate ion with the tellurium species in place of methanol. This would have the effect of slowing down the rate if the formate complex is less reactive. However, I was unable to show whether formate does indeed coordinate to the tellurium species due to the lack of time.

The effect on the rate constant of using different alcohols was investigated. The results are shown in table 5-8. The rate constant varies in the order methanol > ethanol > propan-1-ol > propan-2-ol > butan-1-ol $\simeq$ 2-methylpropan-1-ol. Now, from the solvent composition data I have argued that methanol is not involved in the rate determining step. If this is correct then the effect of the various alcohols cannot be due to steric effects, ie entering group effects.

Various parameters have been constructed for various solvents[125,126] for example Y values (Grunwald and Winstein), Dielectric constant(D), pK_a, Kosower's Z value, Rheinhardt's E_T parmeter and Brownstein's S value. Using these parameters we can find the most likely property to explain the effect obtained.

	SOLVENT PARAMETER				
SOLVENT	pK_a	E_T	D	Y	S
Water	14	63.1	78.4	3.493	0.154
Methanol	15.09	55.5	32.7	-1.090	0.0499
Ethanol	15.9	51.9	24.6	-2.033	
Propan-1-ol	16.1	50.7	20.3		-0.0158
Propan-2-ol	17.1	48.6	19.9		
Butan-1-ol	16.1	50.2	17.5		-0.0240
2-Methylpropan-1-ol	19.2	49.0	17.9		-0.0413

Although all the solvent parameters appear to vary in order of the rate of solvolysis, the pK_a values are the most likely property to affect the rate. The solvolysis reaction is acid catalysed and as such the initial hydrogen ion concentration will affect the rate of solvolysis. A similar arguement has been advanced for the solvolysis of N(trialkylsilyl)amines[116] which is acid catalysed. The rate determining step involves a protonated species and as such the concentration of this species will depend on the initial hydrogen ion concentration, that is the pK_a of the solvent. However, consideration must be given to steric hindrance during interaction of the alcohol and the tellurium species. It is probable that the best explanation is due to a combination of the pK_a and steric hindrance of the alcohol in question.

Characterisation of the product was the most difficult part of the investigation. Addition of methanol to p-EtOPhTeCl_3 resulted in a white precipitate, upon both filtering and evaporation of the solvent a yellow solid reappeared, showing that the solvolysis reaction is reversible. It is obvious that the acid produced from the reaction becomes more concentrated as the solvent is removed. Hence the reaction

$$\text{p-EtOPhTeCl}_3 + 3\text{MeOH} \longrightarrow \text{p-EtOPhTe(OMe)}_3 + 3\text{HCl}$$

is shifted back to the reactants.

Since filtering or evaporation of the solvent was unsuccessful I decided to add methanol to p-EtOPhTeCl_3, then draw off the liquor and successively repeat this procedure until a white solid remained after drying. The solid had no melting point but decomposed at 234°C and the elemental analytical data found were C = 32.2%, H = 2.87% and Cl = 11.5%. The infra-red spectrum of the product, fig 5-9, shows an absorption at 700-600cm^{-1} associated with a Te-O bond vibration. In the introduction it was noted that acid hydrolysis of p-EtOPhTeCl_3 yields p-EtOPhTeOCl as the product.

Two possible solvolysis products p-EtOPhTe$(OCH_3)_2$Cl and pEtOPhTeOCl are summarised in the table below

Element %	Carbon	Hydrogen	Chlorine
1) Found	32.2	2.87	11.5
2) p-EtOPhTe$(OCH_3)_2$Cl	34.6	4.4	10.2
3) p-EtOPhTeOCl	32.0	3.0	11.8

Tahir's product decomposed at 185°C and the analysis suggested compound 2. The product I obtained is different both in elemental analysis and melting point (decomposition). The analysis suggests compound 3, which has been reported by other workers in the acid hydrolysis of p-EtOPhTeCl$_3$. Now, compound 3 could presumably be prepared from p-EtOPhTe(OCH$_3$)$_2$Cl by

$$\text{p-EtOPhTe(OCH}_3)_2\text{Cl} \longrightarrow \text{p-EtOPhTeOCl} + \text{O(CH}_3)_2$$

The problem is to decide whether breaking of a carbon-oxygen bond is feasible under my experimental conditions. The most important finding is that the solvolysis product still contains the aryl group, tellurium and chlorine present. This shows that we need not consider reactions involving tellurium-carbon bond cleavage. The decomposition point[51] of p-EtOPhTeOCl has been reported to be 224-6°C and is similar to that found for the methanolysis product. Since the methanol used was dry it is unlikely that compound 3 could be due to the presence of traces of water. Thus the nature of the product is not totally resolved, although it is probably compound 3.

Any explanation for the pathway of the preceding solvolysis reaction must take account of the geometrical structure of p-EtOPhTeCl$_3$ in solution. The structure of p-EtOPhTeCl$_3$ has been reported to be polymeric[30]. However, Raina and Khandelwal[32] have reported that p-EtOPhTeCl$_3$ is present in its molecular form in solution, that is as p-EtOPhTeCl$_3$ molecules. Therefore on this basis I argue that the trichloride is present in solution as p-EtOPhTeCl$_3$ molecules. Now molecules such as MX$_4$ having a lone pair of electrons are expected to be based on the trigonal bipyramid. Now, the lone pair of electrons will take up the equatorial position together with the aryl group. This is due to the fact that equatorial positions have more s character in the tellurium orbitals. The third equatorial position will be taken up by one of the chlorides. This leads to the structure, R = p-EtOPh

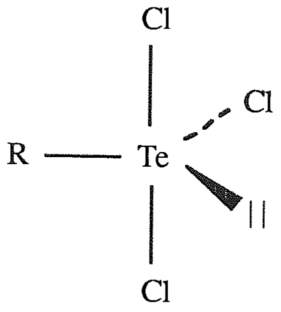


Fig 5-11

Next the identity of the leaving group must be established. During the reaction, acid is released observed as a drop in the pH-meter reading and the reaction is also acid catalysed. Whether the process is associative or dissociative, the tellurium species is protonated first to give

$$[RTe(H)Cl_3]^+$$

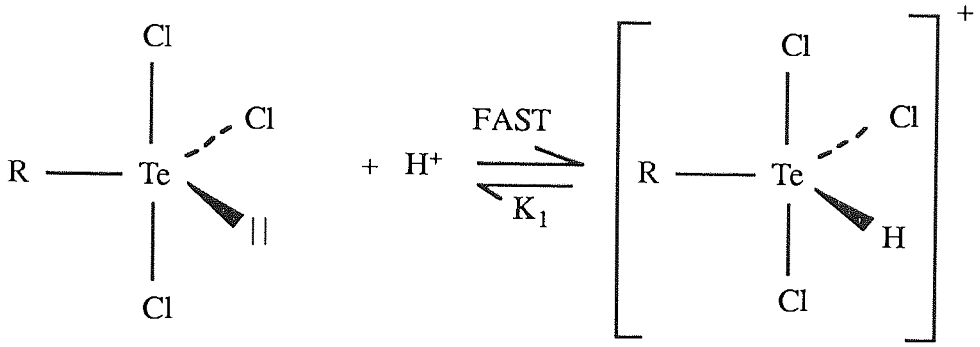
or a solvated derivative thereof

$$[RTe(H)Cl_3(MeOH)_n]^+$$

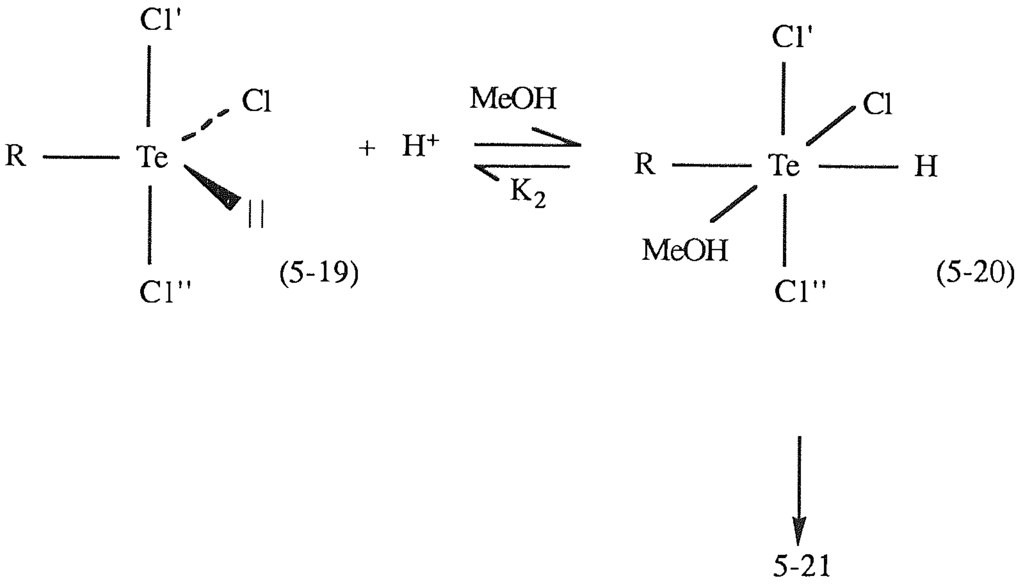
Now, if one of the chlorides were to leave as Cl^- the result would be a doubly charged cation. This would be expected to be more difficult after protonation as an anion would be leaving a cation, rather than leaving a neutral reagent . Therefore on this basis I argue that the leaving group is HCl.

$$[RTe(H)Cl_3(MeOH)_n]^+ \longrightarrow [RTeCl_2(MeOH)_n]^+ + HCl \qquad \text{---(5-19)}$$

The species $[RTeCl_2]^+$, has been suggested as an intermediate by Petragnani[108] to explain the condensation reaction of various aryltellurium trihalides with acetone, acetophenone, N-dimethylaniline and resorcinol. However, earlier I argued that p-EtOPhTeCl_3 is present in its molecular form in solution and this would rule out the species p-EtOPhTeCl_2^+. Since a dissociative mechanism requires an intermediate of lower coordination number, the conclusion is that the solvolysis is not dissociative in nature. Also, the large negative entropy of activation, -222 J mol^{-1} K^{-1}, is indicative of an associative process. The size of the tellurium atom would enable a methanol molecule to form an octahedral intermediate with little steric strain. So it would appear that essentially we are dealing with an associative process. Here I show protonation of the tellurium species is the first step

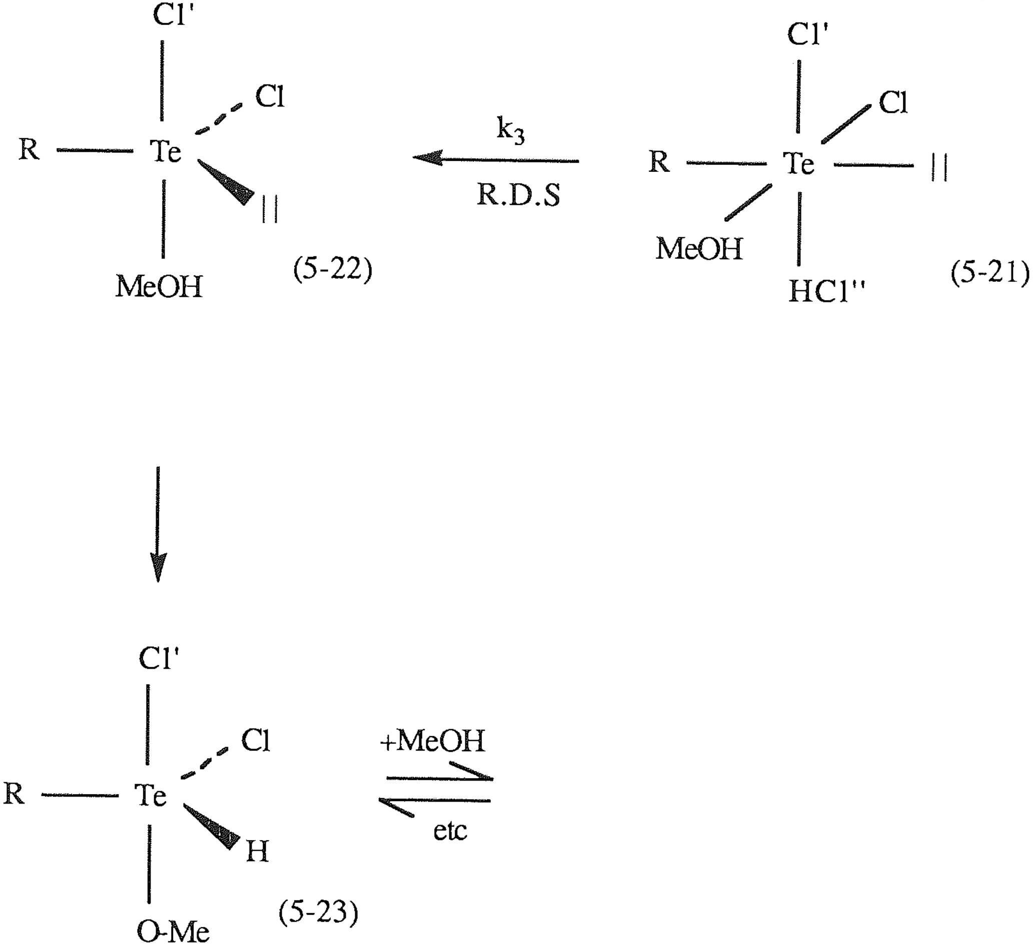


The scheme presented for an associative process would then be 5-20 - 5-23, where R = p-EtOPh and R.D.S = Rate Determining Step, Cl', Cl" and Cl distinguish between the chlorines present. Note equations 5-19 to 5-23 are positively charged, due to protonation and for convenience the charge is not shown.



(5-19)

(5-20)



Note that in order to produce an acceptable trigonal bipyramial product, two of a set of aryl, lone pair and leaving group must be trans to each other. Thus it can be seen that attack by methanol trans to the aryl group will force the aryl group or lone pair to take up the unacceptable apical position if HCl is to be lost. Therefore attack by methanol on the protonated tellurium species occurs cis to the aryl group. This gives the intermediate 5-20 and shows that all the chlorines are cis to the lone pair, thus protonation of one of the chlorines is achieved easily. HCl will be a good leaving group under my experimental conditions and thus 5-21 is able to lose HCl to give the trigonal bipyramidal product 5-22 with R, Cl' and lone pair in the equatorial positions.

The feature of acid catalysis would presumably be due to protonation of the lone pair. This would provide a very mobile proton which can migrate rapidly around the intermediate. Under my experimental conditions the rate determining step is loss of the first chloride, k_3. Since the reaction is autocatalytic and acid catalysed, loss of the remaining chlorides is likely to be fast and thus no kinetic information is available.

Further evidence that acid catalysis is necessary comes from the observation that the solvolysis occurs in protic solvents such as water and alcohols. In aprotic solvents such as benzene, THF and 1,4-dioxane under dinitrogen, p-$EtOPhTeCl_3$ does not undergo solvolysis, observed by the persistent yellow colour of the trichloride.

Now, the suggested scheme involves two equilibria involving protonation followed by attack by methanol to form an intermediate which then loses HCl. The full scheme for the loss of the first chloride can be written as

$$RTeCl_3 \quad + \quad H^+ \quad \underset{\text{FAST}}{\overset{K_1}{\rightleftharpoons}} \quad [RTe(H)Cl_3]^+ \qquad \text{---(5-20)}$$

$$[RTe(H)Cl_3]^+ \quad + \quad MeOH \quad \underset{\text{FAST}}{\overset{K_2}{\rightleftharpoons}} \quad [RTe(H)Cl_3(MeOH)]^+ \qquad \text{---(5-21)}$$

$$[RTe(H)Cl_3(MeOH)]^+ \quad \xrightarrow[\text{slow}]{k_3} \quad [RTeCl_2(MeOH)]^+ \quad + \quad HCl \qquad \text{---(5-22)}$$

this gives

$$k_{obs} = k_3 \left[\frac{K_1[H^+]}{1 + K_1[H^+]}\right]\left[\frac{K_2[MeOH]}{1 + K_2[MeOH]}\right] \qquad \text{---(5-23)}$$

Since methanol is in a large excess then we can assume that $K_2[MeOH] >> 1$ then we have

$$k_{obs} = k_3 \left[\frac{K_1[H^+]}{1 + K_1[H^+]}\right] \qquad \text{---(5-24)}$$

Now, if $1 >> K_1[H^+]$ then

$$k_{obs} = k_3 K_1 [H^+]$$

where $k_s = k_3 K_1$

ie the rate of solvolysis is related to the final acid concentration which is found experimentally. Notice we need the two equilibria to be in sequence in order to obtain this relationship, although K_1 and K_2 could be interchanged. Note that the rate constant, k_s, is made up of two terms K_1 and k_3.

CONCLUSION

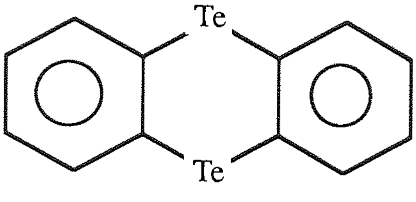
The solvolysis of p-$EtOPhTeCl_3$ has been studied in methanol/benzene media. The solvolysis is acid catalysed and substitution of the first chlorine is rate determining. Acetic acid has no effect on the rate whereas sodium acetate retards the rate because the acetate removes hydrogen ions as undissociated acid. Different alcohols show different effects on the rate due to changes in their acidities. A large negative entropy of activation, -222 J mol^{-1} K^{-1}, indicates that the reaction is associative. The scheme suggested involves two equilibrium steps, protonation and attack by methanol, to form an intermediate octahedral tellurium species, followed by the rate determining step, loss of HCl.

CHAPTER SIX

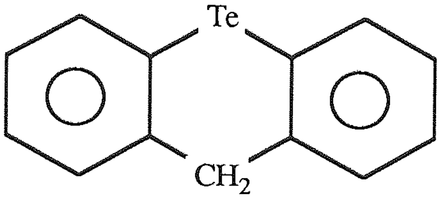
TELLURIUM HETEROCYCLICS

6-1 INTRODUCTION

In this chapter I describe the synthesis of Telluranthrene(A) and the attempts to synthesise Telluraxanthene(B).



A



B

The kinetic and mechanistic studies undertaken described earlier involve using the diaryl ditellurides and aryl tellurium trichlorides. My attention is now being turned to compounds of tellurium in which the tellurium atom is in a rigid position. One possible method of achieving this is by putting the tellurium atom in a cyclic structure such as telluranthrene and telluraxanthene.

Telluranthrene has been reported twice in the literature. The first reported synthesis was by Schmidt and Schumann[127], who heated tetraphenyltin(IV) and tellurium metal at 310°C under vacuum. The products isolated were reported to be diphenyltelluride, diphenyl and telluranthrene, as a brown substance depositing tellurium on exposure to air.

Dereu and Zingaro[49] synthesised and characterised telluranthrene by heating o-phenylenemercury(II) with tellurium metal in a sublimation apparatus at 250°C for ten hours. Telluranthrene was isolated as a pale yellow solid. The mechanism was suggested to involve a free radical reaction with tellurium(scheme 6-1).

$$-\mathrm{Hg}\text{-}\mathrm{C_6H_4}^{\cdot} + \mathrm{Te} \longrightarrow -\mathrm{Hg}-\mathrm{C_6H_4}\text{-}\mathrm{Te}^{\cdot}$$

$$-\mathrm{Hg}-\mathrm{C_6H_4}-\mathrm{Te}^{\cdot} + {}^{\cdot}\mathrm{C_6H_4}-\mathrm{Hg}- \longrightarrow -\mathrm{Hg}-\mathrm{C_6H_4}-\mathrm{Te}-\mathrm{C_6H_4}-\mathrm{Hg}-$$

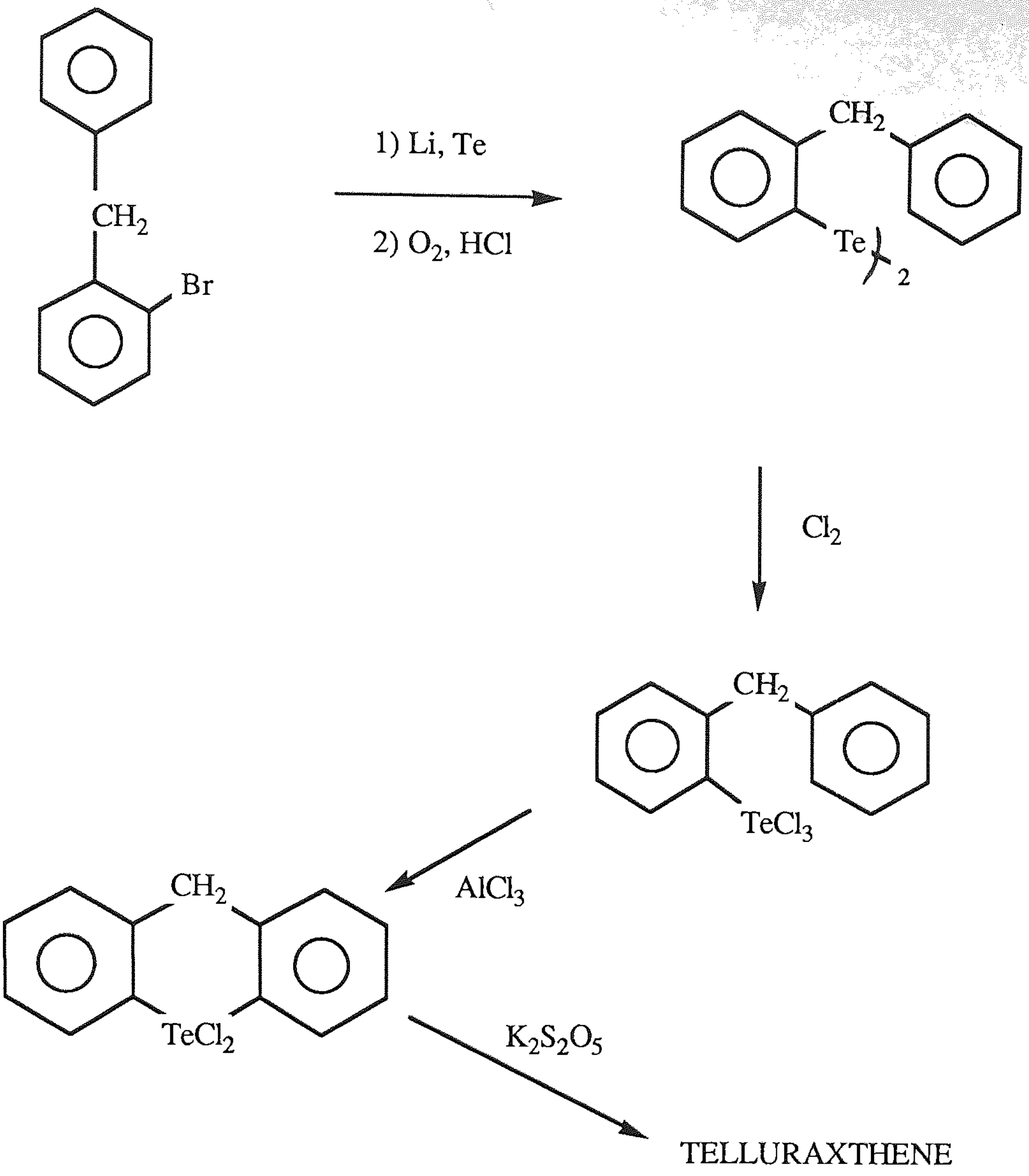
and further steps

$${}^{\cdot}\mathrm{Te}-\mathrm{C_6H_4}-\mathrm{Te}-\mathrm{C_6H_4}^{\cdot} \longrightarrow \text{TELLURANTHRENE}$$

SCHEME 6-1 : Synthesis of Telluranthene

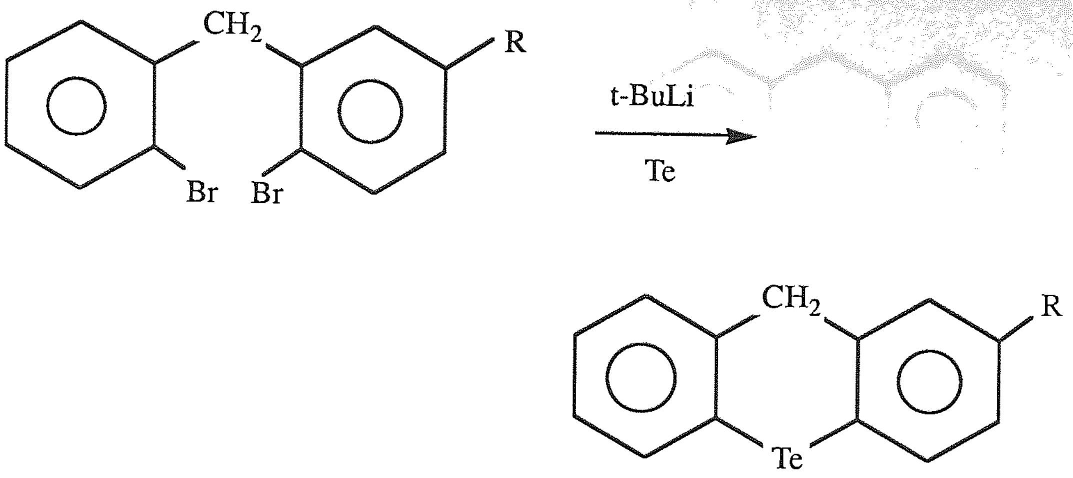
These authors were, however, unable to duplicate the earlier synthesis. One probable explanation is that in the early synthesis a closed vessel was used. Thus any telluranthrene formed in it would probably have decomposed under these experimental conditions. There are no literature reports of any reactions of telluranthrene at the present time.

Telluraxanthene has been reported by three different methods in the literature. The first reported synthesis[128] was in 1978. This involves preparing bis (2-benzyl phenyl) ditelluride followed by oxidation using chlorine to give the trichloride. This was then cyclised to give the 5,5-dichloro compound, which was finally reduced by potassium metabisulphite to give telluraxanthene, with an overall yield of 50% (scheme 6-2).



SCHEME 6-2 : Synthesis of Telluraxanthene

The second method was reported by Lohner and Praefcke[51] and involves the incorporation of tellurium into 2,2'-dibromodiphenylmethane (scheme 6-3)

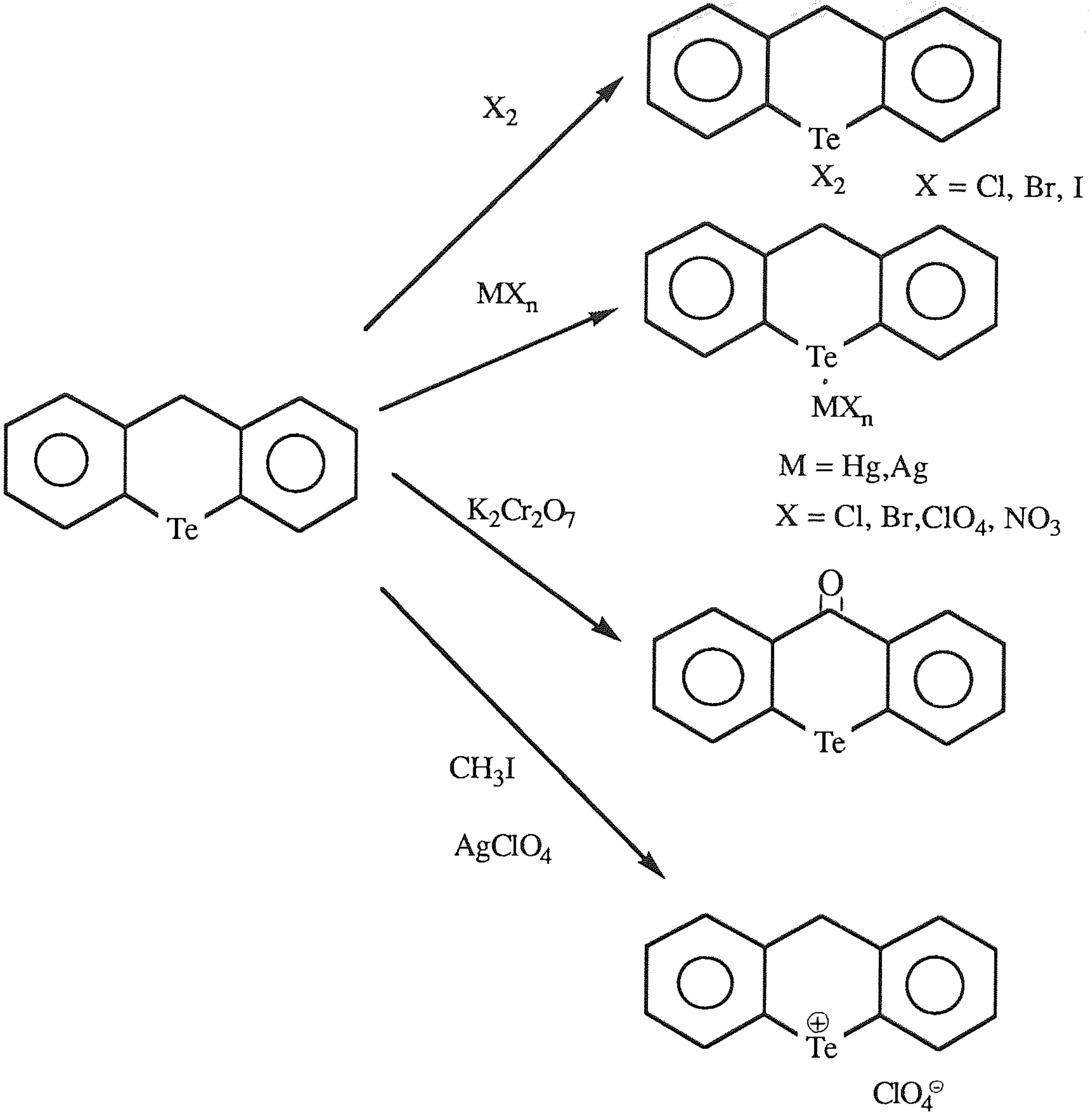


$R = CH_3, H$

SCHEME 6-3 : Synthesis of Telluraxanthene by direct incorporation of tellurium

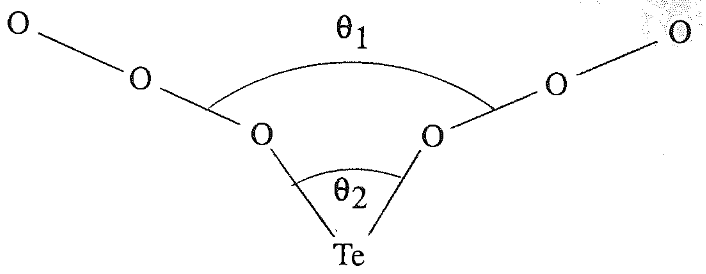
The third method was a low yield (2%) synthesis involving cyclisation of the diazonium salt $[(2N_2^+C_6H_4)CO2Cl^-]$ with sodium telluride (Na_2Te)[129].

Telluraxanthene is characterised by reactions that are usually observed for diaryl tellurides. It readily adds halogens (chlorine, bromine and iodine) to give the corresponding 10,10-dihalotelluraxanthene. It also forms 1:1 complexes with mercury and silver salts but does not form telluronium salts with methyl iodide[128]. Reactions at the methylene group involve oxidation by potassium dichromate to give telluraxanthone as shown in Scheme 6-4.



Scheme 4 : Reactions of Telluraxanthene

The crystal structures of telluranthrene[130] and telluraxanthene[131] have been reported and both are similar. Both structures can be described as butterfly shaped. A side view of the molecule illustrates this point.



where O represents the carbons of the phenyl rings.

In telluranthrene the dihedral angles between the phenyl rings are $124^{o}(\theta_1)$ and the dihedral angle, θ_2, between the halves of the central ring are 120^{o} whilst the bond angle C-Te-C is 95.6^{o}. The bond length C-Te is 2.11A.

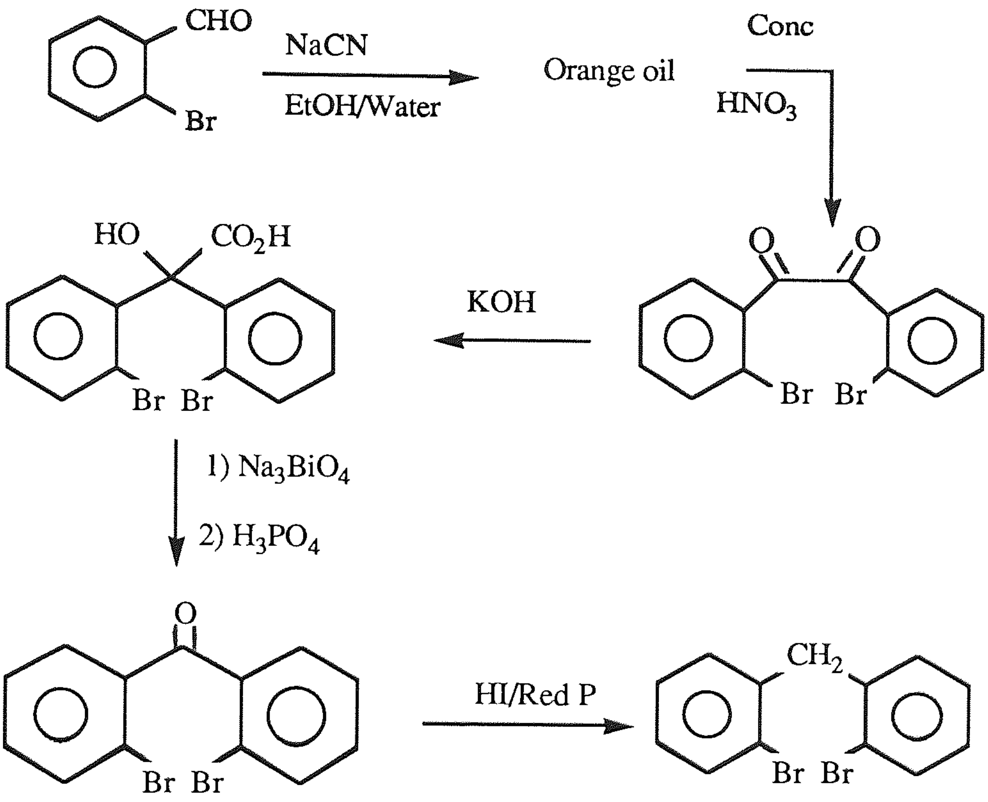
In telluraxanthene the central ring is puckered distorting the shape compared to telluranthrene. In this case the tellurium atom lies above the carbon in the central ring. The dihedral angle θ_1 is 129.6^{o} whereas the dihedral angles, θ_2, at the tellurium and methylene ends of the molecule are 151.9^{o} and 132.7^{o} respectively. The C-Te bond length is 2.14Å similar to that in telluranthrene. It can therefore be seen that the the two structures of the two heterocyclics are similar to the ditellurides when considering the tellurium atoms. In both compounds the tellurium is exposed on one side to attack by various reagents.

6-2 RESULTS

The synthesis of telluranthrene was carried out from the method of Dereu and Zingaro. This requires o-phenylenemercury(II) as one of the starting materials. o-phenylenemercury(II) was prepared by the method of Winkler and Wittig[48]. The operation was successfully undertaken without any problems. The yield was about 20% and involved a very time consuming work up. The product melted at 332°C compared to the literature value of 332-4°C. Elemental analysis, C;26.2%: H; 1.70%: agreed with the expected values C;26.04% : H; 1.46%:

The preparation of telluranthrene in a sublimation apparatus was successfully carried out three times, and gave a yellow crystalline solid. The ^{1}H NMR spectrum (fig 6-1) shows two multiplets at 8.05-7.98δ and 7.13-7.26δ. The proton decoupled ^{13}C spectrum (fig 6-2) shows three signals at 136.53δ, 130.60δ and 128.41δ. The mass spectrum gave the following molecular ion peaks, with intensities relative to the diphenylene peak M= 152 as unity, 412(0.37), 410(0.70), 408(0.74), 406(0.50). Other peaks of interest are 336(0.11), 282(0.88). 206(0.13). The IR spectrum is shown in fig 6-3.

The synthesis of telluraxanthene was attempted by the method of Lohner and Praecke. This involved synthesising 2,2'-dibromodiphenylmethane from 2-bromobenzaldehyde. There were two literature methods in which the dibromo compound could be synthesised. Thorp and Wildman prepared it from 3-nitrobenzaldehyde with an overall yield of ~5%. However, a more recent method was used because it was much simpler and gave a better overall yield (~10% from the literature). The method involves a benzoin condensation of 2-bromobenzaldehyde followed by nitric acid oxidation to give 2,2'-dibromobenzil. Rearrangement of the benzil gives dibromobenzillic acid which is then oxidised by sodium bismuthate in glacial acetic acid to give dibromobenzophenone. Reduction with hydroioiodic acid and red phosphorus yielded 2,2'-dibromodiphenylmethane in 9% yield as shown below in scheme 5



Scheme 5 : Synthesis of 2,2'-dibromodiphenylmethane

The attempted synthesis of telluraxanthene used t-butyl lithium. However, twice I attempted the synthesis and failed. The solid that came from the water layer melted >200°C and the chloroform layer yield a red gum.

Mass	Intensity	Assignment
412	0.37	
410	0.70	Molecular
408	0.74	Ion
406	0.50	
336	0.11	o-Phenylene ditelluride
282	0.88	Dibenzotellurophene
206	0.13	o-Phenylenetelluride
152	1.00	Diphenylene

Table 6-1 Mass spectra of Telluranthrene

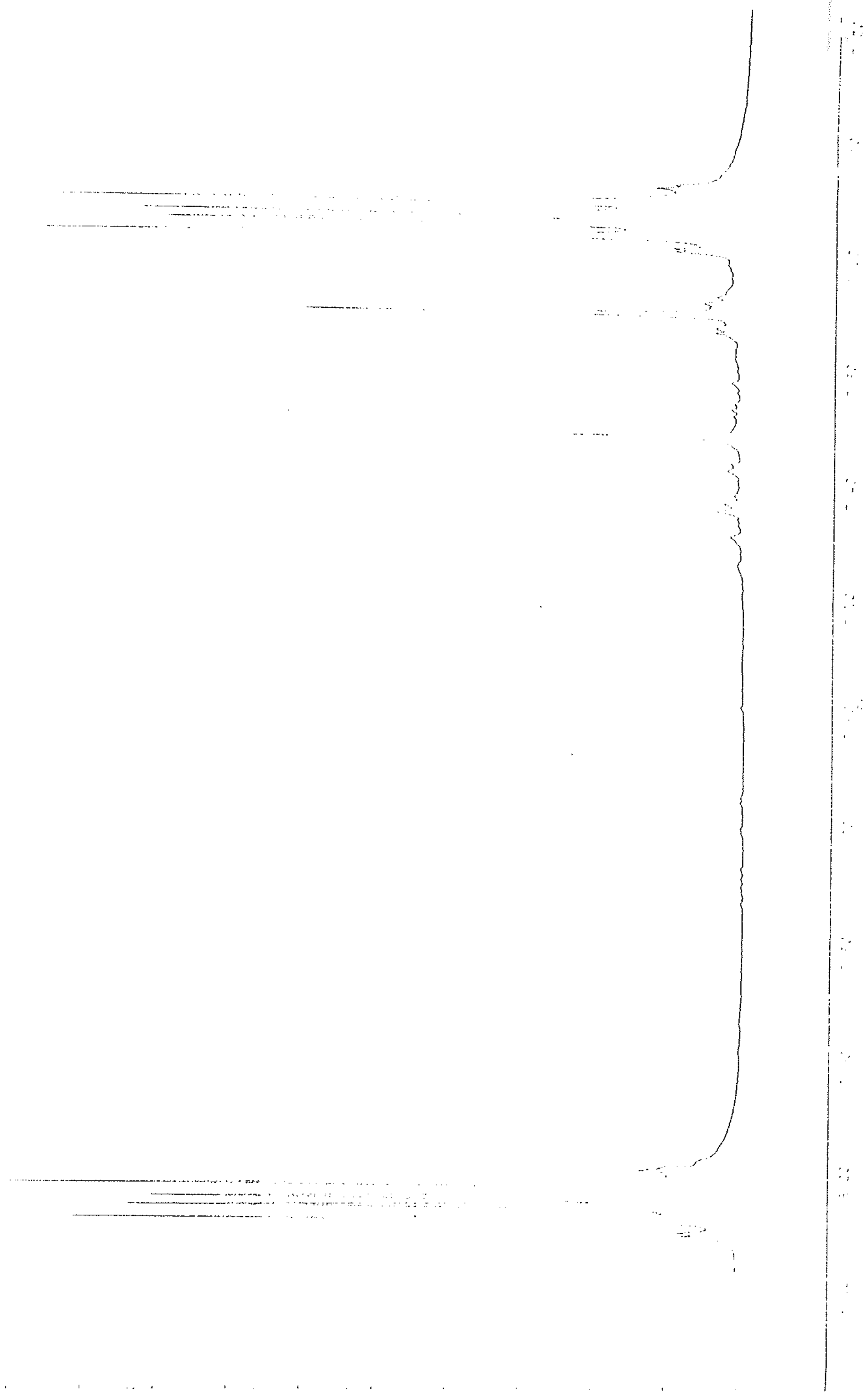


Fig 6-1 ^{1}H NMR spectrum of Telluranthrene in $CDCl_3$.

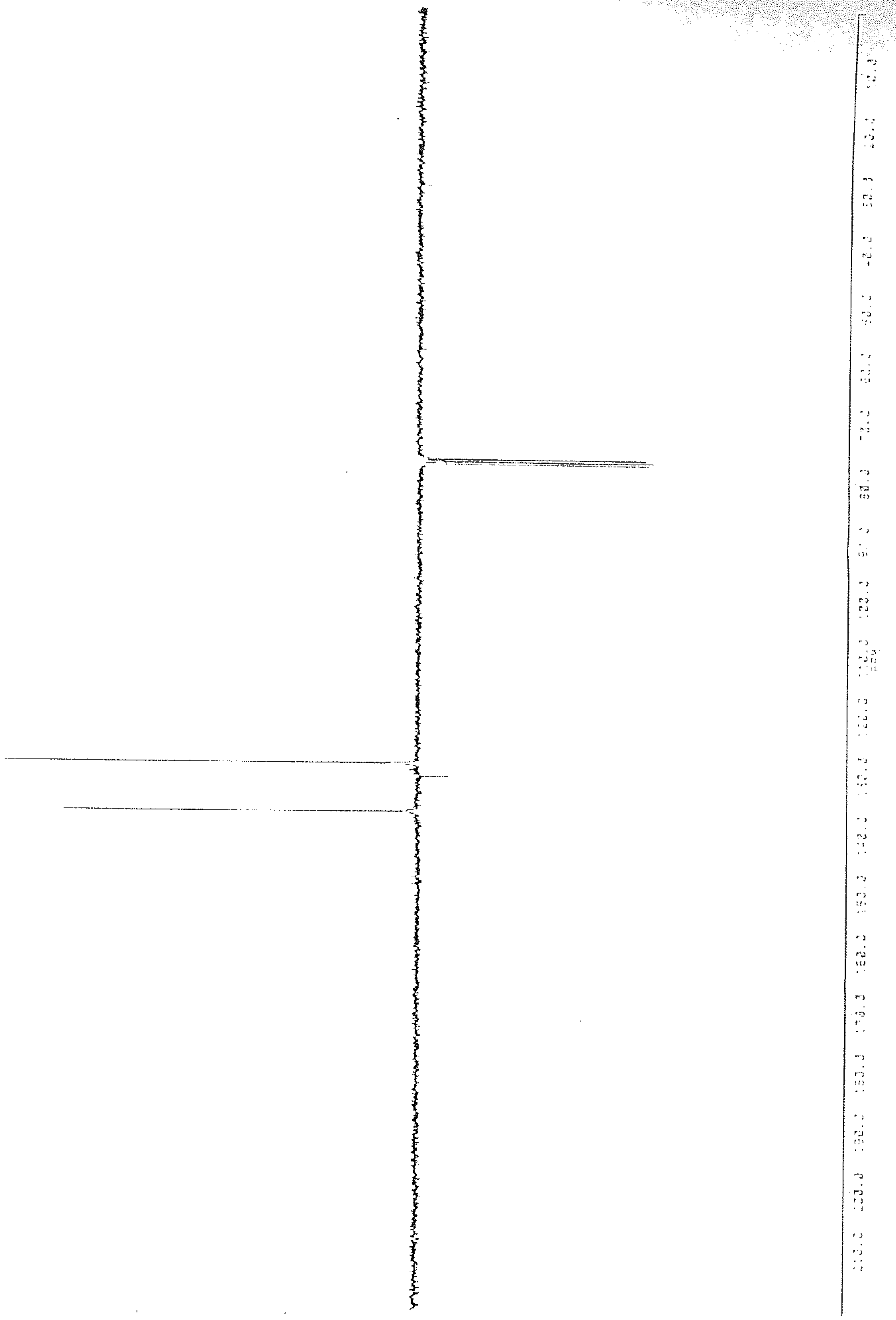


Fig 6-2 ^{13}C NMR spectrum of Telluranthrene in $CDCl_3$.

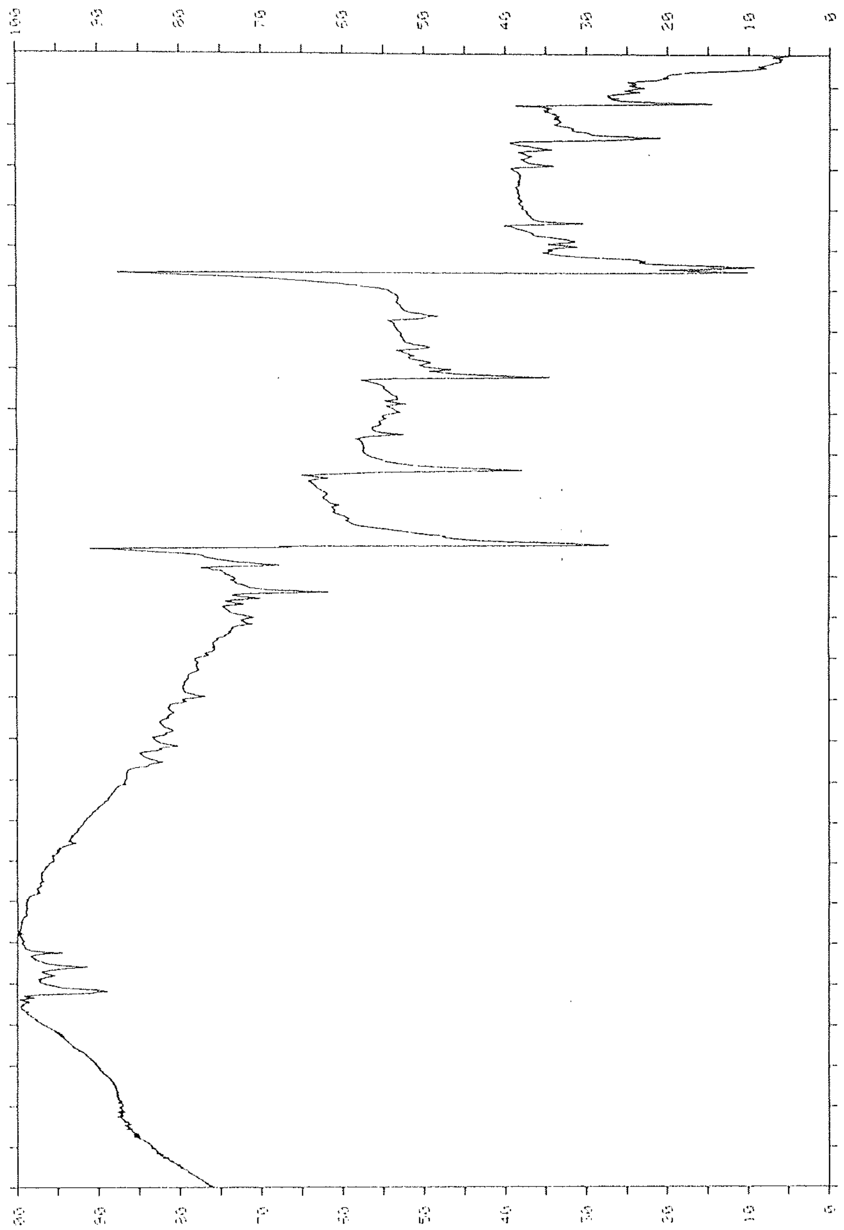


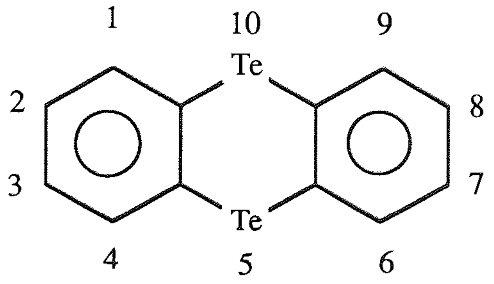
Fig 6-3 IR spectrum of Telluranthrene as a KBr disc.

6-3 DISCUSSION

The results described in this chapter involve the synthesis and characterisation of telluranthrene and attempts to synthesise telluraxanthene.

The synthesis of telluranthrene was carried out successfully by heating in vacuum tellurium metal and o-phenylenemercury(II). The o-phenylenemercury(II) compound was prepared from a sodium-mercury amalgam in contact with an ethereal solution of o-dibromobenzene. The preparation involved considerable work up and a low yield ~10-20%. On the scale used, however, 12g was sufficient for the next stage.

The preparation of telluranthrene resulted in a low yield ~30% and gave ~1g of product. Characterisation of the product indicated that it was telluranthrene. The ^{1}H NMR spectra was characterised by aromatic multiplets at 7.9 and 7.1δ. The latter was attributed to protons attached to carbons 2,3,7 and 8 (shown below) as they are closer to the proton resonances observed in benzene.



The proton decoupled ^{13}C NMR spectrum consists of three peaks, two intense peaks at 136.53δ and 128.41δ, and a weak resonance 130.66δ. This is in agreement with that found in the literature. Unfortunately I did not have ^{125}Te coupling. However, the literature indicated that the weak resonance was due to the carbons bonded directly to the tellurium, whereas the resonance at 136.53δ was attributed to carbons 1,4,6 and 9. Carbons 2,3,7 and 8 due to the 128.41δ.

The mass spectrum is also in agreement with the literature. The molecular ion peaks were 412, 410, 408, 406 with the relative intensities in agreement to that found in the literature. Fragmentation of telluranthrene occurs in the following pattern

$$\begin{tikzcd}
\begin{array}{c}\text{Telluranthrene}\\ 412\end{array} \arrow[r, "-C_6H_4"] \arrow[d, "-Te"] & \begin{array}{c}\text{o-phenylene ditelluride}\\ C_6H_4Te_2^{\ +}\\ 336\end{array} \arrow[d, "-Te"] \\
\begin{array}{c}\text{Dibenzotellurophene}\\ C_{12}H_8Te^{\ +}\\ 282\end{array} \arrow[r, "-C_6H_4"] \arrow[d, "-Te"] & \begin{array}{c}\text{o-phenylenetelluride}\\ C_6H_4Te^{\ +}\\ 206\end{array} \\
\begin{array}{c}\text{Diphenylene}\\ C_{12}H_8^{\ +}\\ 152\end{array} &
\end{tikzcd}$$

Loss of one tellurium results in the formation of dibenzotellurophene, $C_{12}H_8Te^+$ 282. The loss of another tellurium gives the most intense fragment, diphenylene $C_{12}H_8^+$ at 152. Loss of C_6H_4 from telluranthrene yields o-phenyleneditelluride $C_6H_4Te^+$, 336, which upon loss of one tellurium yields o-phenylenetelluride,

$C_6H_4Te^+$ 206.

The IR spectrum, fig 6-3, shows C-H absorptions at 3037 cm^{-1} and 754 cm^{-1} due to aromatic C-H. Unfortunately the lack of time has prevented any kinetic and mechanistic studies from been carried out.

The synthesis of telluraxanthene was the next aim of this chapter. In the literature there are two methods of preparation. I chose the German synthesis because it was a direct method. The overall yield from the German and Russian methods are similar.

The method I chose involves synthesising the organic starting material, 2,2'-dibromo diphenylmethane. Thorp and Wildman used 3-nitrobenzaldehyde and the method required six stages with an overall yield ~5%. However, the more recent method involves four stages and a higher overall yield ~10%. Each stage was carried out and gave compatible yields as in the literature.

The telluraxanthene preparation involved using t-butyl lithium in the final stage and the literature yield was 50%. However, despite doing the reaction twice I was unable to synthesise the tellurium heterocyclic. Two products were obtained. A red gum from the chloroform layer showing no crystalline material. The second product was a pale tan powder which melted >200°C, far higher than that expected for telluraxanthene, 151-2°C .

It therefore appears that I have failed to synthesise telluraxanthene. Exactly what went wrong I am not sure but with hindsight it would probably have been better to use the Russian method.

Telluranthrene was successfully prepared and characterised. The method used could be built up to a larger scale to enable more quantities to be available for studies. The preparation of telluraxanthene was unsuccessful but the Russian method might prove more fruitful.

APPENDIX I

```
10  REM :FIRST ORDER FIT FOR INCREASE IN PRODUCT:VIZ,INCREASE IN R2TE2 I
     N REDU.
11  REM :FOR DECREASE IN REACTANT CONC,CHANGE LINES;60,150,200&410
12  REM :FOR INCREASE IN REACTANT CHANGE LIES,60,150,200,&290
20  DIM A(50),L(50),T(50)
40  REM ;RUN TITLES
45  INPUT "RUN TITLE ?";T$:
50  INPUT "INITIAL TE CONC";TE
60  INPUT "INITIAL H2O2 CONC ";H2
75  INPUT "INITIAL H+ CONC";AC
80  INPUT "TEMP=";DC
90  REM :RECORDER SCALING AND
91  DATA  INPUT
105  INPUT "INITIAL AND FINAL ABSORANCES :-";A,B
115  INPUT "INITIAL AND FINAL PEN READINGS:-";P,Q
120  INPUT "SPEED OF PAPER(S/CM):-";S
130  INPUT "DISTANCE IN CM TO 1ST READING";C
140  INPUT "DISTANCE BETWEEN SUCCESSIVE  READINGS";D
150 P = (A - B) / (P - Q):TT = S * C - D:D = D * S
160  PRINT "INPUT SUCCESSIVE PEN READINGS      "
170  PRINT "TO INDICATE END OF RUN TYPE        -1":N = 1
180  INPUT A: IF A =  - 1 THEN 210
190 A(N) = P * (A - Q):T(N) = N * D
200 L(N) =  LOG (A(N)):N = N + 1: GOTO 180
210 N = N - 1
215  REM :CALCULATION SECTION
217 NN = 1
220 A = 0:B = 0:C = 0:D = 0: FOR I = NN TO N
230 A = A + L(I):B = B + T(I)
240 C = C + L(I) * T(I):D = D + T(I) * T(I): NEXT I
250 Z = (A * D - B * C) / (N * D - B * B)
260 K = (Z * N - A) / B
270  REM  :OUTPUT SECTION
280 S = 0: FOR I = NN TO N
290 A =  EXP (Z - K * T(I)):S = S + (A - A(I)) ^ 2
300  IF  INT (I / 10) = I / 10 THEN  GET A$
310  PRINT TT + T(I),A(I),A: NEXT I
320  PRINT "SUM OR SQUARED DIFFERENCES="S
325  PRINT "REPEAT RUN DROPPING SOME POINTS?TYPE IN NUMBER OF POINTS TO
     BE DROPPED AND OF LATE POINTS": INPUT NE,NL
330  IF NE = 0 AND NL = 0 THEN 350
340 N = N - NE - NL:NN = 1 + NE: GOTO 220
350  PR£ 1: PRINT : PRINT "INITIAL CONCS OF TE,H2O2,H+,TEMP ARE ": PRINT

360  PRINT TE,H2,AC,DC: PRINT
365  PRINT : PRINT T$: PRINT
367  PRINT "RATE CONSTANT ="K"SEC-1": PRINT
370  PRINT "DATA AS TIME OBSERVED A AND  CALC A ARE": PRINT
380  PRINT "SUM OR SQUARED DIFFERENCES="S
390  PRINT "DATA AS TIME OBSERVED A AND  CALC ARE": PRINT
400  FOR I = NN TO N
410 A =  EXP (Z - K * T(I)):S = S + (A - A(I)) ^ 2
420  PRINT TT + T(I),A(I),A: NEXT I
430  PR£ 0: PRINT "ANOTHER RUN?": INPUT A$
440  IF A$ = "Y" THEN 45
450  END
```

APPENDIX II

```
5  REM   STOP ** CUSTOMISED LINEAR REGRESSION ***
10  REM  *** THE PROGRAM CONVERTS THE INPUT DATA TO THE LINEAR FUNCTIONS
      REQUIRED ***
15  REM  - WRITTEN BY S.J.MOSS (20TH MAY 1981)
18  REM  - REVISED 7TH JULY 1982
20  TEXT : HOME :ZX = 0
25  DIM X(40),Y(40),W(40)
26  DIM XO(40),YO(40)
30  GOSUB 4000
32  DEF  FN X(XI) = XI * 1E - 3
34  DEF  FN Y(YI) = (YI * 1E - 3)
40  HOME : PRINT
45  GOSUB 3000: REM  * TITLES *
49 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
50  INPUT "NUMBER OF DATA POINTS = ";N
60  PRINT : PRINT "CHOOSE WEIGHTING OPTION (1,0,-1):- ": PRINT
70  PRINT "+1 FOR UNIT WEIGHTING"
80  PRINT " 0 FOR STATISTICAL WEIGHTING"
90  PRINT "-1 FOR INSTRUMENTAL WEIGHTING"
100  PRINT : INPUT WI: HOME
120  PRINT "ENTER X AND Y SEPARATED BY A COMMA:-"
130  FOR I = 1 TO N
140  INPUT XO(I),YO(I):XI = XO(I):YI = YO(I)
145 X(I) =  FN X(XI):Y(I) =  FN Y(YI)
150  IF WI = 1 THEN W(I) = 1: GOTO 200
160  IF WI = 0 THEN W(I) = 1 / Y(I): GOTO 200
170  INPUT "ENTER INSTRUMENTAL WEIGHTING:- ";S:W(I) = 1 / S ^ 2
200  NEXT I
299 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
300  REM  - CALCULATE APPROPRIATE SUMS
310 SU = 0:SX = 0:SY = 0:XX = 0:YY = 0:XY = 0:SR = 0
320  FOR I = 1 TO N
330 SU = SU + W(I)
340 SX = SX + X(I) * W(I)
350 SY = SY + Y(I) * W(I)
360 XY = XY + X(I) * Y(I) * W(I)
370 XX = XX + X(I) ^ 2 * W(I)
380 YY = YY + Y(I) ^ 2 * W(I)
390  NEXT I
499 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
500  REM  - CALCULATE REGRESSION PARAMETERS
510 D = SU * XX - SX ^ 2
520 C = (XX * SY - SX * XY) / D
530 Q = SU * XY - SX * SY
540 M = Q / D
545 J1 =  ABS (D * (SU * YY - SY ^ 2))
550 J =  SQR (J1)
560 RO = Q / J
799 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
800  REM  - OUTPUT
810  PRINT  CHR$ (4);"PR#1"
812  PRINT : PRINT NA$;"  (";DA$;")": PRINT
814  PRINT " ";TITLE$;" ": PRINT
816  IF S$ <  > "Y" THEN 830
820  PRINT ST$: PRINT
825  PRINT "W = WEIGHTING FACTOR.  ": PRINT
830  IF ZX = 1 THEN  GOSUB 2000: GOTO 975: REM   * PRINT FULL TABLE
840  GOSUB 2500: REM  * PRINT SHORT TABLE
975 SIGMA =  SQR (SR / (N - 2))
980 DC = SIGMA *  SQR (XX / D)
985 DM = SIGMA *  SQR (SU / D)
999 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
```

```
1000  REM  - REGRESSION PARAMETERS
1020  PRINT "     SLOPE = ";M,"+/- ";DM;"  (": INT (1000 * DM / M + .5) /
     10;"%)": PRINT
1030  PRINT "INTERCEPT = ";C,"+/- ";DC;"  (": INT (1000 * DC / C + .5) /
     10;"%)": PRINT
1035  PRINT "THE VARIANCE OF THE FIT IS ";SIGMA
1040  PRINT "THE CORRELATION COEFFICIENT IS "; INT (10000 * RO + .5) / 1
     0000: PRINT
1200  PRINT  CHR$ (4);"PR£0"
1210  HOME : INPUT "RUN AGAIN?  ";ANS$
1220  IF ANS$ = "Y" THEN 1300
1250  END
1300  PRINT : INPUT "SAME FUNCTIONS? ";ANS$
1310  IF ANS$ = "N" THEN 30
1320  HOME : GOSUB 3030: HOME : GOTO 50
1999 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
2000  REM  *** PRINT OUT FULL TABLE ***
2010  PRINT "W";: POKE 36,10: PRINT "X";: POKE 36,25: PRINT "FN(X)";: POKE
     36,40: PRINT "Y";: POKE 36,55: PRINT "FN(Y)";
2020  POKE 36,70: PRINT "M*FN(X) + C";: POKE 36,85: PRINT "DIFFERENCE"
2030  POKE 36,25: PRINT X$;: POKE 36,55: PRINT Y$
2050  FOR I = 1 TO 100: PRINT "-";: NEXT : PRINT
2100  FOR I = 1 TO N
2110  PRINT W(I);: POKE 36,10: PRINT XO(I);: POKE 36,25: PRINT X(I);: POKE
     36,40: PRINT YO(I);: POKE 36,55: PRINT Y(I);
2120 YCALC = M * X(I) + C:R1 = Y(I) - YCALC
2130  POKE 36,70: PRINT YCALC;: POKE 36,85: PRINT R1
2150 R = W(I) * R1 * R1:SR = SR + R
2160  NEXT I
2190  FOR I = 1 TO 100: PRINT "-";: NEXT : PRINT : PRINT
2200  RETURN
2499 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
2500  REM  *** PRINT OUT SHORT TABLE ***
2510  PRINT "W";: POKE 36,10: PRINT "X";: POKE 36,25: PRINT "Y";
2520  POKE 36,40: PRINT "M*FN(X) + C";: POKE 36,55: PRINT "DIFFERENCE"
2530  POKE 36,10: PRINT X$;: POKE 36,25: PRINT Y$
2550  FOR I = 1 TO 70: PRINT "-";: NEXT : PRINT
2600  FOR I = 1 TO N
2610  PRINT W(I);: POKE 36,10: PRINT X(I);: POKE 36,25: PRINT Y(I);
2620 YCALC = M * X(I) + C:R1 = Y(I) - YCALC
2630  POKE 36,40: PRINT YCALC;: POKE 36,55: PRINT R1
2650 R = W(I) * R1 * R1:SR = SR + R
2660  NEXT I
2690  FOR I = 1 TO 70: PRINT "-";: NEXT : PRINT : PRINT
2700  RETURN
2999 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
```

```
3000  REM  *** TITLES & COLUMN HEADINGS ***
3010  HOME : INPUT "NAME?  ";NA$: PRINT
3020  INPUT "DATE? ";DA$: PRINT
3030  INPUT "TITLE FOR TABLE?  ";TITLE$: PRINT
3040  INPUT "LIKE A SUB-TITLE? (Y OR N)  ";S$
3050  IF S$ <  > "Y" THEN 3100
3060  PRINT : INPUT "SUBTITLE?  ";ST$: PRINT
3100  PRINT : PRINT "WHAT COLUMN HEADINGS WOULD YOU LIKE? ": PRINT
3110  INPUT "FOR THE 'X' COLUMN?  ";X$: PRINT
3120  INPUT "FOR THE 'Y' COLUMN?  ";Y$: PRINT
3200  HOME : RETURN
3999 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
     ::::::::
4000  REM  - TITLE PAGE
4010  PRINT "      **********************"
4020  PRINT "      * LINEAR REGRESSION *"
4030  PRINT "      **********************"
4040  PRINT : PRINT " BASED ON PROGRAM BY K.J.JOHNSON,"
4050  PRINT "<NUMERICAL METHODS IN CHEMISTRY> P. 246"
4060  PRINT : PRINT "THIS PROGRAM FITS DATA Y(X) TO"
4070  PRINT : PRINT "      Y = M*X + C"
4080  PRINT : PRINT "A MAXIMUM OF 40 DATA POINTS MAY BE USED"
4090  PRINT : PRINT "THE METHOD ALLOWS AN OPTIONAL WEIGHTING"
4095  PRINT "OF DATA ACCORDING TO:-"
4100  PRINT : PRINT "+1 FOR UNIT WEIGHTING (W=1)"
4110  PRINT " 0 FOR STATISTICAL WEIGHTING (W=1/Y)"
4120  PRINT "-1 FOR INSTRUMENTAL WEIGHTING (W=1/S^2)
4122  PRINT "    (WHERE S IS THE STD. DEV. OF Y)"
4130  PRINT : INPUT "PRESS <RETURN> TO CONTINUE ";A$
4200  HOME : PRINT "THIS PROGRAM WILL CONVERT YOUR INPUT    DATA TO FUNC
     TIONS WHICH YOU EXPECT TO BELINEARLY RELATED. ": PRINT
4210  PRINT "THE CURRENT FUNCTIONS ARE ": PRINT
4220  LIST 32,34
4230  PRINT "WHERE XI AND YI ARE THE VALUES ENTERED.": PRINT
4240  PRINT "PRESS <ESC> TO TYPE IN NEW FUNCTIONS, ORANY OTHER KEY TO US
     E THE SAME FUNCTIONS.": GET A$
4250  IF  ASC (A$) <  > 27 THEN 4500
4260 ZX = 1: HOME : LIST 32,34
4270  PRINT : PRINT "DEFINE NEW FUNCTIONS IN THE FORM USED   ABOVE.  USE
      XI AND YI FOR THE INPUT     VALUES. ": PRINT
4300  END
4500  PRINT "HIT <ESC> IF ONE OR BOTH FUNCTIONS ARE  NOT IDENTITIES.  ":
      GET A$
4510  IF  ASC (A$) = 27 THEN ZX = 1
4600  RETURN
```

APPENDIX III

```
10   DIM C(30),D(30),DD(30),X(30)
20   INPUT "RUN TITLE ?";T$: IF T$ = "END" THEN 500
21   TEXT : HOME : VTAB (5): PR£ 1: PRINT "NUMERICAL INTEGRATION OF R2TE2
       + H2O2, WITH FOLLOWING SCHEME"
22   PRINT "PROGRAM ENTITLED <H2O2SS> AND COMPILED AS COMPSS>"
23   PRINT "P = H2O2, Q = R2TE2, R = RTE,                  T = RTE(OH)2 & U = RT
      EOH"
24   PRINT : PRINT "P + Q --K1--> R + T"
25   PRINT "Q + T --K2--> R +2U"
26   PRINT "P + R --K3--> T"
27   PRINT "R + T --K4--> INERT"
29   PRINT "STEADY STATE APPLIED TO R WITH RATIO = K4/K3"
33   PR£ 0
40   INPUT "H2O2 CONC    ";HO
42   INPUT "MULTIPLIER TO CONVERT READING TO CONC";Z
45   INPUT "INIT AND FINAL READINGS  ";C,B:C(0) = (C - B) * Z
50   INPUT "TIME INTERVAL = ";E
55   INPUT "TIME OF FIRST READING";TT:TT = TT / E
60   PRINT "ENTER READINGS, USE -1 AS TERMINATOR":N = 0
70   INPUT F: IF F < 0 THEN 90
80 N = N + 1:C(N) = (F - B) * Z: GOTO 70
90 SS = 100
100  FOR I = 1 TO N:J = I - 1:X(I) = 2 +  INT (100 * (C(J) - C(I)) / C(0
      )): IF C(I) > C(0) / 10 THEN 120
110 N = J: GOTO 200
120  NEXT I
200  PRINT "TYPE IN UPPER AND LOWER LIMITS OF RANGE OF K TO BE TRIED AND
       NUMBER OF TRIALS"
201  PRINT "TO FIX A VALUE ENTER <VAL,-1,1>"
205  INPUT "RANGE FOR K1K2  ";ZL,ZU,ZN
210  INPUT "RANGE FOR K2        ";WL,WU,WN
215  INPUT "RANGE FOR RATIO    ";YL,YU,YN
230  FOR I = 0 TO ZN: IF ZU =  - 1 THEN I = ZN
240 Z = (ZU + (ZL - ZU) * I / ZN) * E * E
243  FOR II = 0 TO WN: IF WU =  - 1 THEN II = WN
246 W = (WU + (WL - WU) * II / WN) * E
248 Z = Z / W
250  FOR J = 0 TO YN: IF YU =  - 1 THEN J = YN
260 Y = YU + (YL - YU) * J / YN
285 Q = C(0):S = 0:T = 0:P = HO
290  FOR L = 1 TO N:ST = X(L): FOR M = 1 TO ST
295 KA = Z * P * Q / ST
296 KB = W * Q * T / ST
297 KC = (KA + KB) * P / (P + Y * T)
299 KD = KA + KB - KC: IF L > 1 THEN 308
300 KA = TT * KA:KB = TT * KB:KC = TT * KC:KD = TT * KD
308 Q = Q - KA - KB
309 P = P - KA - KC
310 T = T + KA - KB + KC - KD
315  NEXT M:DD(L) = Q
319 C = (C(L) - Q) / C(0)
320 S = S + C * C / N: IF S > SS THEN 340
330  NEXT L:SS = S:SZ = Z / E:SY = Y:SW = W / E
335  FOR L = 1 TO N:D(L) = DD(L): NEXT L
340  NEXT J: NEXT II: NEXT I
350  PRINT "BEST FITS HAVE SSD = "SS
360  PRINT "AND K VALUES ARE  ": PRINT SZ * SW" "SW" "SY
370  INPUT "ANOTHER TRIAL";A$
380  IF A$ = "Y" THEN 200
390  IF A$ = "N" THEN 410
400  GOTO 370
410  PR£ 1: PRINT : PRINT T$: PRINT : PRINT "AVERAGE FRACTIONAL SSD = "S
     S: PRINT : PRINT "CONSTANTS IN ORDER OF ENTRY ARE": PRINT SZ"    "SW
     "    "SY: PRINT : PRINT
415  PRINT "INITIAL CONCS ARE  "C(0)"    "HO
420  FOR I = 1 TO N: PRINT C(I)"    "D(I): NEXT I
430  FOR I = 1 TO 5: PRINT : NEXT I: PR£ 0: INPUT "SAME DATA? ";A$: IF A
     $ = "N" THEN 20
440  IF A$ = "Y" THEN 460
450  GOTO 430
460 SS = 1000 * SS: PR£ 1: PRINT "SAME DATA": PRINT : PRINT : PR£ 0: GOTO
     200
500  END
```

APPENDIX IV

Consider the following scheme

$$H_2O_2 + R_2Te_2 \xrightarrow{k_1} RTe + RTe(OH)_2$$

$$RTe(OH)_2 + R_2Te_2 \xrightarrow{k_2} RTe + \text{Prods.}$$

$$RTe + H_2O_2 \xrightarrow{k_3} RTe(OH)_2$$

For simplicity

Let $A = R_2Te_2$, $B = H_2O_2$, $C = RTe$, $D = RTe(OH)_2$

If steady state holds for C

then $k_1 A B + k_2 A D = k_3 B C$

$$\frac{dD}{dt} = k_1 A B - k_2 A D + k_3 B C = 2 k_1 A B$$

If B is in large excess ($k_1 B = l$) and if $k_2 A D >> k_1 A B$ ($k_2 = k$)

$$\frac{-dA}{dt} = k A D \qquad \frac{dD}{dt} = 2 l A$$

then

$$-\frac{d^2A}{dt^2} = k. \frac{dA}{dt}. D + k A \frac{dD}{dt} = \frac{dA}{dt} (-dA/dt)/A + k A (2 l A)$$

ie

$$A. \frac{d^2A}{dt^2} = \frac{dA}{dt}^2 - 2 k l A^3 \qquad \text{--- (1)}$$

Consider the trial solution

$$A = Z e^{-y t} / (x + e^{-y t})^2 \qquad \text{--- (2)}$$

Let $e = e^{-y t}$

$$\frac{dA}{dt} = Z \{(x + e) (-ye) - 2(-ye) e\} / (x + e)^3$$

ie $$\frac{dA}{dt} = -y\,Z\,e\,(x - e)/(x + e)^3$$

and

$$\frac{d^2A}{dt^2} = -y\,Z\ \{(x + e)(x - 2e)(-ye) - 3(-ye)(x - e)e\}\ /(x + e)^4$$

ie

$$\frac{d^2A}{dt^2} = y^2 Z\,e\,(x^2 - 4xe + e^2)/(x + e)^4$$

Equation (1) is a solution to (2) as long as $y^2 x = k\,1\,Z$

$$A = \frac{y^2 x\,e^{-yt}}{k\,1\,(x + e^{-yt})^2} \qquad \text{--- (3)}$$

ie $Z = A$

and

$$D = -(dA/dt)/k\,A = y\,(x - e)/k\,(x + e)$$

Consider a general set of boundary conditions, $A = A_o$, $D = d$, $t = 0$

ie at $e^{-yt} = 1$

$$A_o = y^2 x/k\,1\,(x + 1)^2 \qquad \text{--- (4)}$$

$$(A/A_o) = (x + 1)^2 e/(x + e)^2 = f$$

$$d = y\,(x - 1)/(x + 1)$$

$$x = (-y - d)/(d - y)$$

$$x = (y + d)/(y - d)$$

$$x + 1 = 2y/(y - d)$$

$$f = 4\,y^2 e^{-yt}/\{(y-d) + (y - d)\,e^{-yt}\}^2 \qquad \text{--- (5)}$$

Substitute for x and x + 1 to equation (4)

$$\frac{4\,A_o\,k\,1\,y^2}{(y - d)^2} = \frac{y^2(y + d)}{(y - d)}$$

$$4\,A_o\,k\,1 = (y^2 - d^2)$$

$$y = \sqrt{4\,A_o\,k\,1 + d^2}$$

However, if $d = 0$ then $y = \sqrt{4\,A_o\,k\,1}$

$$f = 4\, e^{-yt} / (1 + e^{-yt})^2$$

$$-y\,t = \ln\left\{\frac{2 - f - 2\sqrt{1 - f}}{f}\right\}$$

If d is very small and $d^2 = 0$ then y is still $\sqrt{4\, A_o\, k\, 1}$

Let $\delta = d / y$ and $e^{-yt} = e$

then equation (5) becomes

$$f = 4\, e / \{ 1 + \delta + (1 - \delta)\, e\}^2$$

$$f(1 + \delta)^2 + 2 f (1 + \delta)(1-\delta)\, e + f(1 - \delta)^2 e^2 = 4\, e$$

ie $f(1 + 2\delta) + 2 f e + f(1 - 2\delta)\, e^2 = 4\, e$

ie $e^2 [f(1 - 2\delta)] - 2 e (2 - f) + f(1 + 2\delta) = 0$

$$e^2 = \frac{(2 - f) \pm \sqrt{(2 - f)^2 - f^2(1 - 4\delta^2)}}{f(1 - 2\delta)}$$

$d^2 = 0$ then

$$e^{-yt} = \frac{(2 - f) \pm 2\sqrt{1 - f}}{f(1 - 2\delta)}$$

however e^{-yt} then tends to 0 sign is negative

$$e^{-yt} = \left\{\frac{(2 - f) - 2\sqrt{1 - f}}{f}\right\} / (1 - 2\delta)$$

$$-y\,t = \ln\left\{\frac{2 - f - 2\sqrt{1 - f}}{f}\right\} - \ln(1 - 2\delta)$$

ie $\ln\left\{\frac{2 - f - 2\sqrt{1 - f}}{f}\right\} = \text{Constant} - y\,t$

where $y = k_{obs} = \sqrt{4\, k_1\, k_2\, A_o\, B_o^2}$

APPENDIX V

```
1  TEXT : HOME : VTAB (5): PRINT "AN INTEGRATED FORM FOR H2O2, FOR
        TE2 + H2O2 --K1--> R + S"
2  PRINT " TE2 + S    --K2--> R + PRODS                R + H2O2    --K3--> S"

3  PRINT "STEADY STATE ASSUMPTION HOLDS FOR R,    WHILE K2 TERM IS ONLY
     SIGNIFICANT ONE    FOR TE2 LOSS"
4 TE = 0.3:P = 0.1
5  PRINT "WHEN ENTERING DATA USE -1 AS TERMINATOR, BOTH >70% COMPLETION
     AND >10% CHANGE IN H2O2 CONC WILL END INPUT LOOP"
6  VTAB (18)
10  DIM F(50),L(50),T(50)
15  INPUT "TITLE ";A$
20  INPUT "TE2 AND H2O2 ";E,F
30  INPUT "PEN ZERO AND INF ";A,B
40  INPUT "TIME1 AND INT ";C,D:C = C - D
50 N = 0: PRINT "NOW ENTER PEN READINGS"
60  INPUT Z: IF Z =  - 1 THEN 90
70 N = N + 1:F(N) = (Z - B) / (A - B):L(N) =  LOG ((2 - F(N) - 2 *  SQR
     (1 - F(N))) / F(N))
73  IF F(N) < TE THEN 220
75  IF E * (1 - F(N)) / F > P THEN 220
80 T(N) = D * N + C: GOTO 60
90  PR£ 1: PRINT : PRINT "DATA FOR "A$" , WITH TE2 AND H2O2 CONCS OF "E"
      AND "F
100 G = 0:H = 0:J = 0:K = 0
103  FOR I = 1 TO N
104 G = G + L(I) * T(I):H = H + T(I) * T(I)
106 J = J + L(I):K = K + T(I)
108  NEXT I
110 W = (J * H - G * K) / (H * N - K * K):Z = (W * K - G) / H
111 Y = Z * Z / (4 * E * F)
112  PRINT "K OBS = "Z: PRINT "OTHER CONSTANT ="W
115  PRINT "K1K2 = "Y: PRINT : PRINT "DATA FIT IS"
120  FOR I = 1 TO N
125 Y =  EXP (W - Z * T(I)):X = 4 * Y / ((1 + Y) * (1 + Y))
130  PRINT T(I) + C,F(I),X
135  NEXT I: PRINT : PRINT : PRINT : PR£ 0
140  INPUT "REPEAT? ";A$: IF A$ = "N" THEN 190
150  IF A$ = "Y" THEN 170
160  GOTO 140
170  INPUT "NO OF POINTS TO BE DROPPED = ";M:N = N - M
180  PR£ 1: PRINT : PRINT "REPEAT": GOTO 100
190  INPUT "ANOTHER RUN? ";A$: IF A$ = "N" THEN  END
200  IF A$ = "Y" THEN 15
210  GOTO 190
220 N = N - 1: GOTO 90
230  REM  PROGRAM SAVED AS H2O2EQ
```

APPENDIX VI

```
3   REM  N2H4 INTERGRATION COMPLIED AS N2H5+
5   DIM C(40),D(10),E(40),B(40),X(40),DD(10)
7   INPUT "RUN TITLE?";T$
8   REM  DATA INPUT
9   INPUT "MUTIPLER TO CONVERT READING TO CONC ";G
10   INPUT "INITIAL AND FINAL READINGS ";C,B:C(0) = ((B - C) * G)
11   INPUT "TIME INTERVAL = ";T
12   INPUT "TIME OF FIRST READING ";TT:TM = TT / T
13   PRINT "ENTER READINGS,USE -1 AS TERMINATOR ":N = 0
14   INPUT F: IF F < 0 THEN 16
15 N = N + 1:C(N) = (F - C) * G: GOTO 14
16 TE = (C(0) * 2):SS = 1E6
20   TEXT : HOME : PR£ 1: PRINT "NUMERICAL INTERGRATION FOR N2H4 DATA"
22   PRINT "TE(IV) + N2H4--K1-->TE(II) N2H2 "
23   PRINT "2TE(II) +N2H4 --K2-->(TE)2 + N2H2
24   PRINT "TE(IV) +N2H2 --K3--> TE(II) +N2 "
25   PRINT "2TE(II) + N2H2 --K4--> (TE)2 + N2"
26   PRINT "K1(N2H4) USED AS K1,SAME FOR K2": PR£ 0
30   INPUT "K1 = ";AU,AL,AN
35   INPUT "K2 = ";BU,BL,BN
40   INPUT "K3 = ";CU,CL,CN
45   INPUT "K4 = ";DU,DL,DN
50   FOR E = 0 TO AN: IF AL =  - 1 THEN E = AN
60 KA = ((AL + E * (AU - AL) / AN) / 4) * T
70   FOR F = 0 TO BN: IF BL =  - 1 THEN F = BN
80 KB = ((BL + F * (BU - BL) / BN) / 4) * T
90   FOR G = O TO CN: IF CL =  - 1 THEN G = CN
100 KC = ((CL + G * (CU - CL) / CN) / 4) * T
110  FOR H = 0 TO DN: IF DL =  - 1 THEN H = DN
120 KD = ((DL + H * (DU - DL) / DN) / 4) * T
130 Z = TE:Y = 0:W = 0:S = 0
140  FOR I = 0 TO N:X(I) = C(0) - ((Z + Y) / 2)
142  IF I > 0 THEN 150
144  IF TM = 1 THEN 150
146 KA = KA * TM:KB = KB * TM:KC = KC * TM:KD = KD * TM
150 M = C(I) - X(I):S = S + M * M: IF S > SS THEN 200
160  FOR J = 1 TO 4:LA = KA * Z:LB = KB * Y * Y:LC = KC * Z * W:LD = KD *
     Y * Y * W
170 Z = Z - LA - LC:Y = Y + LA + LC - 2 * (LB + LD):W = W + LA + LB - LC
     - LD: NEXT J
172  IF I > 0 THEN 180
174  IF TM = 1 THEN 180
176 KA = KA / TM:KB = KB / TM:KC = KC / TM:KD = KD / TM
180  NEXT I
190 SS = S:QA = 4 * KA:QB = 4 * KB:QC = 4 * KC:QD = 4 * KD
200  NEXT H: NEXT G: NEXT F: NEXT E
205 SA = QA / T:SB = QB / T:SC = QC / T:SD = QD / T
210  PRINT SS: PRINT "K VALVES ARE": PRINT SA" "SB" "SC" "SD
220  INPUT "ANOTHER TRY?";A$: IF A$ = "Y" THEN 30
230  IF A$ = "N" THEN 250
240  GOTO 220
250  PR£ 1: PRINT T$: PRINT "DATA FIT HAS SSD = "SS
260  PRINT "WITH RATE CONSTANTS OF ": PRINT SA"        "SB"        "SC"
        "SD
270  PRINT "AND DATA AS OBS AND CALC"
275  PRINT "INITIAL CONC TE(IV) IS  "TE    .
280  FOR I = 1 TO N: PRINT C(I)"  "X(I): NEXT I
290  PR£ 0: INPUT "ANOTHER RUN?";P$:
300  IF P$ = "Y" THEN 7
310  IF P$ = "N" THEN  END
```

APPENDIX VII

The solvolysis of p-EtOPhTeCl$_3$ in general is represented in the following sequence

$$A + [H^+] \underset{}{\overset{K_1}{\rightleftharpoons}} B$$

$$B \xrightarrow{k_2} \text{Prod.} + (n+1)[H^+]$$

$$A \xrightarrow{k_3} \text{Prod.} + [H^+]$$

Where A represents p-EtOPhTeCl$_3$, B is an intermediate and $[H^+]$ is the hydrogen ion concentration . At time = 0 the hydrogen ion concentration is very small, and $A >> B$. For simplicity let Prod = C

Let $L = A + B + C$

Assuming B is negligible at time = 0, then

$A = L - C$

$B = K_1 A [H^+]$

$[H^+] = n C$

And $A = L - ([H^+] / n)$

Then $d [H^+] / dt = n k_3 A + n k_2 B$

$$= n (k_3 + K_1 k_2 [H^+]) A$$

$$= n (k_2 + K_1 k_2 [H^+]) (n L - [H^+])$$

$$\int_{H_o}^{H_t} \frac{d [H^+]}{(k_3 + K_1 k_2 [H^+]) (n L - [H^+])} = \int_o^t dt$$

$$\frac{1}{(k_3 + K_1 k_2 [H^+]) (n L - [H^+])} = \frac{Z}{k_3 + K_1 k_2 [H^+]} + \frac{Y}{n L - [H^+]}$$

Then $K_1\, k_2\, Y - Z = 0\,, \qquad Z = K_1\, k_2\, Y$

And $k_3\, Y + n\, L\, Z = 1\,, \qquad Y\,(\,k_3 + n\, K_1\, k_2\, L\,) = 1$

$$Y = \frac{1}{k_3 + n\, K_1\, k_2\, L} \qquad\qquad Z = \frac{K_1\, k_2}{k_3 + n\, K_1\, k_2\, L}$$

$$\int_{[H^+]_o}^{[H^+]_t} \frac{K_1\, k_2\, d[H^+]}{k_3 + K_1\, k_2\, [H^+]} + \int_{[H^+]_o}^{[H^+]_t} \frac{d[H^+]}{n\, L - [H^+]} = (k_3 + n\, K_1\, k_2\, L\,)\, t$$

$$(\,k_3 + n\, K_1\, k_2\, L\,)\, t = \ln\, \{(\,k_3 + K_1\, k_2\, [H^+] - \ln\,(n\, L - [H^+])\}\Big|_{[H^+]_o}^{[H^+]_t}$$

Let $X = K_1\, k_2 \,/\, k_3$ then

$$k_3\,(\,1 + n\, L\, X\,)\, t = \ln \frac{(\,1 + X\,[H^+]_t)\,(\,nL - [H^+]_o)}{(\,1 + X\,[H^+]_o)\,(\,n\, L - [H^+]_t)}$$

If $n\, L = [H\ \,]_o$ this becomes

$$k_3\,(\,1 + [H^+]_o\ X)\, t = \ln \frac{\{(1/X) + [H^+]_t\,([H^+]_{oo} - [H^+]_o)\}}{\{(1/X) + [H^+]_o\,([H^+]_{oo} - [H^+]_t)\}}$$

If $k_3 = 0$ then

$$K_1\, k_2\, [H^+]_o\ \, t = \ln\, \{[H^+]_t\,(\,[H^+]_{oo} - [H^+]_o)\,/\ [H^+]_o\,([H^+]_{oo} - [H^+]_t)\}$$

$$k_{obs} = K_1\, k_2\, [H^+]_{oo}$$

$$k_{obs}\, t = \ln\ \{\ [H^+]_t\,(\,[H^+]_{\infty} - [H^+]_o)\,/\ [H^+]_o\,([H^+]_{\infty} - [H^+]_t)\}$$

APPENDIX VIII

```
5   REM :SOLVOLYSIS OF ARTECL3
6   REM :SAVED AS SOL
10   DIM T(30),L(30),H(30),P(30),BB(30)
20   INPUT "RUN TITLE ";T$
25   REM :DATA AND RECORDER SCALING INPUT
30   INPUT "TIME INTERVAL ";X
40   INPUT "INITIAL AND FINAL PH VALVES ";C0,C1
50   INPUT "INITIAL AND FINAL PEN READINGS ";R0,R1
51   INPUT "FIRST PEN READING ";RF
52 D = (C0 - C1) / (R1 - R0)
53 C0 = C1 - (D * (RF - R1))
55 V = 2.303
56 H0 =  EXP ( - V * C0):H1 = ( - V * C1)
57  REM :CALCULATION SECTION
60  PRINT "ENTER READINGS":N = 1
70  INPUT F: IF F =  - 1 THEN 123
75 P(N) = C1 - (D * (F - R1))
80 T(N) = X * (N)
85 H(N) =  EXP ( - V * P(N))
110 L(N) =  LOG ((H(N) * (H1 - H0)) / (H0 * (H1 - H(N))))
115 N = N + 1: GOTO 70
120  REM :LEAST SQUARES
123 N = N - 1:NN = 1
130 K = 0:J = 0:A = 0:U = 0: FOR I = NN TO N
140 K = K + T(I):J = J + L(I):A = A + T(I) * L(I):U = U + T(I) * T(I): NEXT
     I
160 ZA = (J * U - K * A) / (N * U - K * K)
165 KK = (N * A - K * J) / (N * U - K * K)
167  FOR I = NN TO N
169 XX = (L(I) - (KK * T(I)) - ZA) ^ 2 + XX
171  NEXT I
173 XY = (XX / (N - 2)) ^ 2
175 YY =  SQR ((N * XY) / (N * U - K * K))
179  REM :OUTPUT SECTION
180 S = 0: FOR I = NN TO N
190 A = (KK * T(I)) + ZA:S = S + (A - L(I)) ^ 2
200  IF  INT (I / 10) = I / 10 THEN  GET A$
210  PRINT T(I),L(I),A: NEXT I
220  PRINT "SUM OR SQUARED DIFFERENCES=";S
230  PRINT "REPEAT RUN DROPPING SOME POINTS?TYPE IN NUMBER OF PTS TO BE
     DROPPED"
235  INPUT NE,NL
240  IF NE = 0 AND NL = 0 THEN 300
250 MN = N - NE - NL:NN = 1 + NE: GOTO 130
300  PR£ 1: PRINT T$
310  PRINT "RATE CONSTANT IS= " INT (1000 * KK + 0.5) / 1000" SEC-1": PRINT

315  PRINT "INTERCEPT = " INT (100 * ZA + 0.5) / 100
317  PRINT "ERROR IS +/- "YY
320  PRINT "DATA AS TIME OBS A AND CALC A ARE ": PRINT
330  PRINT "SUM OR SQUARED DIFFERENCES = " INT (1000 * S + 0.5) / 1000
340  FOR I = 1 TO N
350 A = (KK * T(I)) + ZA:S = S + (A - L(I)) ^ 2
360  PRINT T(I), INT (100 * L(I) + 0.5) / 100, INT (100 * A + 0.5) / 100
     : NEXT I
370  PR£ 0: PRINT "ANOTHER RUN?": INPUT Q$
380  IF Q$ = "Y" THEN 20
390  IF Q$ = "N" THEN 400
400  PRINT "***END***"
```

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