MECHANISTIC STUDIES IN TELLURIUM CHEMISTRY

BY

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A Thesis Submitted for the Degree of
Doctor of Philosophy
in the
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SUMMARY

THE UNIVERSITY OF ASTON IN BIRMINGHAM

MECHANISTIC STUDIES IN TELLURIUM CHEMISTRY

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The reduction of p-ethoxyphenyltellurium trichloride by sodium sulphite and metabisulphite has been investigated. The reactions have stoichiometries of one mol of p-EtOPhTeCl$_3$ to 1.5 and 0.75 mol of SO_3^{2-} and $S_2O_5^{2-}$ respectively. The paths of the reaction mechanisms with both reducing agents are almost identical. The reductions are acid catalysed and proceed via a common two electron process. Both systems obey a second order rate law. The percentage of water in the mixed solvent used plays a role in deciding the rate determining step of the reaction. A mechanism for the above reactions is suggested.

The reduction of p-EtOPhTeCl$_3$ by chromous and vanadous ions was also investigated. The stoichiometric measurements show that one mol of p-EtOPhTeCl$_3$ is equivalent to three mols of Cr (II) or V(II). The rates of the overall reactions are second order. The catalysis by chloride ion of the reactions suggests that they are inner-sphere processes. The chloride group which acts as a bridge is brought in by the tellurium species. The interpretation is that tellurium in p-EtOPhTeCl$_3$ prefers an inner-sphere mechanism for its reactions.

The solvolysis of p-EtOPhTeCl$_3$ in aqueous and non-aqueous media has been investigated. The study shows that the solvolysis is a reversible, acid catalysed reaction which is agreed to be associative. The number of chloride ligands on tellurium replaced depends upon the hydrogen and chloride ion concentrations in the solution, and also upon the size of the substituent. The rate of solvolysis in aqueous media is faster than in non-aqueous media and varies in the order of trichloride $>$ tribromide $>$ triiodide.

KEY WORDS

REDUCTION
SOLVOLYSIS
ORGANOTELLURIUM
MECHANISM
KINETICS

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DECLARATION

The work described in this thesis was carried out between 1981 - 1984 at the University of Aston in Birmingham. It has been done independently, and has not been submitted for any other degree.

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Tahir Ahmad Tahir

August 1984

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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 VIB with electronic structure of $\left|Kr\right| 4d^{10}5s^{2}5p^{4}$. The metallic nature of this group increases as the atomic weight increases from oxygen to polonium. This can be observed by looking at the insulator properties of oxygen and sulphur, semi-conductivity of selenium and tellurium and the more positively metallic nature of polonium.

Tellurium with an atomic weight of 127.6 and atomic number of 52 has twenty two known isotopes, with atomic masses ranging from 114 to 135. The element has s, p, and d orbitals available for use in bonding so it can form more than four sigma bonds to other atoms. The most common oxidation states of tellurium are II and IV, represented by TeO and $TeCl_4$. Other known oxidation states are -II, I and VI represented by H_2Te, Ar_2Te_2 and TeF_6.

Since its discovery, tellurium and its derivatives have been used in industry e.g. 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, in chemical reactions as a catalyst and as an antioxidant in lubricating oils.

In this thesis, I describe attempts to investigate the the effect of various reaction conditions on the rate of reduction of p-EtOPhTeCl$_3$ with different reducing agents (i.e. SO_3^{2-}, $S_2O_5^{2-}$, Cr(II) and V(II)). The studies were carried out over a range of concentrations of the reducing agents, temperature, solvent compositions, hydrogen ion concentrations, ionic strengths and chloride ion concentrations. Other studies concerned the solvolysis of p-EtOPhTeX$_3$ (X=Cl, Br, I) in water or methanol.

It is hoped that this work will ultimately help to provide a general understanding of this kind of redox-reaction as well as of the kinetics and mechanism of the particular reactions of organotellurium compounds.

The mechanism of reactions of carbon compounds, of square planar and of octahedral transition metal complexes have been extensively studied, but little attention has been given to tellurium compounds. It is probable that tellurium shows behaviour in between those of carbon and transition metals. For example, its compounds may show both associative and dissociative mechanisms in their reactions.

Organotellurium compounds have a history dating back to 1840(1) when Wöhler prepared some dialkyltellurides. These were the first organic compounds of tellurium.

Morgan and Drew(2) in 1925 first synthesized an aryltellurium trichloride by treating tellurium tetrachloride with phenetole.

$$TeCl_4+C_2H_5\text{-}O\text{-}C_6H_5 \longrightarrow C_2H_5\text{-}O\text{-}C_6H_4\text{-}TeCl_3+HCl$$

The mechanism of this reaction probably involves electrophilic attack by $TeCl_3^+$ at the activated position of the aromatic nucleus.

Campbell and Turner(3) prepared aryltellurium trichloride by the reaction of arylmercuric halides with $TeCl_4$

$$ArHgCl+TeCl_4 \longrightarrow ArTeCl_3+HgCl_2$$

which is a more general method, as it does not depend on the reactivity of the aromatic nucleus. The advantage of this method lies in the possibility of obtaining compounds with any relative arrangement of substituents.

The preparation of a large number of aryltellurium trichlorides employing these methods was described by Petragnani(4), Rheinboldt and Vicentini(5) and Reichel and co-workers.(6,7)

To date, very little work has been published on the kinetics, or mechanism, of the reactions of organotellurium compounds. Very little is known about the common preparative routes to organotellurium compounds, often because of the practical problems involved in making measurements. Many reactions are incomplete, producing by-products, or are not suitably homogeneous.

Mehdi(8) carried out some mechanistic studies of organotellurium compounds, especially the diarylditellurides. These included studying the effect of visible irradiation on diarylditellurides in a solution containing alcohol;and the reaction of iodine with diarylditellurides through attack on the tellurium-tellurium bond. He also investigated the reaction of the diarylditellurides with a transition metal complex, Vaska's compound.

Al-Shali(9)made an experimental study of the kinetics of the reduction of some inorganic compounds of selenium and tellurium in aqueous solutions by a number of well-known inorganic reducing agents. He attempted to make deductions about the mechanism of the reactions involved.

The work described in this thesis concentrates on kinetic and mechanistic studies of the formation of diarylditellurides, R-Te-Te-R, because they 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 aliphatic members which, in addition to their relative instability, possess an obnoxiuos, persistant odour. Additionally the diarylditellurides exhibit strong colour which makes it easy to study the appearance of the compound. The present work has mainly been carried out by following this colour spectroscopically.

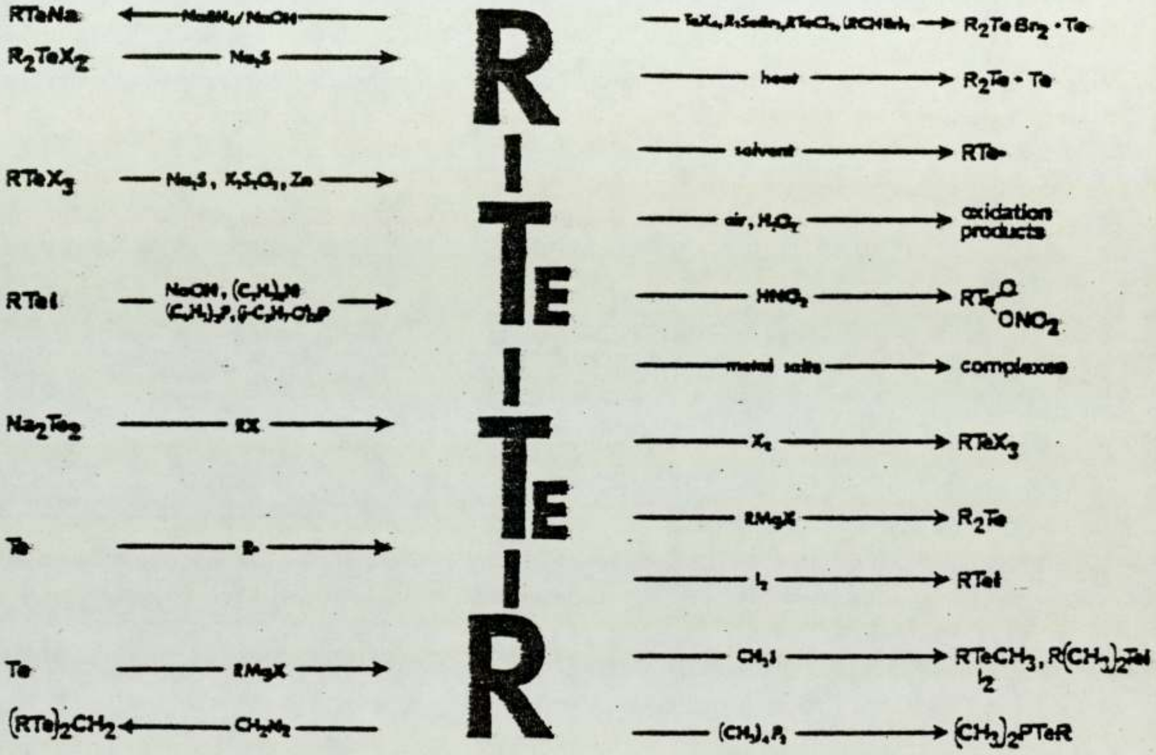


Fig 1:1 Syntheses and Reactions of Diorganyl Ditellurides

The work concerning organotellurium compounds which had been carried out up to 1971 has been reviewed by Irgolic$^{(10)}$. Research during the period 1972-1979 has also been reviewed by Irgolic.$^{(11-16)}$ In 1971, Cooper published a book dealing with all aspects of tellurium, titled "Tellurium".$^{(17)}$

The principal methods for the synthesis of aromatic ditellurides are the reduction of corresponding aryltellurium trihalides using such agents as Na_2S, $Na_2S_2O_5$ and hydrazine.$^{(18,19,20)}$ The corresponding diarylditellurides are formed in almost quantitative yield. A few other modes of formation of ditellurides have been found.$^{(21)}$ Most of them are only of very limited interest for preparative work.

Petragnani and de Moura Campos$^{(22)}$ have explained the formation of diaryltellurides and ditellurides during the reaction of a Grignard reagent with tellurium tetrachloride. Their postulated mechanism is supported only 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 very complex and variable ratios of products can be obtained.

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

$$\mathrm{PhTeMgBr} \longrightarrow \mathrm{PhT\overset{\bullet}{e}{+}MgBr^{\bullet}}$$

$$\mathrm{2PhTe^{\bullet}} \rightleftharpoons \mathrm{PhTe{-}TePh}$$

$$\mathrm{2MgB\overset{\bullet}{r}{+}Te} \longrightarrow \mathrm{Te(MgBr)_2}$$

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

Thavornyutikarn(23) attempted to prepare unsymmetrical ditellurides by reducing a mixture of two different aryltellurium trichlorides using $Na_2S.9H_2O$ and $K_2S_2O_5$ and by irradiating a benzene solution containing diphenylditelluride and $(p\text{-EtOPh})_2Te_2$. He concluded that the ditelluride is not dissociated to 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.

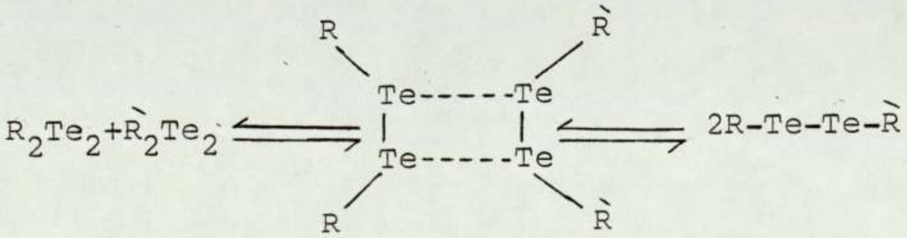
More recent work(24) has demonstrated an exchange reaction between ditellurides R_2Te_2 and R'_2Te_2 and provided the first evidence for the existance of unsymmetrical dairyltellurides, R-Te-Te-R', from mass and proton NMR spectroscopy. An unproven mechanism for the redistribution of R groups might go via radical mechanism

$$R_2Te_2 \rightleftharpoons 2RT\dot{e}$$

$$R'_2Te_2 \rightleftharpoons 2R'T\dot{e}$$

$$RT\dot{e} + R'Te \longrightarrow R\text{-}Te\text{-}Te\text{-}R'$$

Alternatively a dimer intermediate might occur



Dance(24) found no evidence that ditellurides spontaneously produce $RTe^{\bullet}$ radicals, while the dimeric intermediate remains a distinct possibility.

The exchange reaction between two symmetrical ditellurides might be a slow reaction dependant on the mixture, concentration and solvent.(25) Moreover, the exchange reaction, a thermal process, might be disturbed by the presence of oxygen.

One part of my work was designed to study the stoichiometry, kinetic and mechanism of synthesis of diarytellurides by reducing the corresponding aryltellurium trichlorides. The study was carried out in mixed solvents over a wide range of concentrations, temperature, ionic strength, hydrogen ion concentration and solvent composition. The reactions were all found to be first order with respect to each reactant.

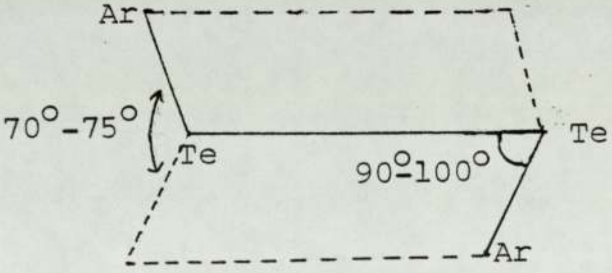
A very few studies have been made on the photo-chemical reactions of diorganylditellurides. The first report on the photo-chemistry of ditellurides was published by Spencer and Cava in 1977.(26) Under aerobic conditions, irradiation of toluene solution of a diarylditelluride containing alcohol with visible light, results in the bleaching of the orange/red colour of the ditelluride.(8) There is an initial induction period, which is then followed by a rate profile which is fitted by the equation:-

$$\sqrt{[Ar_2Te_2]} = K_{obs}\ t\ [EtOH] + \text{constant}$$

The half order equation probably indicates the homolytic cleavage of the Te-Te bond.

Mehdi(8) investigated the effect of visible irradiation on the diarylditellurides in a solution containing added alcohol. He concluded that the presence of oxygen plays an important part in this effect. Also, he deduced that while ethanol is involved in the reaction, it plays a part after the formation of radicals.

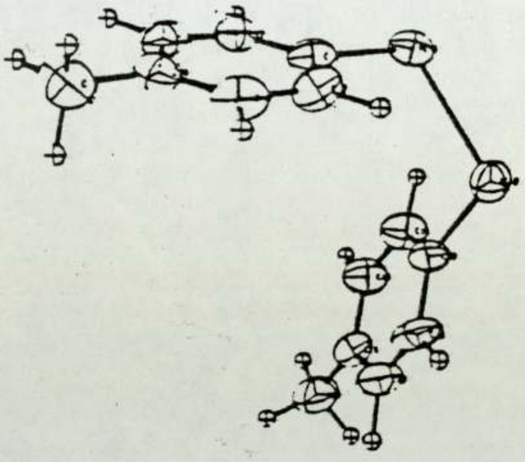
Structural details of diorganylditellurides have been determined from X-ray crystallographic studies.(27,28,29) In all ditellurides examined the C-Te-Te bond angles have been found to be between 90°-100° indicating that the Te-C bonds have a higher degree of p-character and the dihedral C-Te-Te/Te-Te-C angles are 70°-75°



(dihedral angle of diarylditelluride)

In the case of p,p′-dichlorodiphenyl ditelluride the two organic groups bonded to the tellurium atoms form a dihedral angle of 72°.

Recently, the structure of bis(p-tolyl)ditelluride was determined. The molecule was characterized by dihedral angle C-Te-Te/Te-Te-C of 87.7° and Te-C and Te-Te bond lengths of 2.13 and 2.69 A°, respectively. The molecular structure is shown in the following figure:-



Stereoscopic view of bis(p-tolyl)ditelluride

The determination of the crystal and molecular structure of p-EtOPhTe X_3 (X=Cl, Br, I) shows that the tellurium atom has square pyramidal co-ordination with each tellurium atom lying almost exactly in the basal planes formed by the four chlorine atoms while the p-EtOph group is in the apical position. The pyramids are linked in chains through cis-basal chlorine atoms, Fig (1:2)(30). There is quite an acute angle between the basal planes of the pyramids. This presumably results from weak bonding indicated by the short distance between adjacent tellurium atoms. That is, the trichloride crystallizes as a polymer.

The tribromide and trichloride both crystallize with a dimeric molecular unit Fig(1:3,1:4).The co-ordination at tellurium is square pyramidal with the halogen atoms in the basal positions and the organic group apical. Now the pyramids are linked in pairs by two symmetrically bridging halogen atoms. In general (Te-X) terminal distances are slightly shorter than Te-X bridging distances. The Te-aryl distances range between 2.09 and 2.16 A^{o} among the three compounds.

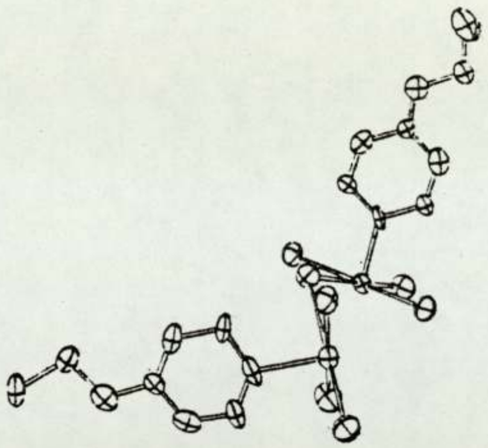


Fig 1:2 Stereoscopic view of p-EtOPhTeCl$_3$

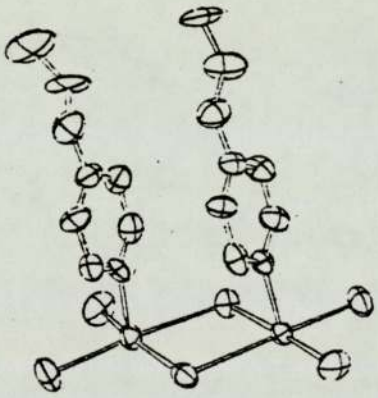


Fig 1:3 Stereoscopic view of p-EtOPhTeBr$_3$

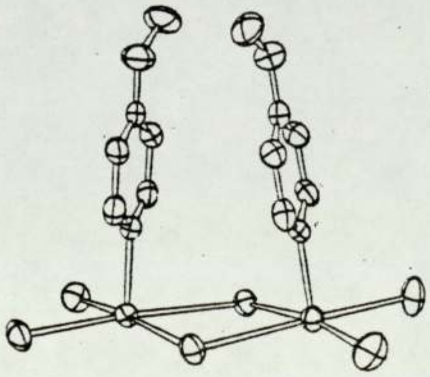


Fig 1:4 Stereoscopic view of p-EtOPhTeI$_3$

McWhinnie(31) made a spectroscopic examination of solid phenyltellurium trichlorides in order to determine the structural properties of aryltellurium trichlorides. It was found that $PhTeBr_3$ may differ from the other two members of the group. The IR spectrum of the tri-iodide indicates that the structure is based on "$PhTeI_2^+$ units" associated via iodide bridges to give 5 - co-ordinate tellurium atoms. The same considerations hold for $PhTeCl_2^+$. There is no indication that the above structures are ionic, but McWhinnie considered that they might be built up from donor-acceptor interactions between $RTeX_2^+$ and X^- to give the molecular structure illustrated in Fig (1;5a). The conclusion is that of $PhTeCl_3$ and $PhTeI_3$ are at least dimeric, $PhTeBr_3$ may even be trimeric as illustrated in Fig (1:5b)

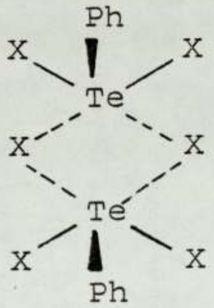
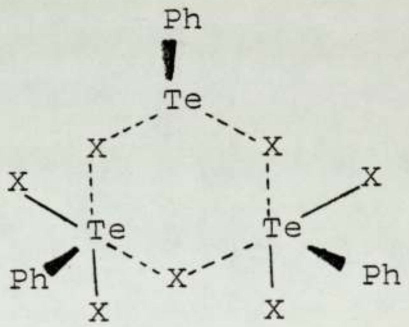


Fig (1:5a)



Fig(1:5b)

Krishna and Khandelwal(32) obtained the I.R. and N.M.R spectra of p-$EtOPhTeCl_3$ and p-$MeOPhTeCl_3$. They also made conductance and molecular weight measurements on their compounds. They found that both compounds present in molecular form in organic solvents and $TeCl_3$ groups are in the para position to the ethoxy or methoxy groups in the ring.

The reaction of tellurium tetrachloride with benzene derivatives containing sufficiantly powerful electron donor groups, implies that the active apical chlorine atom may be that to undergo neucleophilic replacement, because it has a considerably higher negative charge than the equatorial chlorine as shown in Fig$^{(33)}$(1:6).

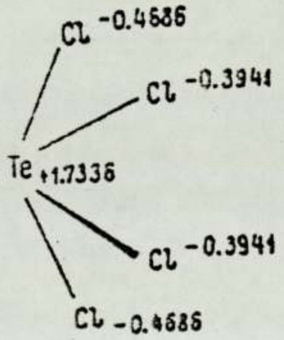


Fig (1:6) The structure of $TeCl_4$

The result of calculations on the various conformations of tellurium trichloride is that the final product of the replacement reaction may be expected to be as in Fig (1:7) with the phenyl ring in the equatorial plane.

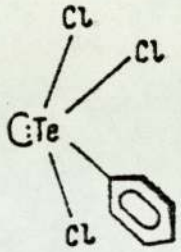
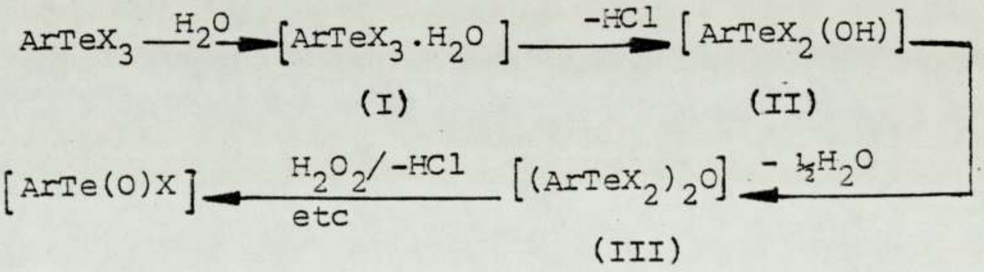


Fig 1:7 The structure of $C_6H_5TeCl_3$

The apical positional ring was unfavoured energetically.(34)

Thavornyutikarn and McWhinnie(23) investigated the hydrolysis of phenyl and 4-ethoxyphenyltellurium trihalides in neutral aqueous media. It was considered to proceed in a stepwise manner. The first stage involves the formation of a monomeric species compound (I), arising from the nucleophilic attack on tellurium in $ArTeCl_3$ by water and the resulting breaking of the halogen bridge bonds, thus



$$ArTeX_3 \xrightarrow{H_2O} \underset{(I)}{[ArTeX_3.H_2O]} \xrightarrow{-HCl} \underset{(II)}{[ArTeX_2(OH)]}$$

$$[ArTe(O)X] \xleftarrow[etc]{H_2O_2/-HCl} \underset{(III)}{[(ArTeX_2)_2O]} \xleftarrow{-\frac{1}{2}H_2O}$$

Attempts to isolate compounds corresponding to (III) failed. Only ArTe(O)X, or a mixture of $ArTeX_3$ and ArTe(O)X, could be obtained at various reaction times and under a range of conditions.

Thus if stages corresponding to (II) and (III) are involved, the intermediates must be short lived.

The hydrolysis of $ArTeX_3$ and ArTe(O)X in alkaline media also lead to the formation of similar compounds, hence the initial stages of these reactions probably follow a scheme similar to the above equation. The product isolated from the alkaline medium shortly after mixing has the composition $(p\text{-}EtOPhTeO)_2O$ therefore, a scheme such as the following is appropriate:-

$$\begin{tikzcd}
ArTe(O)X \arrow[r, "OH^-", "H_2O"'] & ArTe(OH)_3 \arrow[r, "-H_2O"] & ArTe(O)OH \arrow[d, dash] \\
 & \frac{1}{2}\left[(ArTeO)_2O\right] & \arrow[l, "-\frac{1}{2}H_2O", "H^+"']
\end{tikzcd}$$

From the failure to isolate any product of the hydrolysis corresponding to a stage intermediate between $ArTeX_3$ and ArTe(O)X, the intervening stages are probably fast. The limited solubility of $ArTeX_3$ in water is probably the rate determining factor. In an attempt to use a Lewis base other than water to break the bridging halogen bonds in $ArTeX_3$, Pyridine was reacted with phenyl and para ethoxyphenyltellurium tri-chlorides. The products obtained are pyridinium salts $PyH^+ArTeCl_4^-$ rather than the expected compound, $ArTeCl_3Py$. The explanation is that although the reagents were supposedly "dry" they contained sufficient water to hydrolyse some $ArTeCl_3$ to ArTe(O)Cl. The hydrogen chloride released reacted with $ArTeX_3$ to yield $ArTeX_4$, which was subsequently isolated as a pyridinium salt.

No work has been reported concerning the photoreactions of arytellurium trihalide. I have observed that the colour of the aryltellurium trihalide solution exposed to light and air disappears gradually with time. The loss of colour is very slow when the solution is kept in the dark, or under oxygen -free nitrogen. This process has not been followed further, due to the shortage of time.

In my kinetic studies of the solvolysis of aryltellurium tri-halide in solvents of different composition and at different temperature, the reaction of tri-halides with MeONa and MeOH, has been examined.

The solvent used for the reduction of p-EtOPhTeCl_3 is a mixture of 1,4 dioxane with water. The choice of a non-aqueous component of the mixed solvent systems used in this study was limited to those solvents which do not react with aryltellurium tri-halides or diarylditellurides(35) and do not form inner-sphere complexes with transition metal ions (i.e. Cr(III), V(III)).

Dioxane, unlike other solvents (i.e. methanol, acetone, etc.,.) gives no evidence for reaction with aryltellurium trihalides or for co-ordination to both Cr(III) and V(III). The evidence for dioxane not participating in the solvation of the reactions is proved by Frattiello and Douglass(36) who showed that many ions, including the alkali metals, alkaline earths, lanthanium (III) ion, cobalt (II) ion and iron (II) ion are preferentially solvated by water in dioxane water mixtures.

Dioxane was also chosen because, in accordance with its symmetrical structures dioxane has a very small dipole moment, and is completely miscible in all proportions with such a highly polar compound as water. This property, combined with a very low dielectric constant, makes dioxane-water mixtures highly suitable for the study of the behaviour of electrolytes in media of continuously and rapidly varying dielectric constants. The variation of rate constant with dielectric constant has long been used as evidence bearing on mechanisms. We found that the mixture of 75% by volume of dioxane and 25% by volume of water is a suitable solvent for our reactants and products.

Due to the low solubility of the reactants and the products in proper mixed solvents, our experiments were performed in a low concentration which resulted in homogenous solutions and without precipitate.

CHAPTER TWO

EXPERIMENTATION

2- EXPERIMENTATION

In all experiments involving chromium (II) and vanadium (II) ions, oxygen was, of necessity, rigorously excluded by purging all apparatus and solutions with nitrogen for a minimum of 30 minutes. This was accomplished either by using a multi-necked round-bottom flask fitted with a nitrogen bubbler and nitrogen outlet (Fig 2:1) , or the flask containing the solvent was attached to a vacuum pump and then purged with nitrogen. The solutions were transferred using pipettes or all glass graduated hypodermic syringes fitted with stainless steel needles.

2-1 Chemicals

All chemicals used were obtained from the usual commercial sources and "AnalaR" grades were used when necessary. Tellurium tetrachloride ($TeCl_4$) which is the important starting material was supplied by the British Drug House (B.D.H) in a sealed bottle. It was found to be of a satisfactory quality and used without further purification.

2-2 Solvents

All solvents used were obtained from commercial sources, generally they were all redistilled, at least, before use. If pure solvents were needed, they were purified according to literature methods.(37) When a de-oxygenated solvent was required it was placed in a flask and connected to a vacuum pump to remove air, then purged with nitrogen. This procedure was repeated at least twice for each solvent. Generally all the solvents were purified and de-oxygenated prior to use.

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 800-350 n m. The solution and the solvent for comparison were both contained in 1cm quartz cell. 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 599B spectrophotometer, which covers the range 4000-200 cm^{-1}. The samples were examined as solid discs, prepared by pressing a mixture of sample and powdered KBr or CsI. Usually spectra were recorded using medium speed with normal slit parameters while air was used as a reference material.

2-3-3 Melting point

The melting points of all solid compounds were determined using a Gallenkamp melting point apparatus which is heated electrically. The thermometer was calibrated by determining the melting points of several pure compounds of known melting point.

2-3-4 Conductivity measurements

The conductivity of some aqueous solutions containing chromium (III) species was measured at 25°C using a Mullard conductivity bridge (type E7591/B) and a normal cell (Cell constant = 1.46). When solutions had previously been refluxed for an hour, they were subsequently kept in the thermostat bath until their temperature also reached 25°C.

2-3-5 pH Measurements

All pH measurements were obtained using a Corning-EEL Model 12 pH meter, operating range pH (0) to (14), with an accuracy of ∓ 0.02. Potentiometric data were also measured using the same apparatus, with an operating range of (0 to ∓ 1400 m.v), with an accuracy ∓ 2 m.v. For kinetic studies, the pH meter was used in conjunction with a Pye-Unicam AR-55 linear recording unit.

2-3-6 Thin Layer Chromatography (T.L.C)

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

2-3-7 Magnetic Measurements

Magnetic Susceptibilities were determined at room temperature by the Gouy method. The electromagnet used was water cooled and supplied by Newport Instruments Magnet Supply type D104. The field between the pole pieces could be held constant for all measurements by manual regulation of the current to within 0.1 per cent. Weighing were made on a balance supplied by Stanton Instruments Limited, model SM12, sensitivity 0.1 m.g. All weighings were made at field strength at 10 amperes, to give reported values (in milligrams). Susceptibility values were calculated by comparison with $Hg(Co(NCS)_4)$. The latter was found to be more satisfactory because of its higher purity, stability and also because it packs very well.

2-3-7-1 Procedure

To remove paramagnetic impurities, the Gouy tube was cleaned and dried carefully. The empty tube was weighed with the field off and then with the field on. This procedure was then repeated but in this instance the unknown substance and the $Hg(Co(NCS)_4)$ was used instead of water.

2-4 Computation

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

2-5 Analysis

Micro-analysis for carbon, hydrogen and halogen were performed by the microanalytical laboratory of the Chemistry Department; chromium (III) and dithionate were determined as shown below.

2-5-1 Determination of Chromium in Chromic Salt

The sample was accurately weighed (0.2535 gm) and dissolved in 50ml distilled water, after which 20ml of 0.1 N silver nitrate solution and 50ml of 5 per cent solution of potassium persulphate were added.

The mixture was boiled gently for one hour. The cooled solution was finally diluted to 250ml in a volumetric flask. 25ml of the solution was taken from the volumetric flask and added to 50ml of 0.02 N ferrous ammonium sulphate solution and 200ml of 2N-sulphuric acid and 0.2ml of diphenylammine indicator. The excess of the ferrous salt was back titrated against a standard potassium dichromate solution until the colour changed from pale green to violet. The ferrous ammonium sulphate solution was standardized against a standard potassium dichromate solution. The literature method of Yoshio Matsumoto and Michiko Shira(38) was attempted unsuccessfully.

2-5-2 Estimation of Dithionate(39,40)

A solution of p-EtOPhTeCl_3 was reduced by AnalaR Na_2SO_3 to obtain $(p\text{-EtOPh})_2Te_2$. The ditelluride was extracted from the aqueous solution by chloroform. A few drops of NaOH was added to the aqueous layer followed by an excess solution of $BaCl_2$. A white precipitate, $BaSO_4$ and $BaSO_3$ was obtained.(41) The mixture was allowed to stand for 2 hours before it was filtered. A few more drops of $BaCl_2$ was added to the filtrate which was then kept overnight and filtered again to remove any more precipitate. Concentrated HNO_3 (15ml) was added to 200ml of the filtrate and then boiled for 1 hour, after which a few drops of $BaCl_2$ were added, No precipitation was observed. This experiment shows that no dithionate is formed as a by-product from sodium sulphite when it is oxidised by p-EtOPhTeCl$_3$.

2-6 Potentiometric Titration of Cr(II) with CuSO$_4$ Solution

A standard solution 0.01M of AnalaR copper sulphate (25ml) and concentrated hydrochloric acid (25ml) was added to a 250ml,five-necked flask Fig 2:1 . The central neck (1) was fitted with a one hole rubber stopper to insert the tip of the burette. The second neck (2) was fitted with a long tube to bubble nitrogen through the solution. The other necks were fitted with a platinum electrode (3), an out-let paraffin tube (4) and the end of a salt bridge (5).

The salt bridge was prepared from 3% agar gel saturated with potassium sulphate. The outer end of the bridge was placed in a saturated potassium chloride solution in a beaker in which a saturated calomel electrode was dipped. The solution in the titration vessel was freed from oxygen by passing nitrogen through it for 45 minutes before titration and stirred magnetically.

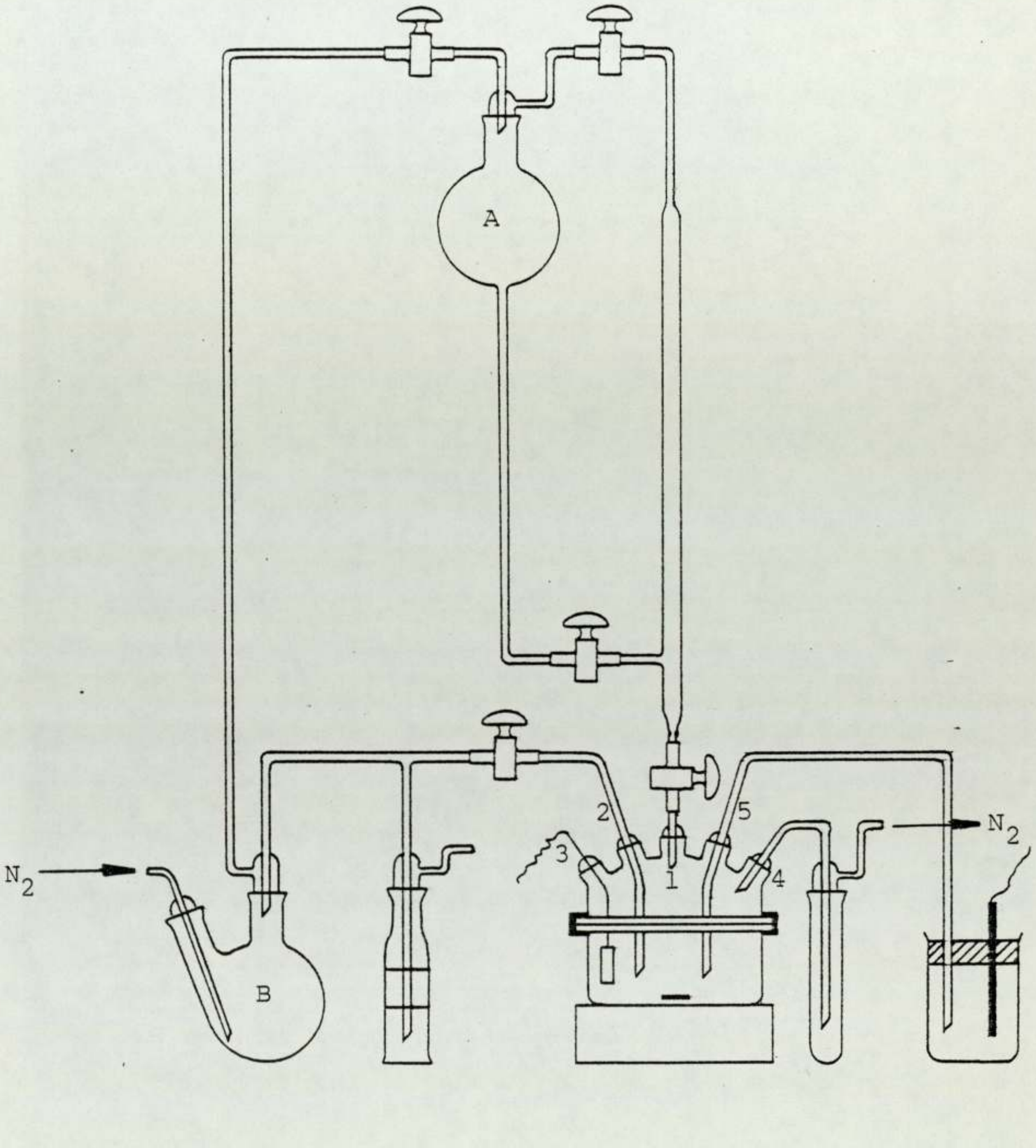


Fig (2:1).Apparatus for Potentiometric Titration of Cr(II) and for preparation of Cr(II) and V(II) solutions.

2-7 Stoichiometry

2-7-1 Determination of $S_2O_5^{2-}$ and SO_3^{2-} consumed by p-EtOPhTeCl$_3$

A solution of p-EtOPhTeCl$_3$ in 1,4-dioxane (6.25×10^{-4}M) was added to ten different concentrations of freshly prepared, deoxygenated solutions of $Na_2S_2O_5$ and Na_2SO_3. The mixture consisted of one volume of distilled water and 3 volumes of 1,4 dioxane. Then the reaction was kept in the dark for two hours. The concentration of (p-EtOPh)$_2$Te$_2$ was determined spectrophotometrically by reading the final absorbance of the product.

2-7-2 Determination of V(II) consumed by p-EtOPhTeCl$_3$

A solution of 20N sulphuric acid (4ml) was added to a round bottom flask Fig 2:1, followed by previously calculated amount of distilled water and 1,4 dioxane, to maintain the final mixed solvent in 3 volumes of 1,4 dioxane to one volume H_2O. The solution was flushed out with nitrogen for one hour. A solution of (1×10^{-3}M) of deoxygenated p-EtOPhTeCl$_3$ (48ml) in 1,4 dioxane was added to the round bottom flask followed by a sufficient amount of V(II) with continuous stirring. The flask was covered with aluminium foil to exclude light. The concentration of the product, (p-EtOPh)$_2$Te$_2$ was determined spectrophotometrically. The experiment was repeated for seven different concentrations of V(II). The system was kept at dilute concentrations to prevent the precipitation of the product.

2-7-3 Determination of Cr(II) consumed by p-EtOPhTeCl$_3$

The determination was carried out by potentiometric titration as described in section 2-6 with-out adding HCl, with a waiting time of approximately 10 minutes after each addition of Cr(II) to the solution of the reaction. The ratio of water to 1,4-dioxane 1:3 was calculated previously. A solution of 0.01M of p-EtOPhTeCl$_3$ (25ml) in 1,4 dioxane followed by 1,4-dioxane (25ml); and distilled water (10ml) was used to keep the system under the same conditions as the kinetic runs, in order to avoid the effect of other conditions on the reaction.

2-8 Preparations

2-8-1 p-EtOPhTeCl$_3$

Tellurium tetrachloride (12gm), phenetole (17gm) and dry chloroform (75ml) were mixed and heated under reflux for 2 hours with stirring and 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$_3$ formed. This was removed after one day, washed with a little cold chloroform and dried. Yellow crystals (14.5gm) were obtained, which melted to a red liquid at 181-182°C (lit 182-183^{o}C)$^{(2)}$ without any further recrystallization. (found: C,27%; H,2.6%; $C_8H_9Cl_3OTe$ requires;C, 27.0%; H,2.5 %)

2-8-2 p-Phenetyltellurium Tribromide

Bromine in carbon tetrachloride (0.5gm) was added dropwise with stirring to a solution of $(p\text{-}EtOPh)_2Te_2$ (0.5gm) at room temperature and magnetically stirred. The solution of $(p\text{-}EtOPh)_2Te_2$ changed from orange-red to yellow with precipitation of yellow compound. Excess bromine was added. This was done by observing the existance of bromine colour in the solvent. The mixture was continuously stirred for another 30 minutes. The precipitate was filtered and dried, and recrystallized from glacial acetic acid. Yellow crystals were obtained and the crystals melted at 196-205^{o}C dec. (lit 195-205^{o}C)$^{(4)}$ (found:C,19.7%;H,1.7%;Br49%;$C_8H_9Br_3OTe$;requires:C,19.7% H,1.8%;Br,49%).

2-8-3 p-Phenetyltellurium Triiodide

The procedure was similar to that used for the corresponding tribromide; $(p\_EtOPh)_2Te_2$ one gram was reacted with iodine (1.6gm) in carbon tetrachloride The product obtained was recrystallized from benzene and afforded black needle crystals which melted at 133-134^{o}C (lit 133-134^{o}C).$^{(4)}$ (Found:C,15.4%;H,1.5%; $C_8H_9I_3OTe$ requires:C,15.3%;H,1.45%)

2-8-4 Bis-p-Phenetyl Ditelluride(2,6,20)

A solution of p-phenetyltellurium trichloride (6gm) in chloroform was reduced with potassium metabisulphite (5gm) in water (50ml), by putting both solutions in a conical flask and placing on a shaker for 30 minutes. The ditelluride was extracted from the chloroform layer and recrystallized from petroleum ether (60-80°C) producing fluffy masses of brilliant golden-orange plates, melting at 102-104°C to a deep red liquid (lit 107-108°C).(2) (Found:C,38.4%;H,3.6%; requires:C,38.6%; H,3.6%).

2-8-5 Chromous Sulphate

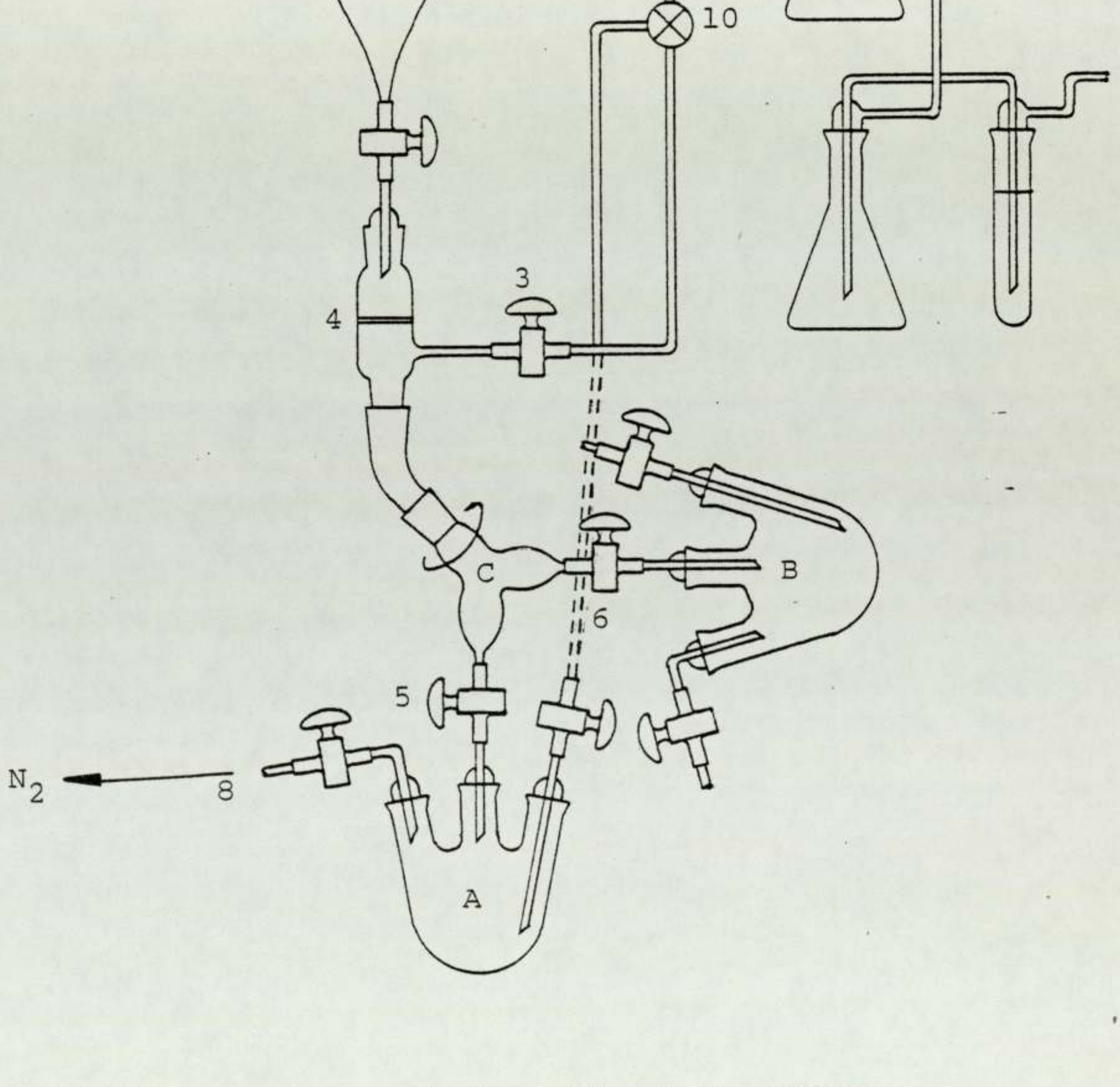
Chromium trioxide AnalaR grade (2gm) dissolved in approximately 250ml of redistilled water in a one litre conical flask, - was then acidified with concentrated sulphuric acid, (60ml), cooled followed by an addition of 35% hydrogen-peroxide (80ml) added slowly in several portions. The solution was heated to boiling point for 30 minutes to evolve oxygen. Then the solution was cooled and diluted to one litre in a volumetric flask. The inlet tube (Fig 2:1) connected to a nitrogen supply. The nitrogen from the latter passed through a vessel (B) containing chromous sulphate to consume any traces of oxygen. The Storage vessel (A) was flushed with nitrogen then half filled with AnalaR zinc. A chromium sulphate solution was placed in the vessel with sufficient quantity to cover the zinc.

2-8-6 Vanadium (II) Sulphate

Vanadyl sulphate, AnalaR grade (9.95gm) was dissolved in approximately 200ml of distilled water. The Solution was filtered through a No.4 Sintered glass crucible. The filtrate was transferred to a one litre volumetric flask and concentrated sulphuric acid (55.6ml) was added to give a solution of 2N with respect to the acid. A quantity of 250 to 350ml of this solution was placed in the storage vessel, enough to cover the zinc (Fig 2:1) as described in section 2-8-5. The colour of the solution changes from deep blue (VO (IV)) through green (V(III)) to pale violet (V(II)). Reduction is complete when the solution has a uniform pale violet colour.

2-8-7 Chromium (II) Acetate Monohydrate

A saturated solution of sodium acetate (100ml) was placed in a 250ml round bottom flask (Fig 2:1). Nitrogen was passed through the solution for 1 hour to flush out the traces of oxygen. A solution of 0.1M chromous sulphate (75ml) was added from the burette to a sodium acetate solution with continuous stirring for 20 minutes. The resultant water slurry, brick-red coloured, was filtered under nitrogen (Fig 2:2). There was no significant



Fig(2:2). Apparatus used for Filtration under Nitrogen effect from atmospheric oxygen on the slurry when it was transferred to the filtration apparatus.

2-8-8 Separation of Cr(III) Complex

Chromium acetate slurry, a brick-red colour, was transferred as quickly as possible from the round bottom flask (Fig 2:1) to a separation flask (Fig 2:2) which was initially flushed with nitrogen. A current of nitrogen was passed from the side tube (1) to maintain the nitrogen atmosphere in the separation funnel. The flask was stoppered, tap (3) was attached to a vacuum tap which caused the solution of chromous acetate to be filtered through the filter disc (4). The precipitate was washed with deoxygenated distilled water and the unwanted filtrate was received into flask (A). A solution of 20 N sulphuric acid (8ml) was cooled to 4°C and this was added to the precipitate. The apparatus was smoothly shaken until the brick-red colour changed to a pale blue of chromous sulphate. The chromous sulphate crystals were washed with a little deoxygenated methanol and also the joint (C) was rotated to replace flask (A) for flask (B). A solution of (0.1M) p-EtOPhTeX_3 (X=Cl,Br,I) (25ml) in deoxygenated, purified 1,4 dioxane was added to flask (B) and nitrogen purged the system for 15 minutes. Redistilled water (10ml) warmed to 30-35°C was added through the separating funnel, and the apparatus was shaken smoothly to let the chromous sulphate dissolve. Flask (B) was attached to the vacuum tap, and tap (5) was turned off. Tap (6) was turned on, this caused the transfer of the chromous solution to flask (B) and reduced p-$EtOPhTeCl_3$. The reaction under nitrogen was left for 30 minutes until completion. The contents of flask (B) were transferred to a 2 litre separation flask. A solution of diethyl ether (750-1000ml) was added to extract $(p\text{-}EtOPh)_2Te_2$. The layer containing the Cr(III) complex was washed several times with diethyl ether until a thick, dark green layer of Cr(III) complex was separated. The layer was transferred to 100ml round bottom flask and warmed to 30-35°C and attached to a vacuum pump for evaporating. The product was dried overnight over P_2O_5 under vacuum.

2-9 Ion Exchange

The elution characteristics of the product chromium (III) complex were studied using an ion exchange technique in order to determine the charge type on the complex. The study utilized cation exchange (H^+) form ZEROLIT 226 (Formerly Zeo-Karb 226) 14 to 52 mesh, standard grade from " Hopkin and Williams Limited."

A column of 35x1cm^2 was packed and washed several times with deionized water until the pH of the eluent was neutral to pH paper. A known concentration of Cr(III) solution was added to this column. The elution of Cr(III) complex was collected and diluted to 50ml in a volumetric flask. 10ml of the elution was taken from the volumetric flask and nitrogen was passed through for 30 minutes to flush out any traces of CO_2, then titrated against sodium hydroxide (0.01M) using bromomethyl blue, pH 6-7, as an indicator. The titration was repeated several times under nitrogen.

2-10 Recycling 1,4 Dioxane

A mixed solvent of 75% 1,4 dioxane and 25% distilled water was used through this project. Since 1,4 dioxane is an expensive solvent, the ether was recovered after use. The used solvent was collected and purified by distillation at 95-105°C to remove any dissolved solutes. An adequate amount of $CaCl_2$ was added to the distillation solvent and then heated to 65-75°C. The solvent was separated into two layers. The 1,4 dioxane layer was separated and dried on $CaCl_2$ for 24 hours, then refluxed on sodium wire for 8 hours, in an attempt to achieve complete dryness of the solvent.

2-11 Kinetic Studies

2-11-1 Apparatus for Stopped Flow Studies

This apparatus, in connection with SP8-100 UV visible spectrophotometer and thermostated water bath was used in our experiments to carry out studies of rates of reaction, either in order to minimize the time before the first readings, or to exclude atmospheric oxygen from the reactants. The apparatus is diagramatically explained in Fig2:3. It consists of two inter-connected glass syringes (25ml) enclosed in glass jackets through which water can flow at a constant temperature. Each of the two syringes is equipped with a tap, the purpose of which is to allow the liquids to be drawn into the syringes from the separate reservoirs(50ml). The separating reservoir is connected to nitrogen, to occupy the volume of reactant when drawn into the syringe. When the taps are turned, and the plungers of both the syringes simultaneously pressed, equal volumes of the two solutions can be delivered into the mixing chamber leading to the spectrophotometer cell. This method was found to reduce the time of the first reading to less than 3 seconds after mixing and to be adequate for work - with concentrations of Cr(II) and V(II) down to $6x10^{-4}M$.

2-11-2 Procedure using Stopped Flow System

The thermostating assembly of the water bath is adjusted to the required temperature and switched on. The required temperature in the bath was monitered using a thermometer divided into tenth of degree centigrade. The apparatus was flushed with nitrogen for a minimum of 30 minutes prior to use. Equal volumes of deoxygenated reactant were transferred from their storage flasks to the separate

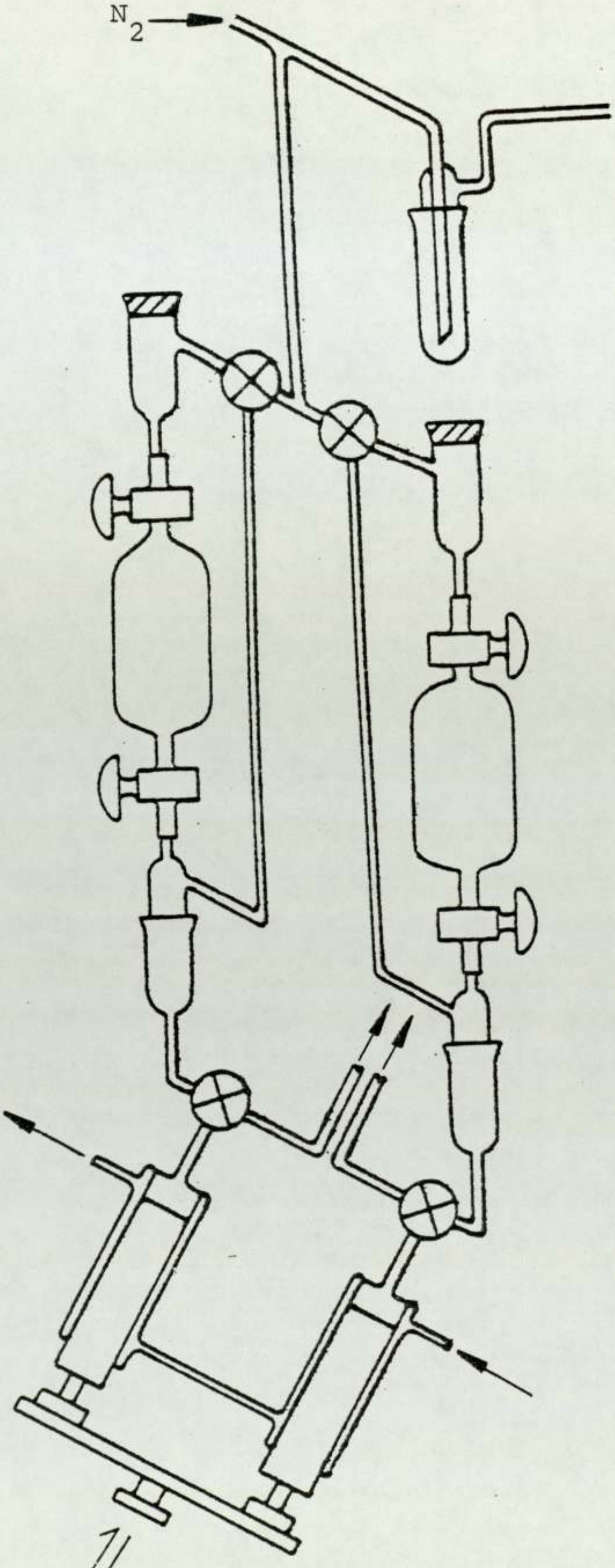
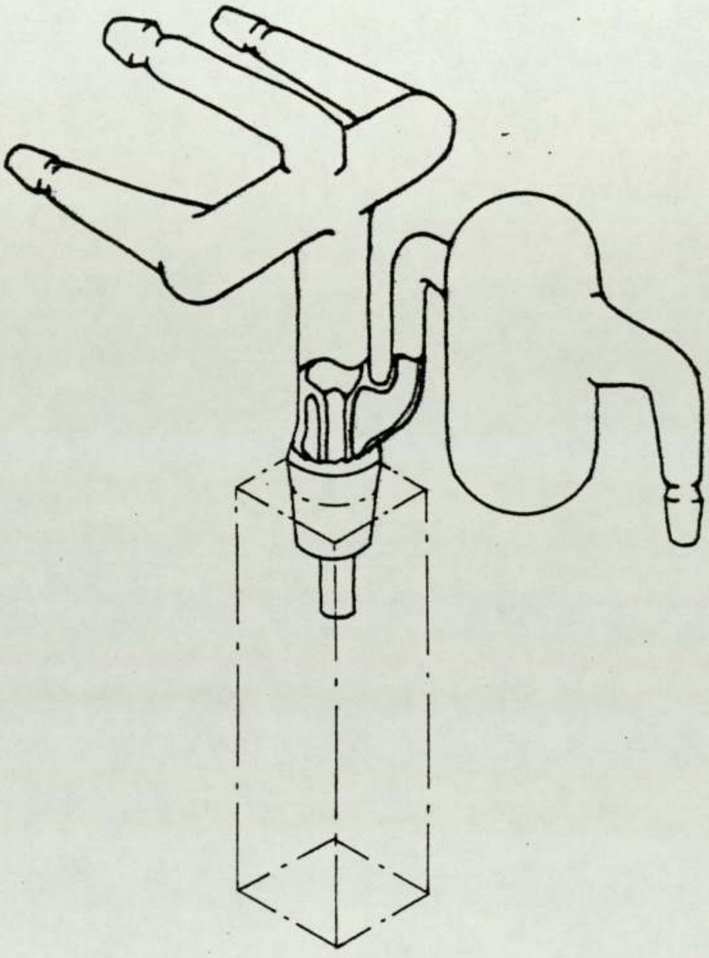


Fig (2:3) Apparatus for stopped flow studies under Nitrogen reservoirs. The reactant solutions were then drawn into the respective syringes from their reservoirs and thermostated for 15-20 minutes. At the start of each experiment, the spectrophotometer is zeroed and the plungers on the syringes are pushed evenly via their connecting bar. This action transfers the two solutions to the cell via mixing chamber (Fig 2:4) where they can react together, the resultant solution is finally delivered to the spectrophotometer cell. The reaction was carried out at controlled temperature by circulating water through the water jacket of the cell holder from the water bath. The absorbance of the product at 400n m. being recorded versus the time. The experiment was repeated at different concentrations and over a temperature range from 15 to 45^{o}C (with 5^{o}C intervals). It was also repeated at different ionic strengths, ratios of mixing solvents and at different pH's. After each experiment the cell was cleaned, first with acetone then dried by passing compressed air through it.

2-11-3 Procedure without Stopped Flow System

In this procedure a three-neck 75ml round bottom flask was put in a thermostat bath, then flushed with deoxygenated nitrogen for approximately 20 minutes, prior to use Predetermined volumes of deoxygenated solvents of distilled water, 1,4 dioxane and 20N H_2SO_4 were added to the flask, to make the final ratio of the solvents 50%



Scale ≃ 2:1

Fig (2:4). The mixing chamber with the Quartz Cell

1,4 dioxane. Lastly, a required volume of Cr(II) or V(II) solution was dispensed from the burette , whose tip passed through a rubber suba seal into the middle neck of the flask. The second neck was used for bubbling nitrogen through the solution and the third for the nitrogen out let.

The quartz cell (4ml) was filled with 2ml of deoxygenated p-EtOPhTeCl_3 and kept in a thermostat bath under nitrogen and 2ml of the solution from the three neck flask was injected from the pipette under the surface of p-EtOPhTeCl_3 solution. The cell was quickly stoppered, shaken well and put into the cell holder of the spectrophotometer. This procedure was found to be satisfactory even though the first reading was taken at 25-30 sec, and was adequate for concentrations of chromium (II) and vanadium (II) down to $6x10^{-4}$M.

In the reduction with $S_2O_5^{2-}$ and SO_3^{2-} the same procedure was carried out without adding 20N H_2SO_4

It was found that using pre-mixed 50% 1,4 dioxane and 50% distilled water for the reducing agents causes a reduction in the mixing time of the reactant and prevents the formation of either the white precipitate of hydrolysed p-EtOPhTeCl_3 or of the turbidity caused by inorganic compounds.

2-11-4 Solvolysis of p-EtOPhTeX_3 (X=Cl, Br, I)

The solvolysis of p-EtOPhTeX_3 in water or methanol was determined at controlled temperatures. The apparatus consisted of 250ml beaker enclosed in a glass jacket. The system can be kept at a constant temperature by circulating water through the water jacket of the beaker from the water bath (Section 2-11-2).

The mixed solvent in the thermostated beaker was stirred continuously by a magnetic stirrer. The pH of the mixing solvent of methanol and benzene was measured on a pH meter mentioned in section 2-3-5. Prior to use all solvents were carefully dried on sodium metal and distilled (Section 2-2).

The mixed solvent was left in the beaker for 15-20 minutes until the desired temperature was reached. At the same time the electrode of the pH meter was immersed in the mixed solvent until the pen on the linear recorder unit showed a constant reading. The solution of p-EtOPhTeX_3 in benzene was added to the mixed solvent and the curve of the pH-time was obtained.

The experiment was repeated in different percentages of methanol and at different temperatures.

2-12 Photochemical Observations

2-12-1 Irradiation of p-EtOPhTeX_3 (X=Cl, Br, I)

Benzene solutions of p-EtOPhTeX_3 were prepared, divided into two equal volumes and placed in separate volumetric flasks. One of the flasks was irradiated by natural light for 15 days and the other flask was kept in the dark for the same period. The colour of the irradiated solutions of p-EtOPhTeCl_3 and p-EtOPhTeBr_3 were considerably bleached. Ultra-violet and visible spectroscopy show considerable changes in the spectra of the solutions, as shown in Figures 2:5, 2:6 and 2:7. A creamy coloured precipitate was obtained from the irradiated solution of p-EtOPhTeBr_3 which gives a strong peak at 600cm^{-1} in its I.R. spectrum, Figures 2:8 and 2:9. Similar observations were made with different solvents (i.e. 1,4 dioxane, toluene, T.H.F. etc.,).

2-12-2 Irradiation of $(p\text{-EtOPh})_2Te_2$

A solution of $(p\text{-EtOPh})_2Te_2$ $3.4x10^{-4}M$ in mixed solvents of toluene and methanol (5:1) was irradiated by a 60 watt domestic light bulb. The experiments were carried out under air and also under oxygen-free nitrogen. No significant change in the absorbance was observed when either oxygen or light was Excluded from the solution. The same experiment was repeated under atmospheric conditions until the absorbance of the solution attained approximately half of the initial readings. Then the solution was kept in the dark and the absorbance reading was carried out at the same periods. The data are listed in Table 2:1. A plot of absorbance versus time for the solution is shown in Fig 2:10.

Absorbance	Time/Minutes
0.409	00
0.381	05
0.330	10
0.245	15
0.174	20
0.174	25
0.174	30
0.174	Constant reading for more than 48 hours in dark or under oxygen-free-nitrogen.

Table (2:1)

Experimental data of absorbance of $(p\text{-EtOPh})_2Te_2$ 3.4×10^{-4}M in a mixed solvent of toluene-ethanol (5:1) irradiated for 20 minutes.

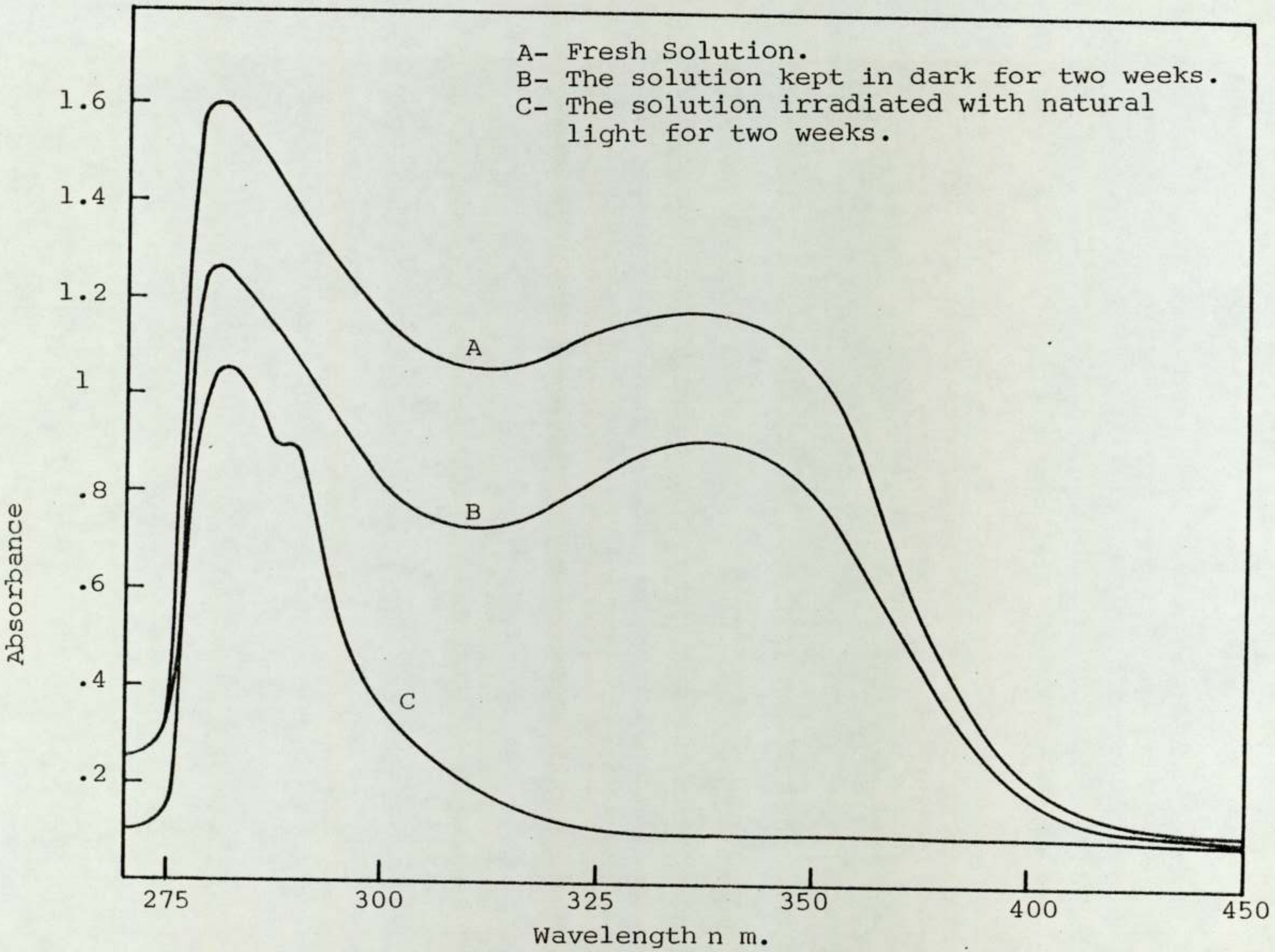


Fig (2:5) UV Visible spectra of p-EtOPhTeCl_3 in Benzene

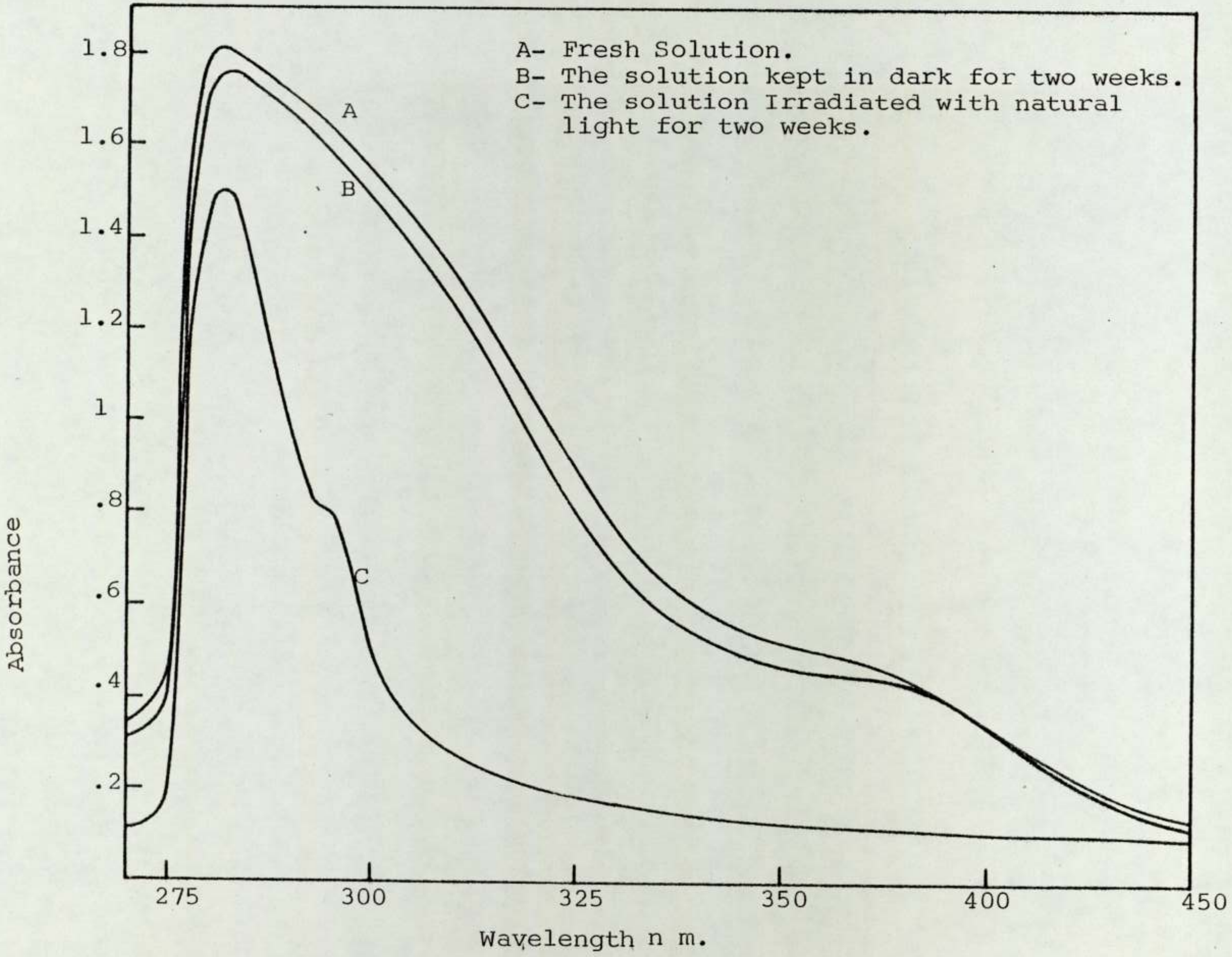


Fig (2:6). UV Visible Spectra of p-$EtOPhTeBr_3$ in Benzene

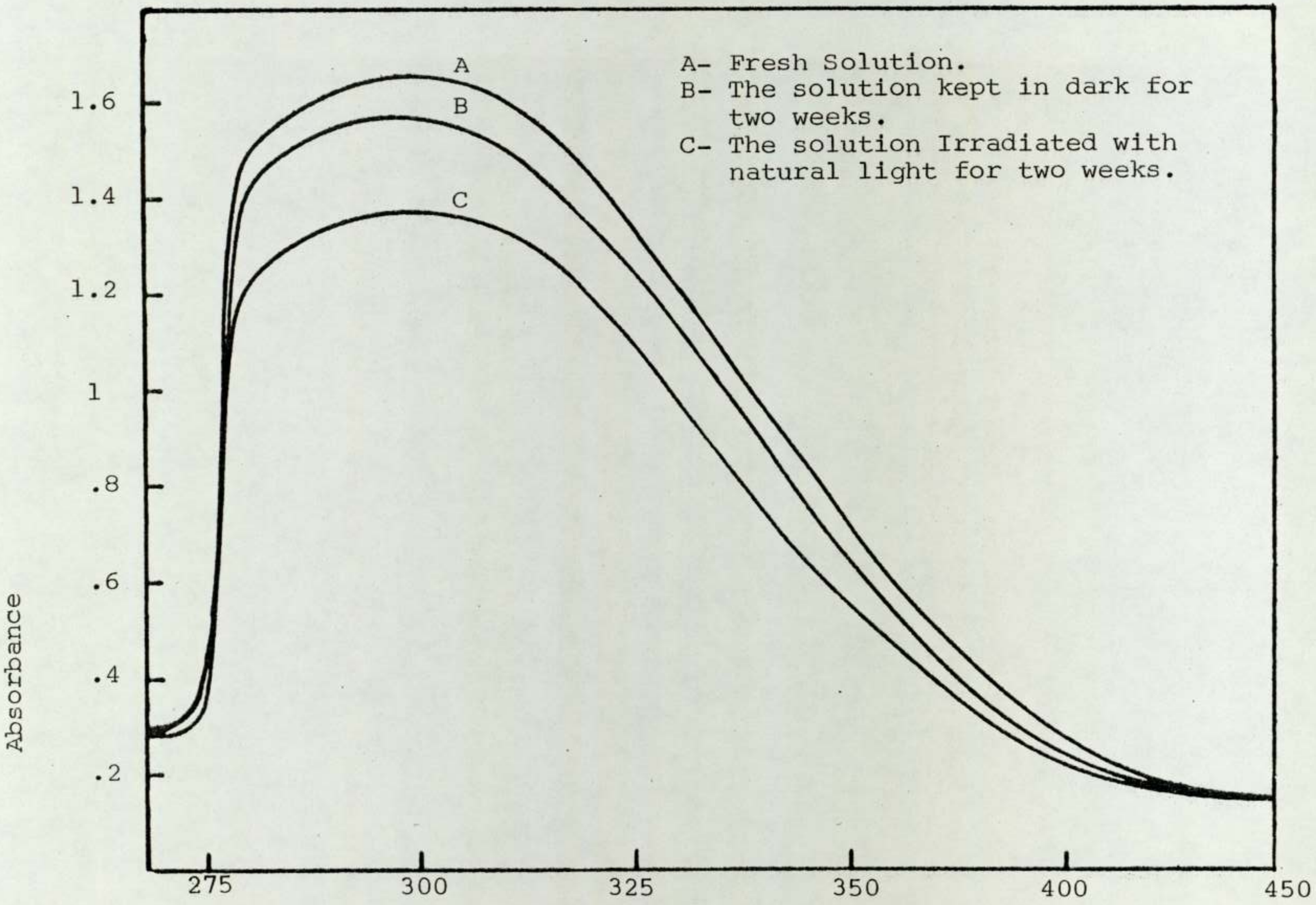


Fig (2:7). UV Visible Spectra of p-EtOPhTeI$_3$ in benzene.

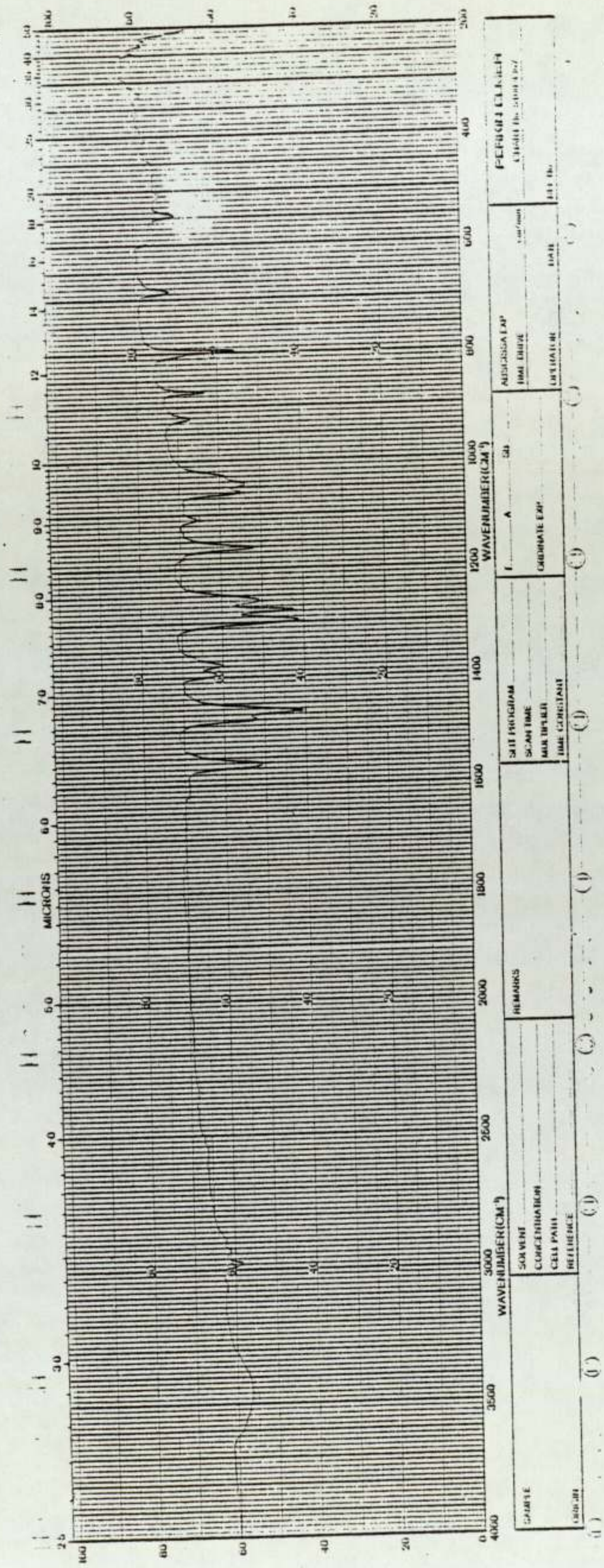


Fig (2:8). I.R. Spectra of p-EtOPhTeBr$_3$ as CsI Disc

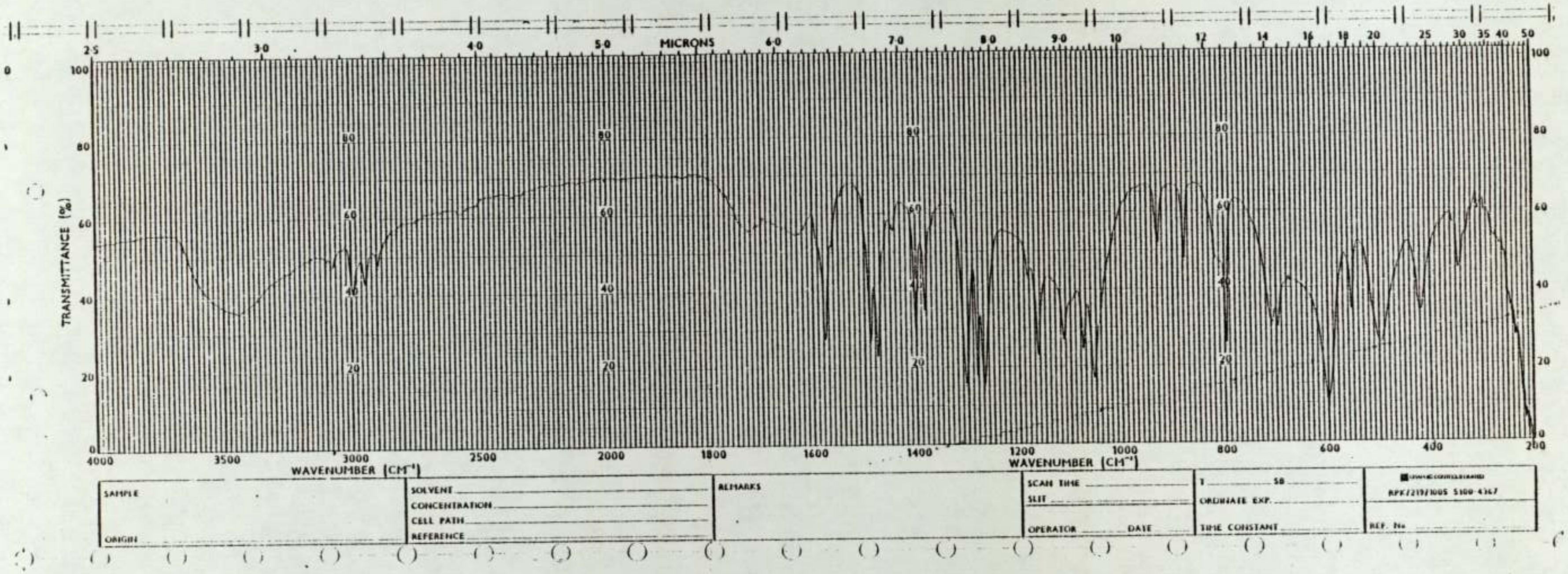


Fig (2:9). I.R. Spectrum of precipitate obtained from Irradiating p-$EtOPhTeBr_3$ as CsI Disc.

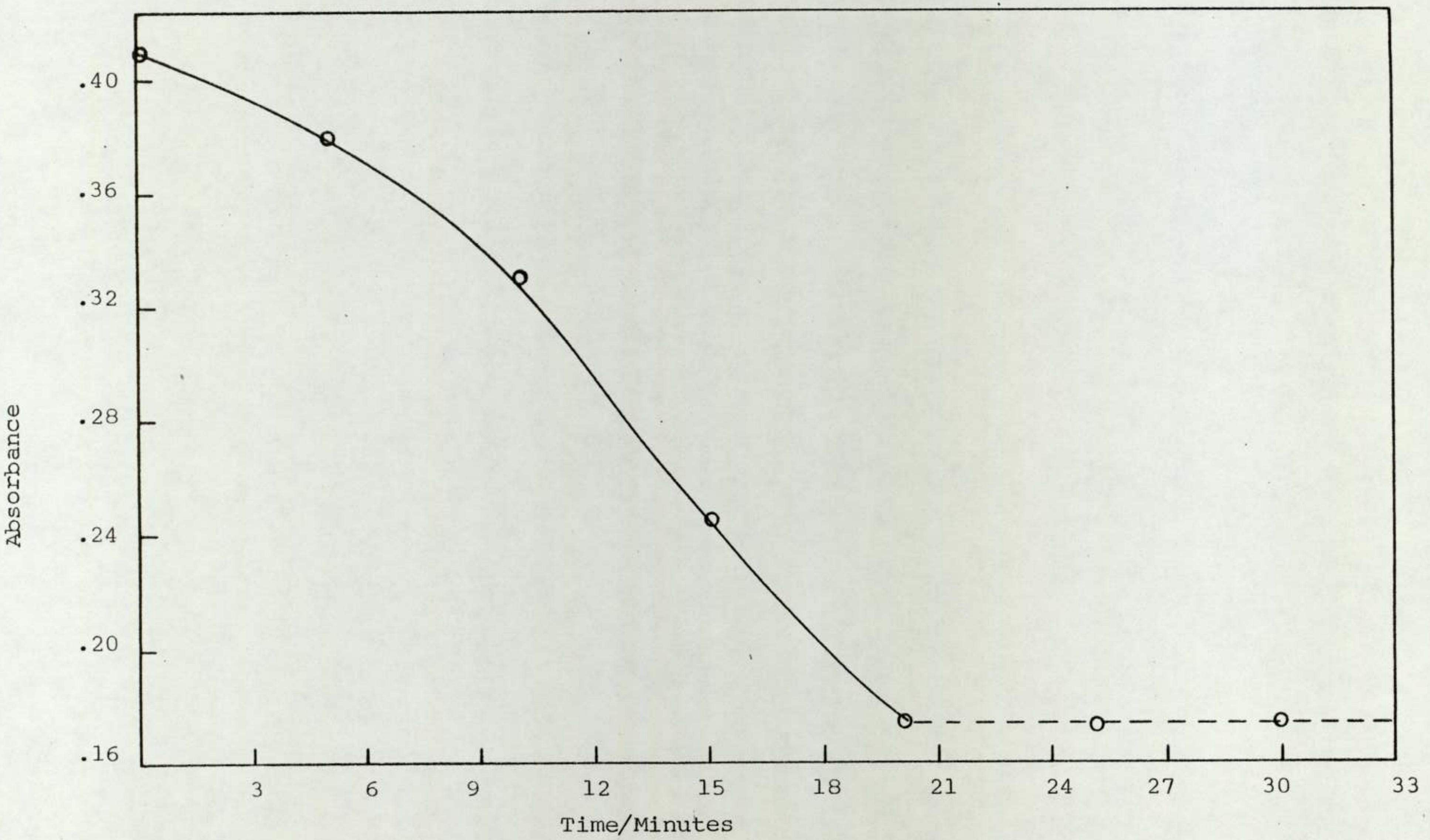


Fig (2:10). A plot of absorbance of $(p\text{-}EtOPh)_2Te_2$ Irradiated by visible light versus Time

CHAPTER THREE

REDUCTION OF p-ETHOXYPHENYLTELLURIUM TRICHLORIDE WITH SODIUM BISULPHITE AND METABISULPHITE

3-1 Introduction

An investigation of the rates of reduction of aryltellurium trihalides by alkali sulphites and metabisulphites was prompted during the synthesis of corresponding diaryl-ditellurides. Although such reactions are important routes extensively used to prepare the diarylditellurides, it appears that no attention has been given to the study of the kinetics and mechanisms involved in the reactions of sulphite and metabisulphite ions, with p-$EtOPhTeCl_3$ under different reaction conditions. Morgan and Drew(2) in 1925 first synthesised bis(p-EtOPh)Te_2 by the reduction of p-$EtOPhTeCl_3$ with **alkaline metabisulphite.** Shortly thereafter, several workers(6,18,20) prepared similar compounds using different reducing agents. Many different methods have been reported for the preparation of new compounds of diorganyl ditellurides.

The chemistry of metabisulphites is largely that of normal sulphites.(42,43) They are related to the equilibria:

$$S_2O_5^{2-} + H_2O \rightleftharpoons 2HSO_3^-$$

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

While at high concentrations only three ions are present ($2M^+$) and $S_2O_5^{2-}$, at lower concentrations four ions are observed corresponding to ($2M^+$) and $2HSO_3^-$ (44).

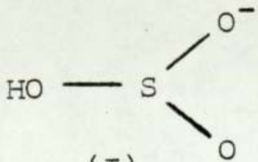
The hydrolysis of metabisulphite solutions occurs rapidly resulting in the formation of the bisulphite. Frederick;(43) Garrett(45) found that both the sodium and potassium metabisulphite solutions behaved in a similar manner to the hydrogen sulphite solutions. Baly and Bailey,(46) stated that freshly prepared solutions of potassium metabisulphite exhibit a characteristic absorption band at λ=257 n.m. and that a similar band is observed in freshly prepared solutions of the alkali metal bisulphites.

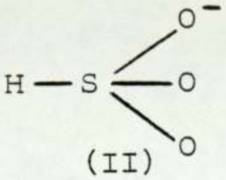
Wilf (47) and co-workers found that HSO_3^- exists in equilibrium with $S_2O_5^{2-}$:-

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

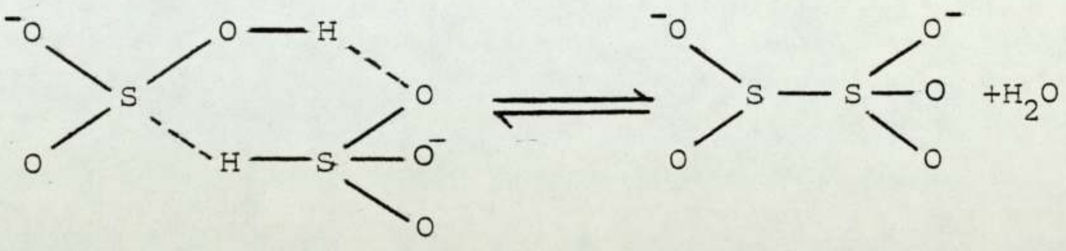
which absorbs strongly at ~255n.m. Lindqvist and Mörstell(48) described the $S_2O_5^{2-}$ ion as a thionite-thionate ion. Their assumption was made on comparison of crystal data of $S_2O_5^{2-}$ with dithionite, $S_2O_4^{2-}$, and dithionate, $S_2O_6^{2-}$, ions. The results show that the thionite groups in $S_2O_4^{2-}$ and $S_2O_5^{2-}$ are very similar, as are the thionate groups in $S_2O_5^{2-}$ and $S_2O_6^{2-}$. Furthermore, the S-S bond length in $S_2O_5^{2-}$ is intermediate between those found in $S_2O_4^{2-}$ and $S_2O_6^{2-}$.

Golding (49) introduced two isomeric species (I) and (II), postulated by Schaefer et al(50) to explain


(I)


(II)

the equilibrium of bisulphite-metabisulphite at high concentrations of bisulphite solution. As the total sulphur concentration increases, hydrogen bonding between species (I) and (II) becomes more favoured, and species (III) is formed



(III)

According to Lindqvist and Morstell(48), the metabisulphite ion has an (S-S) bond and (S-O) bonds and not the (S-O-S) configuration. Golding concluded that the formation of S-S bonded $S_2O_5^{2-}$ ions is much more likely through the hydrogen-bonded bisulphite species(III).

In their general reactions, **sulphites** are moderate reducing agents.(39) On the other hand, they are capable of oxidizing strong reducing agents such as phosphine, hydrophosphorous acid, phosphorous acid and hydrogen sulphide. Oxidation and reduction reactions of sulphites, especially in slightly acidic solutions parallel those of sulphurous acid.

The reactions between different oxidizing and reducing agents may be interpreted in two type of mechanisms:-

I) The outer sphere mechanism which involves electron transfer from reductant to the oxidant while the co-ordination shells or spheres of both reductant and oxidant remain intact. An example of this type of reaction is the oxidation of $(Ru(NH_3)_6)^{2+}$ by complex ions of type $(Co(NH_3)_5L^{-n})^{3-n}$, where L^{-n} is a variety of ligands(51). It is thought that while it is not necessary(52) for the reactants to collide, they must approach to such a distance that there is a slight over-lap of the reactant orbitals.

II) The inner sphere mechanism 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(53). The system involved the reduction of Co(III) by Cr(II):-

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

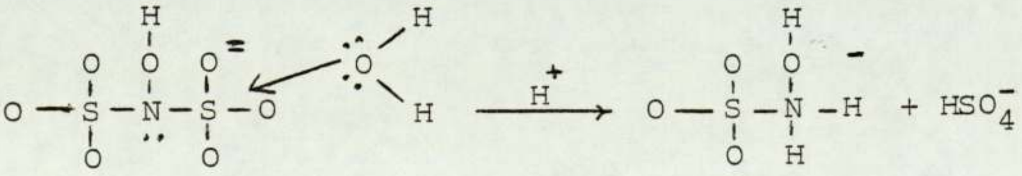
$$\left[(NH_3)_5\,\underset{(A)}{Co\text{-}Cl}\text{-}Cr(H_2O)_5\right]^{4+} \longrightarrow$$

$$\left[CrCl(H_2O)_5\right]^{2+} + Co(II) \text{ species}$$

which takes place within a binuclear complex (A) with the formation of the reduced Co(II) and oxidized Cr(III). Such a reaction consists of the transfer of a chlorine atom from cobalt to chromium.

In a large class of oxidation reduction reactions, the oxidizing agent undergoes a loss of oxygen and reducing agent gains in oxygen content. These reactions involve mainly typical element compounds. The transfer of oxygen from the oxidizing agent to the reducing agent takes place in this type of redox reaction in the absence of any other source of oxygen. However, when the change occurs in an oxide labile solvent, such as water, Halperin and Taube (54,55,56) suggested that there is the possibility that the oxygen which appears on the reducing agent came from the environment. Labelled oxygen was used to distinguish between the two alternative mechanistic routes. The first involving oxygen atom transfer between the reactants, and the second involving electron transfer only. They concluded that the direct transfer of oxygen from the oxidizing agent to the sulphite takes place in the reaction of the sulphite ion with various oxygen containing oxidizing agents.

Rutenburg, Halperin and Taube (57) investigated the reaction of sulphite with nitrite. They concluded that the product (HSO_4^-) of this reaction contains an oxygen atom derived from the solvents. The mechanism proposed for the reaction is:-



where the hydroxylamine disulphonate $(HON(SO_3)_2^{=})$ is an intermediate which can be isolated from the reaction mixture.

Winter and Briscoe(58) studied the oxidation of sodium sulphite by oxygen and hydrogen peroxide in ^{18}O labelled water. In both cases they found that the oxygen atom which was transfered to the sulphite ion came from the oxidizing agent and not from the water.

Higginson and Marshall(59) compared the stoichiometry of the oxidation of sulphurous acid in aqueous solutions by various reagents with the results of those previously obtained in the oxidation of the hydrazine by same reagents. They found that the only common products of the oxidation of sulphurous acid and its related anions were sulphate and dithionate ions. The nature of the products formed depends principally upon whether the oxidizing agents favours a (1) or (2) or (1,2) equivalent reactions. The mechanisms of these types of reactions are generally represented in the form:-

a) reaction with a 1-equivalent oxidizing agent:-

(I) $X(N) \xrightarrow{\text{1 equ.}} x(N+I)$, Initial oxidation process.

(II) $2X(N+I) \longrightarrow (X(N+I))_2$ Dimerisation of radicals

(III) $2X(N+I) \longrightarrow X(N+II) + X(N)$, disproportionation of radicals,

(IV) $X(N+I) \xrightarrow{\text{1 equ.}} X(N+II)$, Further oxidation of radical.

b) Reaction with a 2-equivalnet oxidizing agent:-

(V) $X(N) \xrightarrow{2\ \text{equ.}} X(N+II)$

Where X(N) represents a simple compound of a non-metallic element in oxidation state N. 1,2 equivalent reactions occur according to both these mechanisms. They concluded that the oxidation of sulphite ion to sulphate or dithionate is dependant upon the pH of the solution. In addition to the main reactions, a side reaction involving the formation of dithionate occurs to a limited extent.

Rao and Rao(39) pointed out that most of the oxidometric methods for the estimation of sulphites are incorrect, due mainly to the partial conversion of sulphite to dithionate which resists further oxidation. They point out that if the reaction is carried out in the presence of a suitable catalyst, with control of the acid concentration, the dithionate formed can be further oxidized to sulphate.

Backstrom(60) attributed the variation of the rate of oxidation of sodium sulphite solution to the hydrogen ion concentration. The addition of sulphuric acid serves the purpose of buffering the solution by transforming a definite proportion of the sulphite ions into bisulphite.

Bassett and Henry (61) investigated the mechanism of the formation of dithionate by the oxidation of sulphurous acid and sulphites with different oxidizing agents. They attributed the formation of dithionate, in the oxidation of sulphurous acid solution by free oxygen, to the sulphite concentration and to the increase in the acidity of the solution. This solution becomes more acidic as sulphuric and dithionic acids replace the weaker sulphurous and metabisulphurous acids. The proportion of dithionate formed should increase if it results from direct oxidation of metabisulphite species. With metals like silver, copper or ferric iron, there can readily arise anionic complex sulphite ions such as $(Ag(SO_3)_2)^{\equiv}$ or $(Fe(SO_3)_3)^{\equiv}$. Complexes of this type are likely to undergo self-oxidation and reduction if the metal ion is easily reducible to a lower oxidation state. If two $SO_3^=$ ions of such complexes each surrendered an electron to the metal ions, the SO_3^- groups could readily link up to form the dithionate ion. For sulphate to be formed one electron at a time by a similar mechanism, the $SO_3^=$ ion must lose an electron to the metal ion, and on collision with another complex the second electron must be lost by the partially discharged sulphite group resulting in the formation of neutral SO_3. That trioxide molecule would at once react with water to give sulphuric acid. Since the same complex could give rise to either sulphate or dithionate by reactions of the same order, it follows that the proportions of the two oxidation products should essentially be independent of concentration, acidity, etc.., and depend almost entirely upon the nature of the oxidizing metal ion. Decomposition of a sulphite complex could only give rise to dithionate in cases where just one electron is abstracted from an $SO_3^=$ by the metal ion. If two electrons were removed, the sulphur trioxide formed could only yield sulphate. It is likely that any reduction of metal ion by two Valency Units e.g.:-

$$\text{Pb (IV)} \longrightarrow \text{Pb(II)}$$

would yield only sulphate(62) as long as the mechanistic steps as well as the overall change, involved two electrons at a time. Thus, manganese dioxide affords a large yield of dithionate. Since the tervalent state of manganese is well defined, it is probable that the reduction occurs in two steps. On the other hand in some circumstances the one-stage reduction:-

$\text{Mn(IV)} \longrightarrow \text{Mn(II)}$ may occur yielding only sulphate.

It may be correct to regard ferric chloride as a similar oxidizing agent to p-EtOPhTeCl$_3$. They both contain three chlorine atoms and they have no oxygen atoms to be involved in their redox reactions.

The reduction of ferric chloride by sulphurous acid has been investigated by Bassett and Parker (63). They attributed the decrease in the proportion of dithionate, which formed on reduction of $FeCl_3$ by sulphurous acid, to the stability of the anion $(FeCl_4)^-$. They concluded that anions of high electroaffinity, such as $SO_4^=$ and NO_3^- do not readily form stable complex ions. Complex sulphito-anions can accordingly be formed with ease both in sulphate and nitrate solutions and give high yields of dithionate as they undergo electron transfer. The tetrachloroferrate (III) anion $(FeCl_4)^-$ is, however, very stable so that ferrisulphite anions are not so readily formed in the presence of chloride. The presence of the complex ions $(Fe(SO_3)_2)^-$, $(FeCl_2(SO_3))^-$ and $(FeCl_4)^-$ would appear to be possible in sulphurous acid solutions prepared from ferric chloride, with or without additional chloride ions. It seems unlikely that any $(Fe(SO_3)_3)^{\equiv}$ could be present on account of the very low concentration of $SO_3^=$ ions.

Interactions between two $(Fe(SO_3)_2)^-$, or between an $(Fe(SO_3)_2)^-$ ion and either of the other two might give rise to dithionate or sulphate according to the particular pathway followed during electron transfer. Similarly two $(FeCl_2(SO_3))^-$ ions might yield either dithionate or sulphate, but reactions between $(FeCl_2(SO_3))^-$ and $(FeCl_4)^-$ could give only sulphate. The formation of the latter two ions would be favoured by an increase in the concentration of chloride ions from any source, even by an increase in the original concentration of ferric chloride:-

$$2FeCl_3+H_2SO_3 = H(FeCl_2(SO_3)\ ) + H(FeCl_4)$$

Therefore, a dilute solution of ferric chloride gives rise to a high proportion of dithionate while, in contrast, a solution of ten times the concentration yields hardly any.

Hoffmann and Edwards(64) studied the kinetics of the oxidation of sulphite by hydrogen peroxide in acidic solution. They concluded that the reaction probably proceeds via a nucleophilic displacement by H_2O_2 on HSO_3^- to form a peroxomonosulphurous acid. Species, $HOOSO_2^-$, which then undergoes a rate determining rearrangement.

One may conclude from the literature that the meta-bisulphite solution behaves in a similar way to the sulphite solutions. The oxidation of SO_3^{2-} and $S_2O_5^{2-}$ to sulphate or dithionate depends on whether the oxidizing agents favour one or two-equivalent reactions. The reduction by two-equivalent oxidizing agents will yield sulphate. The production of dithionate is favoured at lower pH and lower chloride ion concentration. In an oxide labile solvent the oxygen appearing on the reducing agents may be derived from the environment. These generalisations may be relevant to the main points of the kinetics and mechanism of our work which included the oxidation of $S_2O_5^{2-}$ and

SO_3^{2-} by p-EtOPhTeCl$_3$.

The purpose of the investigation described in this chapter is to investigate the mechanistic features of the related reduction of aryltellurium trihalides to diarylditellurides through kinetic measurements. Parameters such as temperature, reagent concentration, acidity, electrolyte concentration and solvent composition being varied to help to provide an understanding of the mechanistic features.

It was found that the ratesof the reaction of p-EtOPhTeCl$_3$ with $S_2O_5^{2-}$ and SO_3^{2-} decrease as the pH of the reacting solutions decreases.

Oswald(65) and Arrhenius(66) were the first workers to realise that the ability of an acid to catalyze the reaction of the hydrolysis of esters and the inversion of the cane sugar is independent of the nature of the anion but is approximately proportional to its electrical conductivity. They pointed out that the conductivity of an acid is a measure of its strength, i.e. of the concentration of hydrogen ions. The solvated hydrogen ion is assumed to be the sole effective acid catalyst. It was similarly shown(67) that for catalysis by alkalies the rate is proportional to the concentration of the alkali but independent of the nature of the cation. Thus indicating that the active species is the hydroxide ion. The rates of the reduction of p-EtOPhTeCl_3 by different reducing agents also depend upon the ionic strength of the reacting solutions. The dependence of rates of reaction on ionic strength has been used as evidence to confirm the mechanism of many reactions.(68) The Debye Hückel(69) Theory has been applied to the influence of neutral salts upon the rates of reactions in solution by Brönsted,(70) Bjerrum(71) and Christiansen.(72)

There are two kinds of salt effect:-

i) The primary salt effect. This arises because the presence of added ions alters the activities of reactant particles, whether they are ions or molecules. Therefore, the variation of the reaction rate with ionic strength depends upon the way in which the activity coefficient ratio varies with the ionic strength.

ii) The secondary salt effect. Here the effective concentration of a reactant ion deriving from a weak electrolyte is decreased as the ionization of the electrolyte is suppressed by the added salt. In very dilute solutions the activity coefficient is in accord with the Debye-Hückel limiting law. Then the logarithm of the rate constant of the reaction between ions varies with the square root of the ionic strength. At higher ionic concentrations the rate constant may change because of changes in the activity coefficient of the ions which are not accounted for by the Debye-Hückel theory and because the activity coefficient of neutral molecules are affected by higher ionic strengths. Hückel(73) proposed that the logarithm of the rate constant for a reaction between an ion and neutral molecule should vary with the first power of the ionic strength instead of with the square root.

Olson and Simonson(74) discussed the effect of the addition of "inert" salts on ionic reaction rates. They found that the reaction between ions of like charges is affected both by the concentration and by the magnitude of the charge of salt ions of opposite charge. The rate is not dependent upon the ionic strength of the solution. In reactions between ions of opposite charges, both salt ions can affect the rate although the effect of one may be dominant. They concluded that the further introduction of activity coefficients is not necessary.

In nonpolar solvents more effects of ionic strength are found. Fainberg and Winstein(75,76) investigated the salt effect of several compounds on solvolyses in acetic acid as solvent . They pointed out that the salt effects observed for these compounds only involve their influence on ionization rate. They do not involve any special effects of salts on the behaviour of intermediates. Large salt effects in non-polar solvents have been investigated by Winstein et al.(77) They pointed out that salt effects tend to become quite large in poor ionizing solvents such as acetone, octanoic acid and ethyl acetate, and enormous in solvents such as diethyl ether. This may arise because the relative ionizing power of the solvents are altered by the addition of the salts.

Salt effects may be eliminated from consideration by dealing with rate constants for conditions of zero ionic strength. In ionic reactions the factor having the most pronounced influence upon rate constants at zero ionic strength and constant temperature is usually the dielectric constant of the solvent medium. The variation of rate constant with dielectric constant (D) has long been used as a source of evidence concerning mechanisms(68). Kinetic studies in mixed solvents offer both advantages and disadvantages compared with those in single solvents. For example, where it is not possible to study the role of the solvent in the aquation reactions of the octahedral complexes without having recourse to mixed solvents, it appears to be disadvantageous to work with a mixed solvent. Firstly, it is difficult or even impossible to decide on the composition of the immediate 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 solvent components 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.

Amis and La Mer(78) plotted log k at zero ionic strength ($k_{x=o}$) versus (1/D) for the reaction between negative divalent tetrabromophenol sulphonphthalein and negative univalent hydroxide ions in water-methyl alcohol and water ethyl alcohol 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 curvature in the region of pure water. The deviation of the ($\ln k_{x=0}$) versus 1/D plots from linearity in the low dieletric constant region of the solvent were attributed to the preferential adsorption of water on the ions. The authors concluded that when solvents of lower dielectric constant are added the effects are not as great as would have been the case if the solvent molecules had been randomly orientated.

Hückel(79), Debye and Mc Ulay (80) 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(81) pointed out that sets of data, describing variations of rate constant with dielectric constant, that can be extrapolated to zero ionic strength are scarce. Since Hückel, Debye and McUlay tend to discount the effect of ionic strength, Eyring plotted log k versus 1/D for different reactions.(82) Good straight lines with positive slopes were obtained. The slopes of such lines are always positive, irrespective of the sign of the charge of the ion, since they are governed by the square of the charge. Martin and co-workers(83-86) have plotted log k versus $(D-1)/(2D+1)$ for dipole-dipole reactions. They obtained straight lines from such plots. Deviations from linearity were found only at low values of the dielectric constant.

It is against a background of these various reported findings that the reductive formation of diarylditellurides will be discussed. They provide sufficient documentation to enable much of the mechanistic detail of the present system to be unravelled.

3-2 Results

3-2-1 Reduction with Sodium Metabisulphite

The reaction of p-EtOPhTeCl_3 with sodium metabisulphite has been investigated under different reaction conditions. The absorption spectrum of $(p\text{-EtOPh})_2Te_2$ in aqueous 1,4 dioxane (1:3 by volume) is shown in Fig (3:1). It is found that the maximum absorbance is at 400 n.m. This represents the best wavelength to follow the rate of reaction between p-EtOPhTeCl_3 and sodium metabisulphite. No absorbance in this is found for the solution of sodium metabisulphite. The mixed solvent of 75% 1,4 dioxane and 25% by volume distilled water was used as it is capable of dissolving both the products and the reactants.

A plot of absorbance versus concentration of $(p\text{-EtOPh})_2Te_2$ is a straight line as shown in Fig (3:2). The slope represents the molar extinction coefficient of $(p\text{-EtOPh})_2Te_2$. The experimental value obtained for the slope is 1200 $dm^3\ mol^{-1}\ cm^{-1}$ The plot shows that Beer's law is valid over a considerable range of concentrations for the solution of $(p\text{-EtOPh})_2Te_2$ in aqueous 1,4 dioxane (1:3 by volume).

The determination of the stoichiometry of the reaction of metabisulphite ion was made by spectrophotometric measurement. The data are listed in Table(3:1) and the plot of the molar concentration of $(p\text{-EtOPh})_2Te_2$ produced versus the molar concentration ratio of ($S_2O_5^{2-}$/p-EtOPhTeCl$_3$) is shown in Fig (3:3). The plot shows that one mol of p-EtOPhTeCl$_3$ reacts with 0.75 mol of the metabisulphite, with in experimental error to yield half a mol of product.

No dithionate was detected as a product of the reduction of p-EtOPhTeCl$_3$ with the metabisulphite ion . The kinetic studies for the reaction were made by measuring the increase of the concentration of the product (p-EtOPh)$_2$Te$_2$ with time. Usually a period of between 3 and 10 minutes was adequate. The reaction was followed at wavelength of 400 n m. using an SP8-100 UV visible spectrophotometer. It was confirmed that all results obtained are reproducible.

Up to 80 to 90% completion, the absorbance-time graphs can be fitted to the equation for a second order reaction. The values of the rate constant were obtained by considering particular values set into the more general equations,

$$aA + bB \longrightarrow C + \text{other products} \qquad (3:1)$$

The rate of reaction of p-EtOPhTeCl$_3$ with different reducing agents may be described by:-

$$\frac{d[C]}{dt} = k[A][B] \qquad (3:2)$$

Where A, B, C are the concentrations of the oxidizing agent, the reducing agent and the product (p-EtOPh)$_2$Te$_2$

respectiveley, when:-

$$A/B > b/a$$

Where (a) is the number of electrons gained by the oxidizing agent, and (b) is the number of electrons lost by the reducing agent per molecule, i.e. when the oxidizing agent is in excess, equation (3:3) can be obtained:-

$$k_{obs}\ t = -\ln\left\{\frac{D_f - (D_t/R)}{D_f - D_t}\right\} \qquad (3:3)$$

Where D_f and D_t are the final absorbance and absorbance at time (t) of the solution, also:-

$$R = a[B]_o / b[A]_o$$

Then k_{obs} is given by:-

$$k_{obs} = k_r\left\{b[\text{Red.}]_o - a[\text{p-EtOPhTeCl}_3]_o\right\} \qquad (3:4)$$

Alternatively, when $A/B < b/a$, i.e. when the reducing agent is in excess the following equation is obtained:

$$k_{obs}\ t = \ln\left\{\frac{D_f - R.D_t}{D_f - D_t}\right\} \qquad (3:5)$$

and when $A/B = b/a$ the equation is :-

$$k_{obs} t = D_t/\left[D_f\ (D_f - D_t)\right] \qquad (3:6)$$

The derivation of the above equations are explained in appendix (1)

The value for (a) is (3) in the reduction of Te^{IV} to Te^{I}

$$Te^{IV} + 3e \longrightarrow Te^{I}$$

The value of b=4 in the oxidation of $S_2O_5^{2-}$ according to the following equation:-

$$3H_2O + \overset{IV}{S}_2O_5^{2-} \longrightarrow 2\overset{VI}{S}O_4^{2-} + 6H^+ + 4e$$

Equations (3:3) and (3:5) were used in a BASIC program (appendix 2) to determine (k_{obs}) of the reaction of P-EtOPhTeCl$_3$ with different initial concentrations of sodium metabisulphite. The initial concentration of p-EtOPhTeCl$_3$ used in these runs was (1.25×10^{-3}M). The initial concentration of sodium metabisulphite ranged from 1.25×10^{-4}M to 1.2×10^{-3}M. The values of the rates of reactions (k_{obs}) are listed in table (3:2). The plot of the rate of reaction (k_{obs}) versus the molar concentration of the metabisulphite gives a straight line, as shown in Fig (3:4). The slope was determined by a least square equation, yielding a value of $k_r = 2.1 dm^3 mol^{-1} s^{-1}$. The intercept corresponds to the concentration of metabisulphite equivalent to the concentration of p-EtOPhTeCl$_3$ and is in agreement with the stoichiometric calculations. The plot shows the reaction to be first order in each reactant. The rate of reaction of p-EtOPhTeBr$_3$ with sodium metabisulphite was found to be 0.9 $dm^3 mol^{-1} s^{-1}$.

The reaction of p-EtOPhTeCl$_3$ with metabisulphite ion was repeated under the same conditions but at different temperatures (15-45°C) at 5°C intervals. The data are listed in Table (3:3).

According to the Arrhenius equation

$$k_r = A\exp(-\Delta E^{\#}/RT) \qquad (3:7)$$

where A is a constant known as a frequency factor, R is gas constant 8.314 JK^{-1} $mole^{-1}$. A plot of log k_r versus K/T is linear as shown in Fig (3:5). The least squares computer program written in BASIC (Appendix 3) was used to obtain the slope of the plot. Equation (3:7) was used to determine the activation energy ($\Delta E^{\#}$) of the reaction. The activation energy ($\Delta E^{\#}$) is related to the enthalpy of activation by the equation:-

$$\Delta H^{\#} = \Delta E^{\#} - nRT \qquad (3:8)$$

where (n) is unity for unimolecular reactions and all liquid-phase reactions. The value of the entropy of activation $\Delta S^{\#}$ can be calculated by the following equation:-

$$k_r = \frac{k_B T}{h}\exp\left(\frac{\Delta S^{\#}}{R}\right)\exp\left(\frac{-\Delta H^{\#}}{RT}\right) \qquad (3:9)$$

where k_B is Boltzmann's constant and h is Planck's constant. The data of $\Delta E^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ are:-

$\Delta E^{\#} = 28 \mp 0.4$ $kJmol^{-1}$

$\Delta H^{\#} = 25.5 \mp 0.4$ $kJmol^{-1}$

$\Delta S^{\#} = -154 \mp 1$ $J.K^{-1}$ mol^{-1}

The above experiments were repeated in solutions of different pH. Sodium sulphate was used to maintain a constant ionic strength of 2.3×10^{-3} mol dm^{-3} in the solution while sulphuric acid and sodium hydroxide solutions were used to alter the initial pH of the solution over the range from (3.11) to (11.1). The data are listed in Table (3:4). A plot of logk_r versus pH is shown in Fig (3:6). The plot indicates a region of intermediate pH where log k_r becomes independent of $[H_3O^+]$ and $[OH^-]$.

The effect of varying the composition of the mixed solvent of 1,4 dioxane and water was determined. The volume percentage of 1,4 dioxane ranged from (50%) to (83.3%). The values of the dielectric constant for the mixed solvent in different ratios of volumes and at different temperatures are taken from the work of G.Akerlöf(87). The data of the rate of the reaction are listed in Table (3:5) plot of log k_r versus (I/D) is shown in Fig (3:7).

In the case of a mixed solvent of 93% by volume 1,4 dioxane, spectroscopic measurement on the reduction of p-EtOPhTeCl$_3$, dissolved before mixing in pure 1,4 dioxane (48ml), shows a detectable induction period graph (1) Fig (3:8). When one cm^3 of 2N sulphuric acid is added to the solution of p-EtOPhTeCl$_3$ (47ml) in dry 1,4 dioxane 30 minutes prior to the reduction, the induction period is shorter, graph (2) Fig (3:8), while it disappears when one cm^3 of water is added in place of sulphuric acid graph (3) Fig(3:8).

In this case the reaction can be satisfactorily described by the rate equation appropriate to the following scheme:-

$$p\text{-EtOPhTeCl}_3 + mH_2O + [H^+] \xrightarrow{k_1} I + (1+n)[H^+] + \text{other species}$$

followed by several subsequent reactions which can be written overall as:-

$$I + (3/4)S_2O_5^{2-} + [(9/4) - m]H_2O \xrightarrow{k_2} (1/2)R_2Te_2$$

$$+ ((9/2) - n)[H^+] + \text{other species}$$

Where m and n are constants and I is tellurium containing intermediate. The differential rate equation for the above scheme can be written as:-

$$\frac{d[Pt]}{dt} = k\{[Te]_o - [Pt]\}\{[H^+]_o + 4.5\ [Pt]\} \qquad (3:10)$$

where $[Te]_o$ is the initial concentration of p-EtOPhTeCl$_3$. Pt= $2[(p\text{-EtOPh})_2Te_2]$ at time t, and $[H^+]$ is the initial hydrogen ion concentration in the solution.

The integration of equation (3:10) is demonstrated in appendix (iv) and results in a final equation of:-

$$k_{obs}\ t = \ln\left\{\frac{1+f/A}{1-f}\right\} \qquad (3:11)$$

where $A = [H^+]_o / 4.5\ [Te]_o$ (3:12)

$$f = (D_t - D_o)/(D_f - D_o) \qquad (3:13)$$

As usual the subscript relate to time, thus D_o, D_t and D_f are the initial, at time (t) and final absorbances of the solution.

$$k_{obs} = k_r \left\{ 4.5 \left[Te \right]_o + \left[H^+ \right]_o \right\} \qquad (3:14)$$

$$\left[H^+ \right]_o = 4.5\ A \left[Te \right]_o$$

$$k_r = k_{obs} / (4.5 \left[Te \right]_o . (1+A))$$

Equation 3:11 was used in a BASIC computer (appendix V) to determine (k_{obs}) of the reaction in mixed solvent of dioxane 93% by volume. The data are listed in table (3:6). They show that (k_{obs}) is independent of the concentration of the reducing agent (i.e. $S_2O_5^{2-}$). The reaction is first order in both p-EtOPhTeCl$_3$ and H_3O^+. The plot of k_{obs} versus $(4.5 \left[Te \right]_o . (1 + A))$ gives a straight line with slope of 0.3 dm^3. mol^{-1}. s^{-1} which represents the rate constant (k_r) of the reaction as shown in Fig (3:9)

3-2-2 Reduction with Sodium Sulphite

The reduction of p-EtOPhTeCl_3 by sodium sulphite has also been investigated in a similar manner to that by metabisulphite. The study in general was carried out in a mixed solvent of aqueous 1,4 dioxane (1:3) by volume; at 400n m. which represents the maximum absorbance of the product $(p\text{-EtOPh})_2Te_2$.

Spectrophotometric measurements were used to determine the stoichiometry of the reaction. The data are listed in Table (3:7) and the plot of molar concentrations of $(p\text{-EtOPh})_2Te_2$ versus the molar ratio $[SO_3^{2-}]/[p\text{-EtOPhTeCl}_3]$ is shown in Fig (3:10). The plot shows that 1.5mol of SO_3^{2-} is consumed by 1 mol of p-EtOPhTeCl_3. No dithionate was detected as a product of the reduction of p-EtOPhTeCl_3 with SO_3^{2-} ion. The kinetic studies from the reaction were carried out in the same way as for $S_2O_5^{2-}$, except that the value of (b) is 2, as shown by the equation:-

$$H_2O + \overset{IV}{S}O_3^{2-} \longrightarrow \overset{VI}{S}O_4^{2-} + 2H^+ + 2e$$

the effect of varying the initial concentration of the SO_3^{2-} was investigated over the range from 3.13×10^{-4}M to 2.5×10^{-3}M. The initial concentration of p-EtOPhTeCl_3 was maintained at 1.25×10^{-3}M. The values of the rates of reactions (k_{obs}) are listed in Table (3:8). The plot of the rate of reaction (k_{obs}) versus the molar concentration of the sulphite gives a straight line, as shown in Fig (3:11) the experimental value of (k_r) is found to be 2.1 $dm^3mol^{-1}s^{-1}$ the intercept of the plot represents the concentration of sodium sulphite which is equivalent to the concentration of p-EtOPhTeCl$_3$. This is in agreement with the stoichiometric measurements. The plot shows that the reaction is first order in each reactant. The energy, entropy and enthalpy of activation were calculated as previously described. The data are:-

$$\Delta E^{\#} = 24.9 \mp 0.3 \text{ kJ mol}^{-1}$$

$$\Delta H^{\#} = 22.4 \mp 0.3 \text{ kJ mol}^{-1}$$

$$\Delta S^{\#} = -164 \mp 1 \text{ JK}^{-1}\text{mol}^{-1}$$

A plot of logk_r versus K/T gives a straight line as shown in Fig (3:12). The data are listed in Table (3:9). A sodium sulphate range from 2.08×10^{-4} to 18.8×10^{-4}M was used to study the effect of the ionic strength on the rate of reaction. The data are listed in Table (3:10). According to the relationship:-

$$\log k_r = \log k_o + 2A\ Z_A Z_B \sqrt{I} \qquad (3:15)$$

a plot of log k_r versus $\sqrt{I}$ is shown in Fig (3:13).

Sodium sulphate was also used to maintain a constant ionic strength of 2.3×10^{-3} mol.dm^{-3} while the pH of the reaction solution was varied for the usual reagent, p-EtOPhTeCl$_3$. Sulphuric acid (3.65×10^{-5} to 7.80×10^{-4}M) and sodium hydroxide (1.04×10^{-5} to 1.35×10^{-3}M) were used to vary the initial pH of the solution. The experimental data are listed in Table (3:11). A plot of log k_r versus pH is shown in Fig (3:14). The plot shows a region of intermediate pH where log k_r becomes independent of $[H_3O^+]$ or $[OH^-]$.

The effect of varying the composition of the mixed solvent was determined in the same way as for $S_2O_5^{2-}$. The data of the rate of reaction are listed in Table (3:12). Plots of log k_r versus (1/D) is shown in Fig (3:15)

10^4x $[S_2O_5^{2-}]$ M	10^5x $[(p\text{-EtOPh})_2Te_2]$ M	$[S_2O_5^{2-}]$ / $[p\text{-EtOPhTeCl}_3]$
1	0.75	0.16
2	64	0.32
3	130	0.48
4	190	0.64
5	250	0.80
6	280	0.96
7	300	1.12
8	300	1.28
9	300	1.44
10	300	1.60

Table (3:1) Experimental data for determination of the equivalent weight of p-EtOPhTeCl$_3$ against $Na_2S_2O_5$ at 25°C in aqueous 1,4 dioxane (1:3). Initial concentration of p-EtOPhTeCl$_3$ is 6.25×10^{-4}M

$10^4 \times [S_2O_5^{2-}]$ M	$10^3 \times k_{obs}^{(a)}$ s^{-1}	k_r $dm^3\ mol^{-1} s^{-1}$
1.25	-6.5	2.0
2.50	-5.9	2.1
3.13	-5.0	2.0
6.25	-2.7	2.2
12.00	+2.2	2.1

(a) The sign of the k_{obs} changes as the ratio $[S_2O_5^{2-}]/[ArTeCl_3]$ passes through the value of 3/4

$$k_r = k_{obs} / (4(S_2O_5^{2-}) - 3(p\text{-EtOPhTeCl}_3))$$

Table (3:2) Rate constant for the reaction of p-EtOPhTeCl$_3$ 1.25×10^{-3} M with different molar concentration of $Na_2S_2O_5$ in aqueous 1,4 dioxane.

Temp^{o}C	10^{3}xK/T	$k_r$dm^{3}mol^{-1}S^{-1}	logk_r
15	3.472	1.20	0.080
20	3.413	1.43	0.155
25	3.356	1.73	0.238
30	3.300	2.14	0.330
35	3.247	2.49	0.396
40	3.195	3.03	0.481
45	3.145	3.59	0.555

Table (3:3) Rate constant for the reaction of p-EtOPhTeCl$_3$(1.25x10^{-3}M) with Na$_2$S$_2$O$_5$ (6.25x10^{-4}M) in aqueous 1,4 dioxane at different temperature

$10^4 x [K_2SO_4] M$	$10^3 x [NaOH] M$	$k_r dm^3 mol^{-1} S^{-1}$	Log k_r	pH
3.13	1.35	2.64	0.422	11.13
4.17	1.04	2.47	0.393	11.02
5.20	0.73	2.20	0.342	10.86
6.25	0.42	1.92	0.283	10.62
7.30	0.10	1.89	0.277	10.02
8.30	----	1.96	0.292	6.30
	$10^4 x [H_2SO_4] M$			
7.30	1.04	1.92	0.283	3.68
5.20	3.13	1.82	0.260	3.20
3.13	5.20	1.61	0.207	2.98
1.04	7.30	1.46	0.164	2.84

Table (3:4) variation of the rate constant with the hydrogen ion concentration for the reaction of p-EtOPhTeCl$_3$ 1.25 x 10^{-3}M with $Na_2S_2O_5$ 3.13 x 10^{-4}M in aqueous 1,4 dioxane solution of constant ionic strength of 2.3 x 10^{-3} mol.dm^{-3}.

1,4 dioxane Vol.%	D	$10^2/D$	k_r $dm^3 mol^{-1} s^{-1}$	Log k_r
50.0	49.7	2.01	7.2	0.86
58.3	47.8	2.09	5.2	0.71
66.7	45.8	2.18	3.3	0.52
75.0	43.9	2.28	2.1	0.33
83.3	41.7	2.40	1.5	0.18

Table (3:5) Rate constant for the reaction of p-EtOPhTeCl_3 1.25×10^{-3} M with $Na_2S_2O_5$ 6.25×10^{-4}M in aqueous 1,4 dioxane solution of different dielectric constant

10^4 [p-EtOPhTeCl_3] M	$A=\frac{[H_3O^+]_o}{4.5[Te]_o}$	k_{obs} S^{-1}	k_r $dm^3.mol^{-1}.S^{-1}$
6.25	0.085	$9.2x10^{-4}$	0.302
5.20	0.061	$7.5x10^{-4}$	0.302
4.40	0.049	$6.2x10^{-4}$	0.298
3.90	0.03	$5.4x10^{-4}$	0.299

Table (3:6) Experimental data of the rate constant for the reaction of $Na_2S_2O_5$ ($4.5x10^{-4}$M) with different concentrations of p-EtOPhTeCl_3 in aqueous 1,4 dioxane 93% by volume.

$10^4[SO_3^{2-}]$ M	$[(p\text{-EtOPh})_2Te_2]$ M	$[SO_3^{2-}]/[p\text{-EtOPhTeCl}_3]$
2	7.3×10^{-6}	0.32
4	6.5×10^{-5}	0.64
6	1.3×10^{-4}	0.96
8	1.8×10^{-4}	1.28
10	2.4×10^{-4}	1.60
12	2.9×10^{-4}	1.92
14	3.0×10^{-4}	2.24
16	3.1×10^{-4}	2.56
18	3.0×10^{-4}	2.88
20	3.0×10^{-4}	3.20

Table (3:7) Experimental data for determination of the equivalent weight of p-EtOPhTeCl$_3$ against Na$_2$SO$_3$ at 25^{o}C in aqueous 1,4 dioxane (1:3), initial concentration of p-EtOPhTeCl$_3$ is 6.25×10^{-4}M.

$10^4 \times [SO_3^{2-}]$ M	$10^3 \times k_{obs}^{(a)}$ s^{-1}	k_r dm^3 mol^{-1} s^{-1}
3.13	-6.6	2.1
6.25	-5.2	2.1
12.50	-2.7	2.2
25.00	+2.9	2.3

(a) the sign of the k_{obs} changes as the ratio $SO_3^{2-}/(ArTeCl_3)$ passes through the value of 3/2

$$k_r = k_{obs} / \left[2(SO_3^{2-}) - 3(p\text{-}EtOPhTeCl_3) \right]$$

Table (3:8) Rate constant for the reaction of $p\text{-}EtOPhTeCl_3$ 1.25×10^{-3} M with different molar concentraction of Na_2SO_3 in aqueous 1,4 dioxane.

Temp°C	10^3xK/T	k_r dm^3 mol^{-1} S^{-1}	log k_r
15	3.472	1.54	0.188
20	3.413	1.73	0.238
25	3.356	2.20	0.340
30	3.300	2.50	0.405
35	3.247	3.02	0.480
40	3.195	3.46	0.539
45	3.145	4.00	0.602

Table (3:9) Rate constant for the reaction of p-EtOPhTeCl$_3$ (1.25x10^{-3}M) with Na$_2$SO$_3$ (6.25x10^{-4}M) in aqueous 1,4 dioxane at different temperatures.

$10^4[Na_2SO_4]$M	k_r dm^{3}mol^{-1}S^{-1}	Iog k_r	10^3xI mol.dm^{-3}	10^3x $\sqrt{I}$
2.08	2.01	0.303	2.5	50
4.17	2.15	0.332	3.1	56
6.25	2.29	0.360	3.8	61
8.33	2.35	0.371	4.5	67
9.38	2.37	0.375	4.7	68
10.40	2.49	0.396	5.0	71
11.46	2.54	0.405	5.3	73
12.50	2.66	0.425	5.6	75
14.60	2.70	0.431	6.3	80
15.60	3.73	0.572	6.6	81
16.70	4.22	0.625	6.9	83
18.75	6.96	0.843	7.5	87

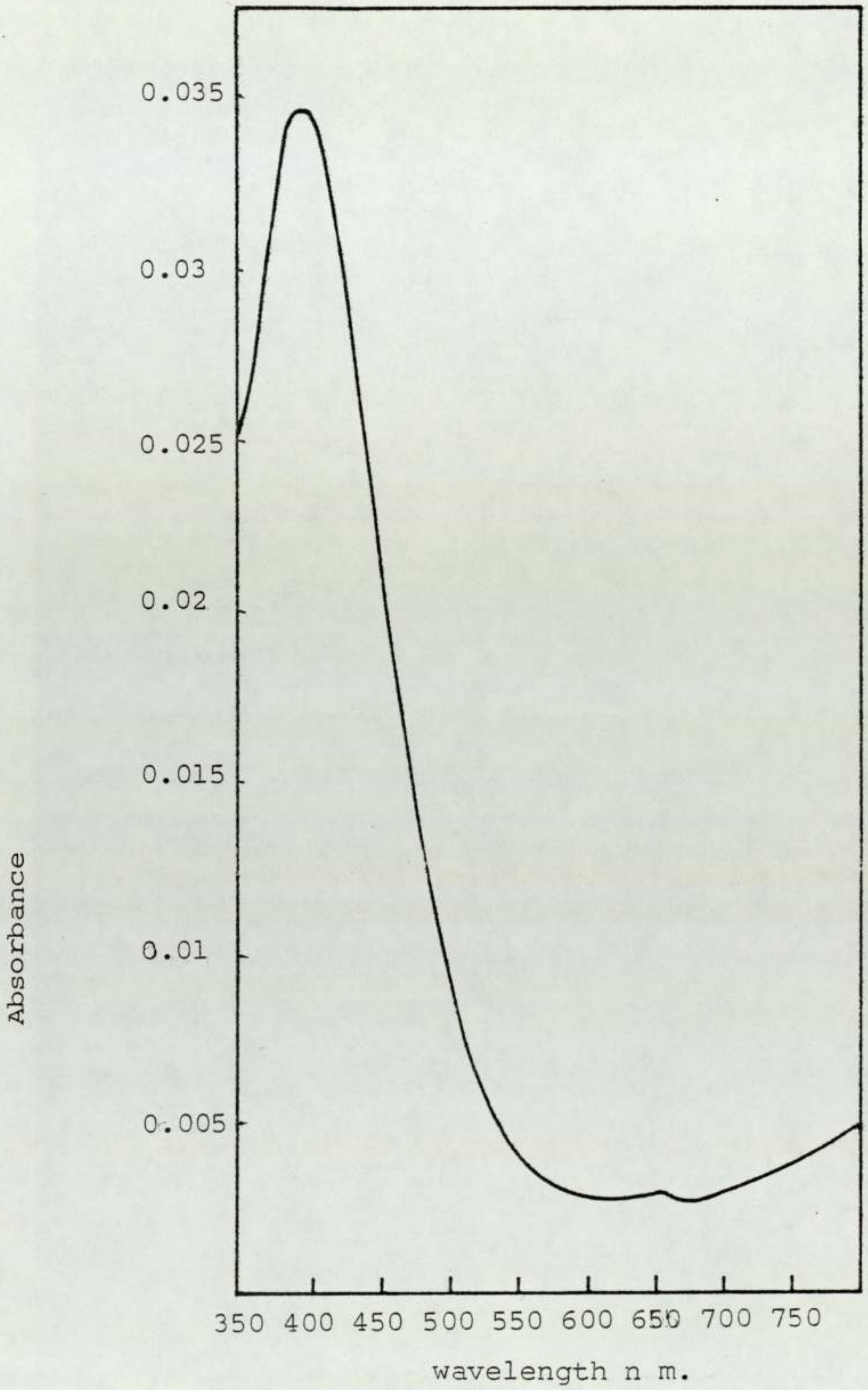
Table(3:10) variation of the rate constant with the ionic strength of the solution for the reaction of p-EtOPhTeCl$_3$ 1.25 x 10^{-3}M with Na$_2$SO$_3$ 6.25 x 10^{-4}M in aqueous 1,4 dioxane

$10^4 x [K_2SO_4]$ M	$10^3 x [NaOH]$ M	$k_r dm^3 mol^{-1} s^{-1}$	log k_r	pH
3.13	13.5	3.65	0.563	11.13
4.17	10.4	2.89	0.461	11.02
5.20	7.3	2.77	0.442	10.86
6.25	4.17	2.46	0.391	10.62
7.29	1.04	2.29	0.360	10.02
7.60	0.10	2.31	0.364	9.02
8.30	—	2.26	0.354	6.84
	$10^4 x [H_2SO_4]$ M			
7.30	0.37	2.20	0.342	4.13
6 .25	1.56	2.17	0.337	3.51
5.20	2.60	2.07	0.316	3.38
4.17	3.65	2.01	0.302	3.14
3.13	4.69	1.98	0.296	3.03
2.08	5.70	1.82	0.260	2.94
1.04	6.77	1.69	0.228	2.87
—	7.80	1.55	0.190	2.81

Table (3:11) rate constants for the reaction of p-EtOPhTeCl$_3$ 1.25 x 10^{-3} M with Na_2SO_3 6.75 x 10^{-4} M in aqueous 1,4 dioxane solution of constant ionic strength of 2.3 x 10^{-3} mol. dm^{-3}. and different hydrogen ion concentration at 25°C.

Dioxane Vol.%	D	$10^3/D$	$k_r dm^3 mol^{-1} S^{-1}$	$\log k_r$
41.7	52.0	19.2	8.2	0.914
50.0	49.7	20.1	7.9	0.898
58.3	47.8	20.9	5.6	0.748
66.7	45.8	21.8	3.4	0.532
75.0	43.9	22.8	2.2	0.342
83.3	41.7	24.0	1.4	0.155

Table (3:12) rate constant for the reaction of $p\text{-EtOPhTeCl}_3$ 1.25×10^{-3} M with Na_2SO_3 6.25×10^{-4} M in aqueous 1,4 dioxane solution of different dielectric constant



Fig(3:1) The visible spectra of $(p\text{-}EtOPh)_2Te_2$ in aqueous 1,4 dioxane 1:3 by volume.

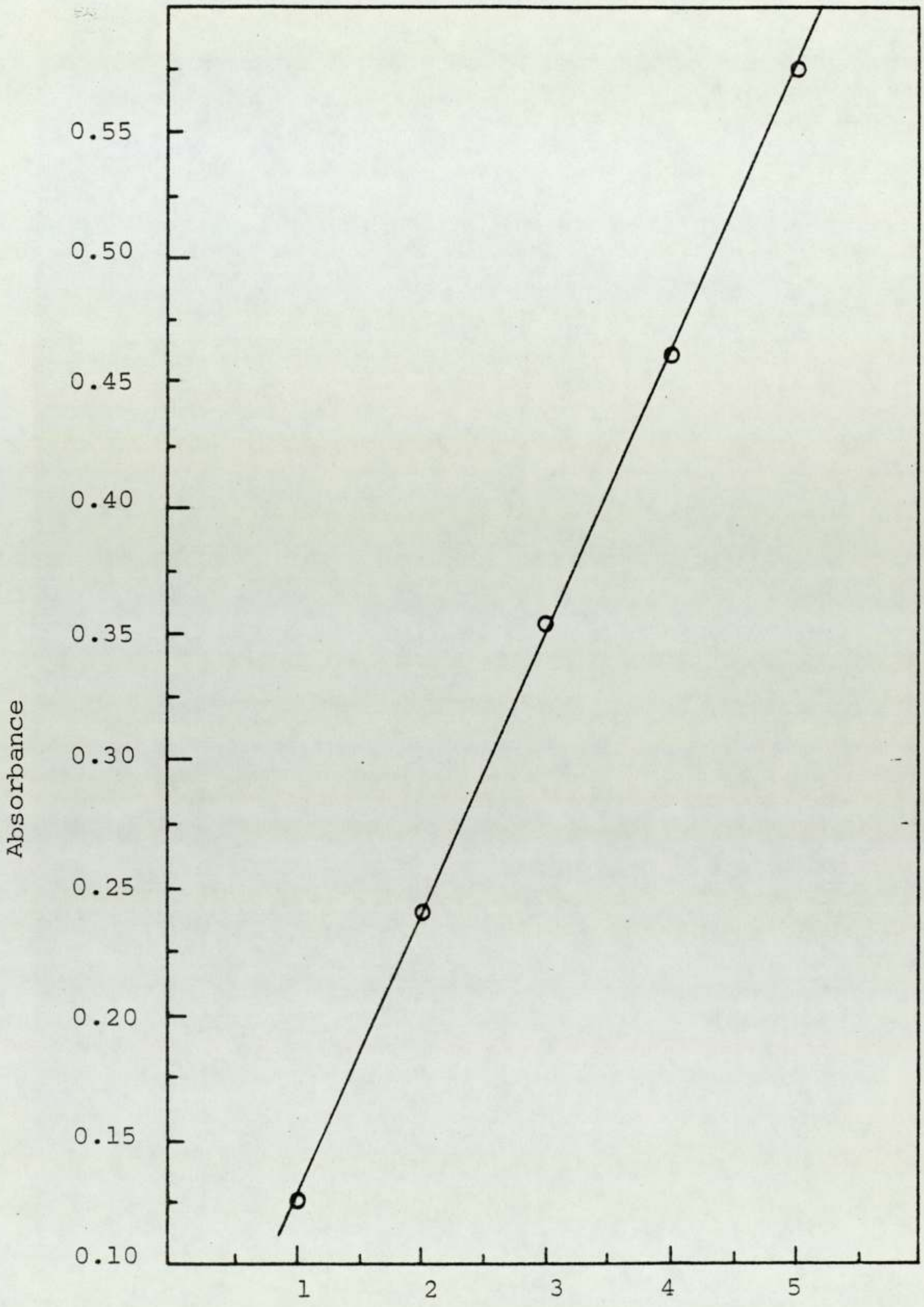
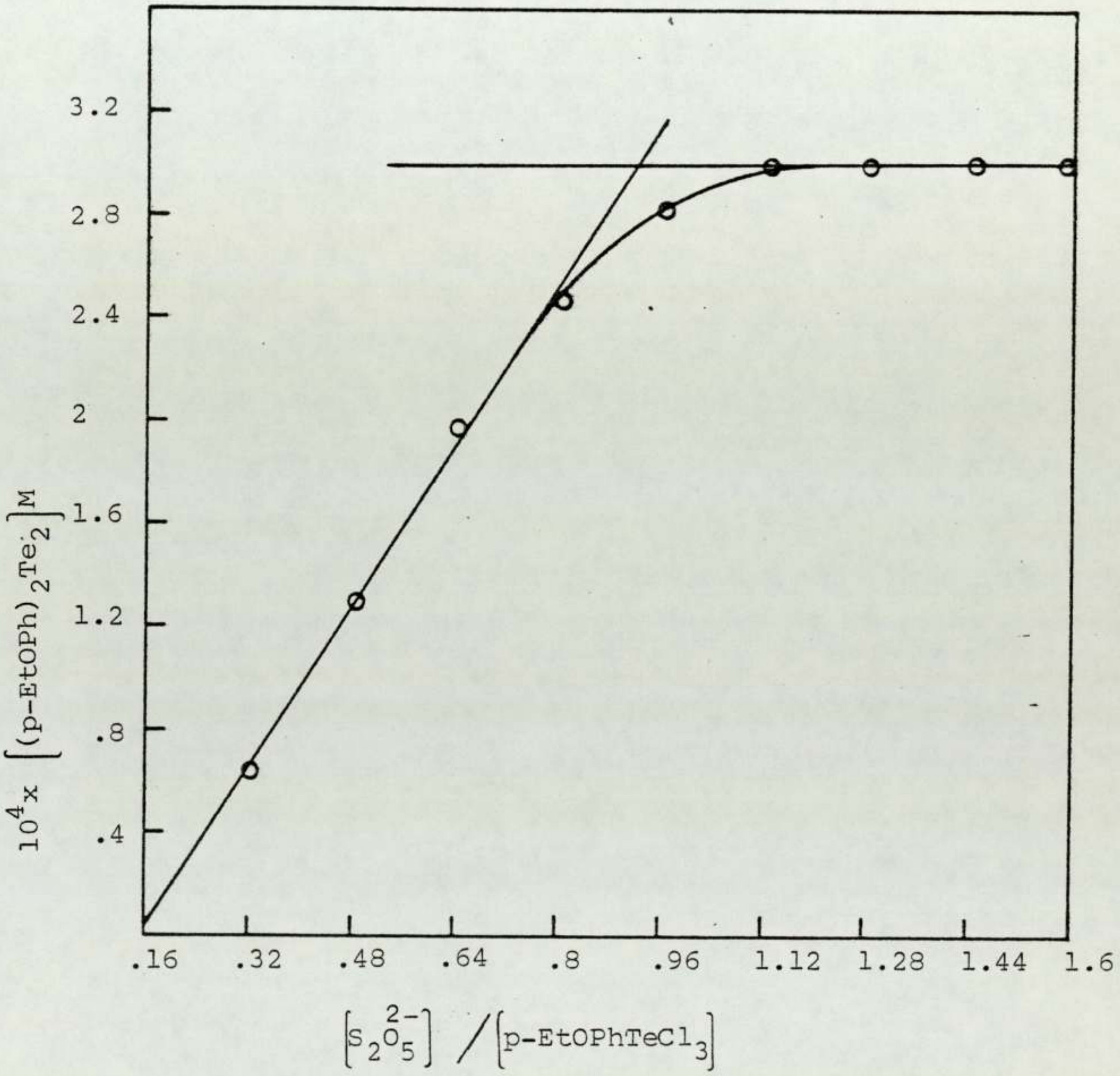


Fig (3:2) Plot of absorbance against concentration for $(p\text{-EtOPh})_2Te_2$



Fig(3:3) plot of molar concentration of $(p\text{-EtOPh})_2Te_2$ in aqueous 1,4 dioxance versus the molar ratio of $S_2O_5^{2-}$ / p-EtOPhTeCl$_3$ at 25°C.

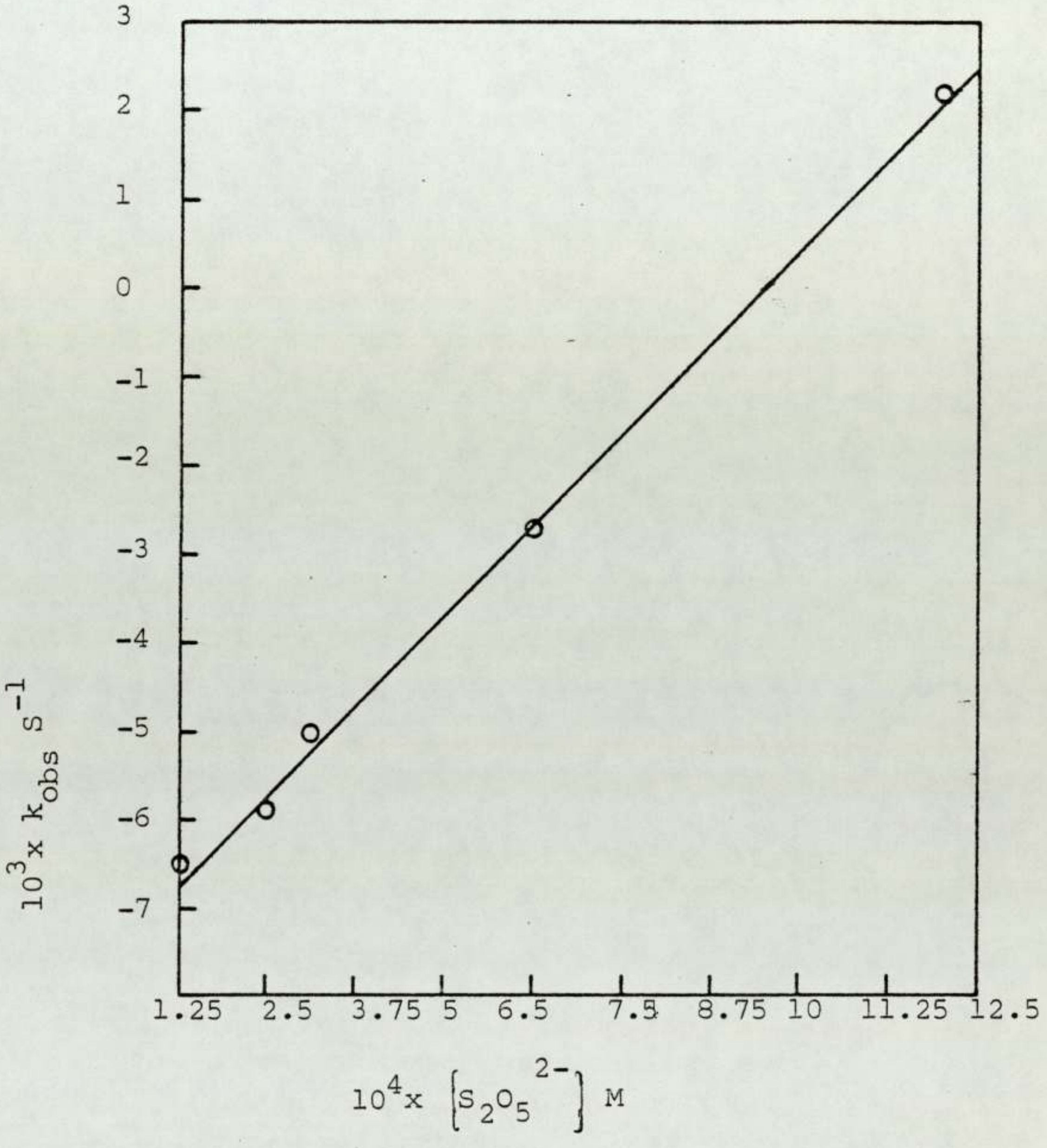
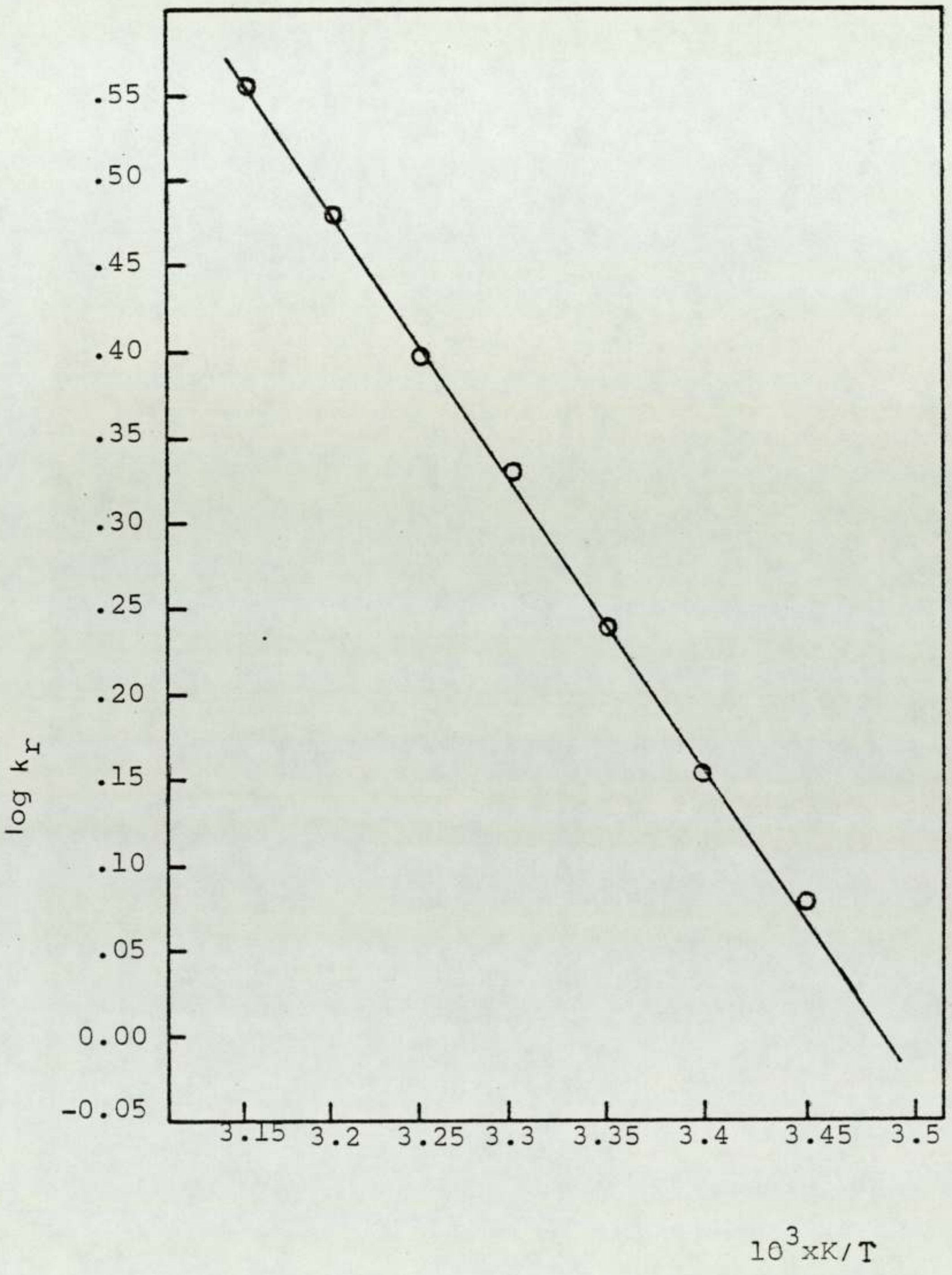


Fig (3:4) Plot of k_{obs} versus molar concentration of $Na_2S_2O_5$ at 25°C



Fig(3:5) Plot of $\log k_r$ versus K/T for the reaction of $Na_2S_2O_5$ with p-EtOPhTeCl$_3$ in aqueous 1,4 dioxane.

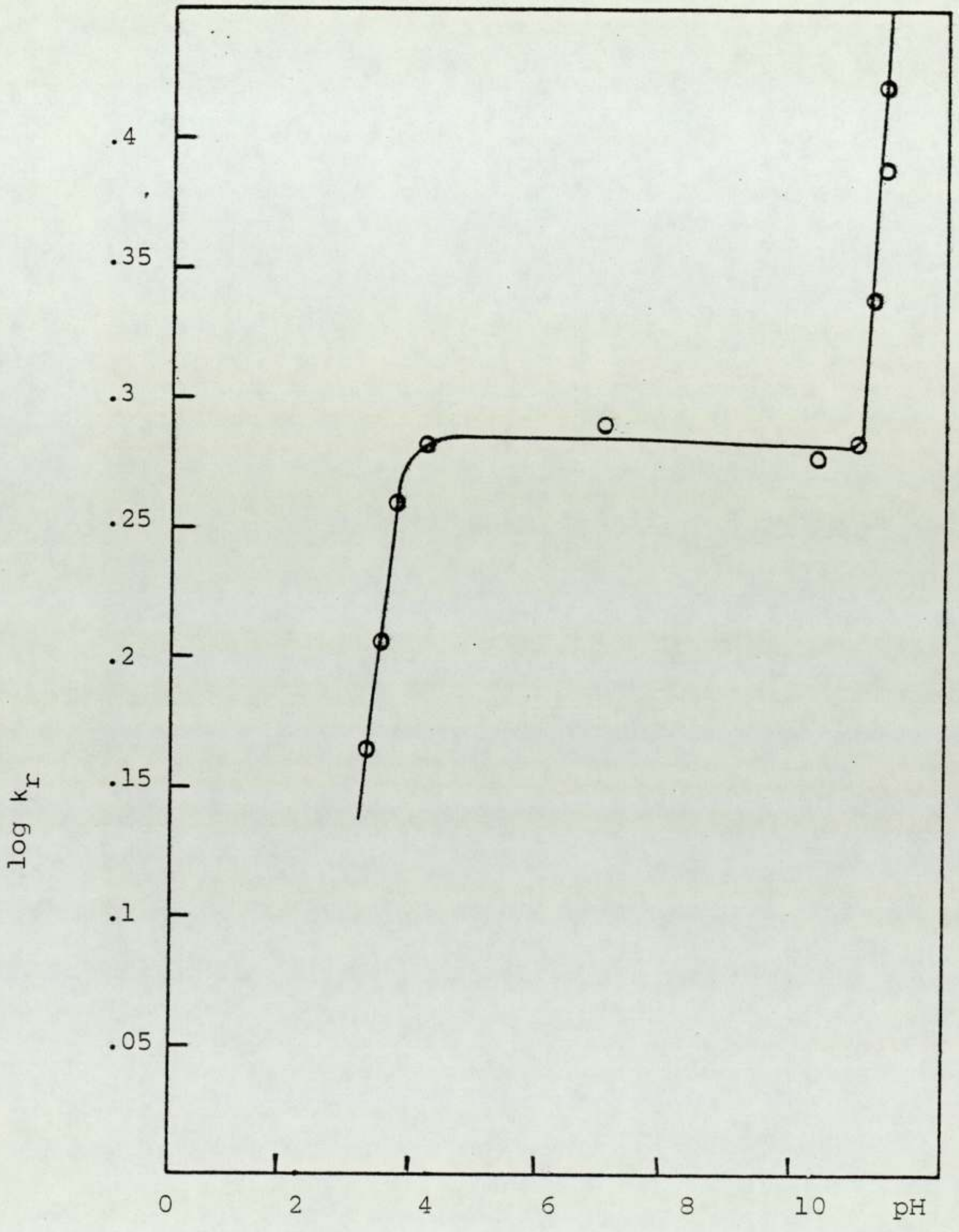
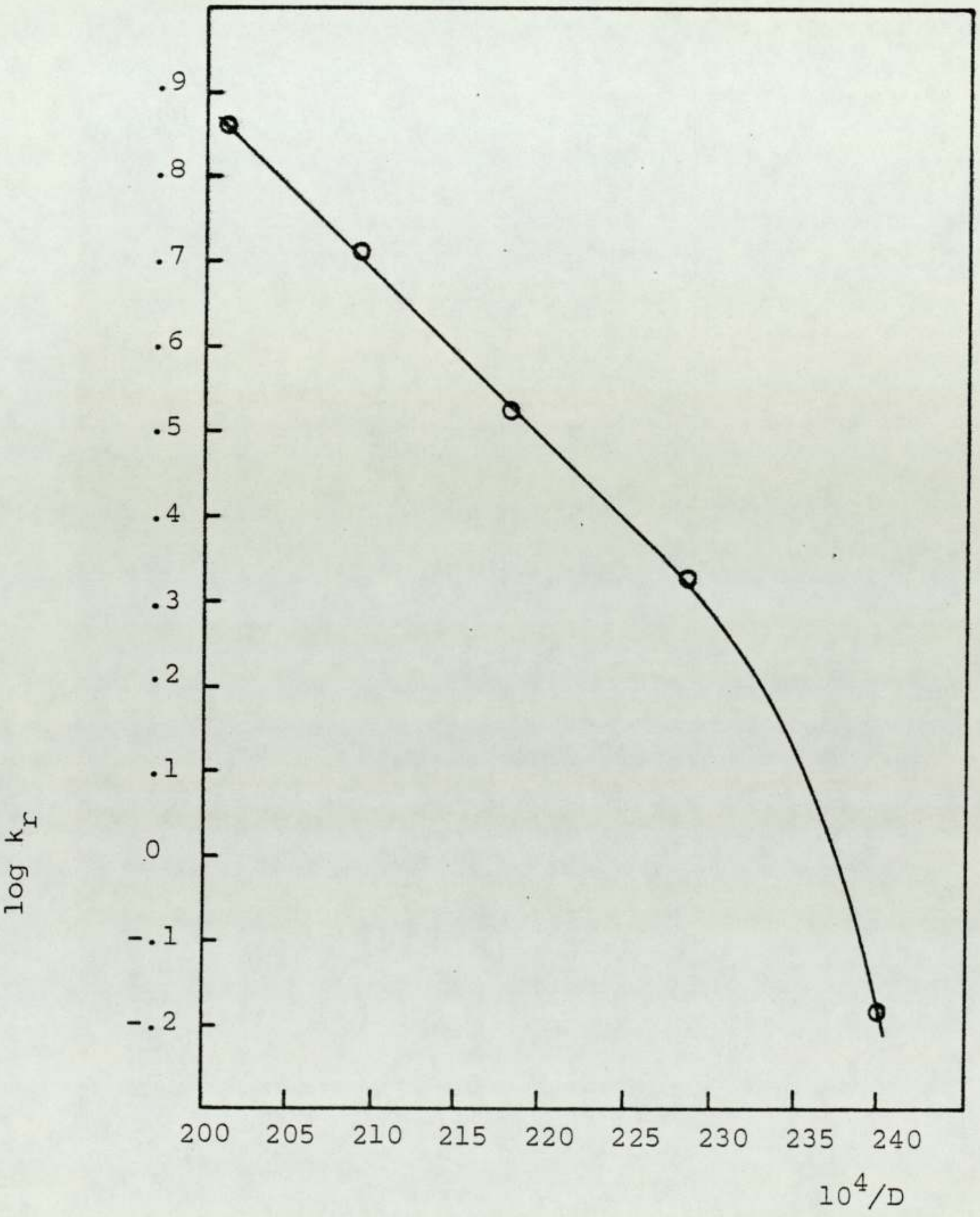


Fig (3:6) Plot of log k_r versus pH for the reaction of $Na_2S_2O_5$ $3.13x10^{-4}M$ with p-EtOPhTeCl$_3$ $1.25x10^{-3}M$ at 25°C and ionic strength of $2.3x10^{-3}$ mol.dm^{-3} in aqueous 1,4 dioxane.



Fig(3:7) plot of log k_r versus 1/D for the reaction of p-EtOPhTeCl$_3$ with $Na_2S_2O_5$ at 25°C

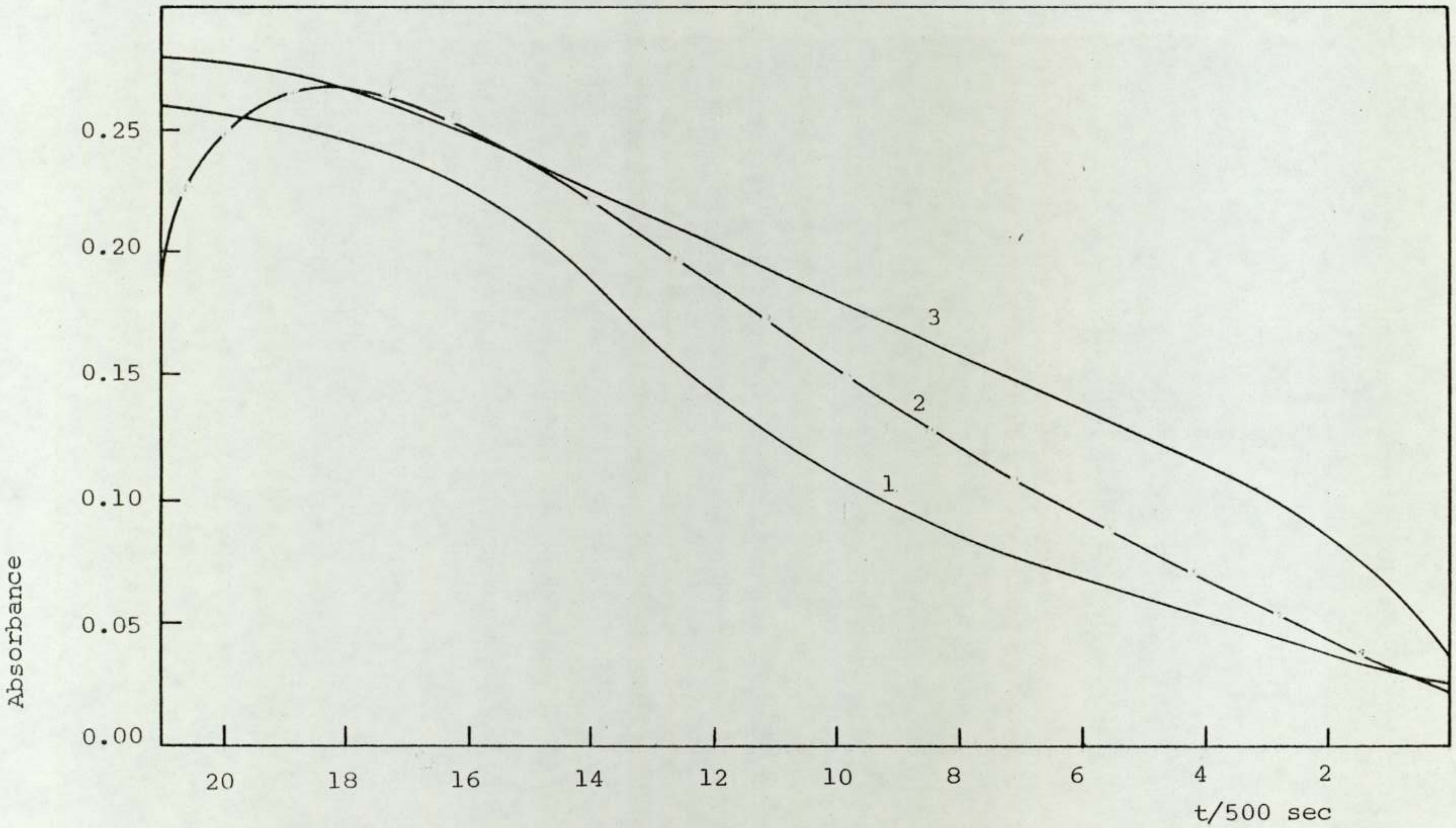


Fig (3:8) Plot of absorbance of (p-EtOPh)$_2$Te$_2$ produced from the reaction of p-EtOPhTeCl$_3$ with Na$_2$S$_2$O$_5$ in aqueous 1,4 dioxane 93% by volume versus time

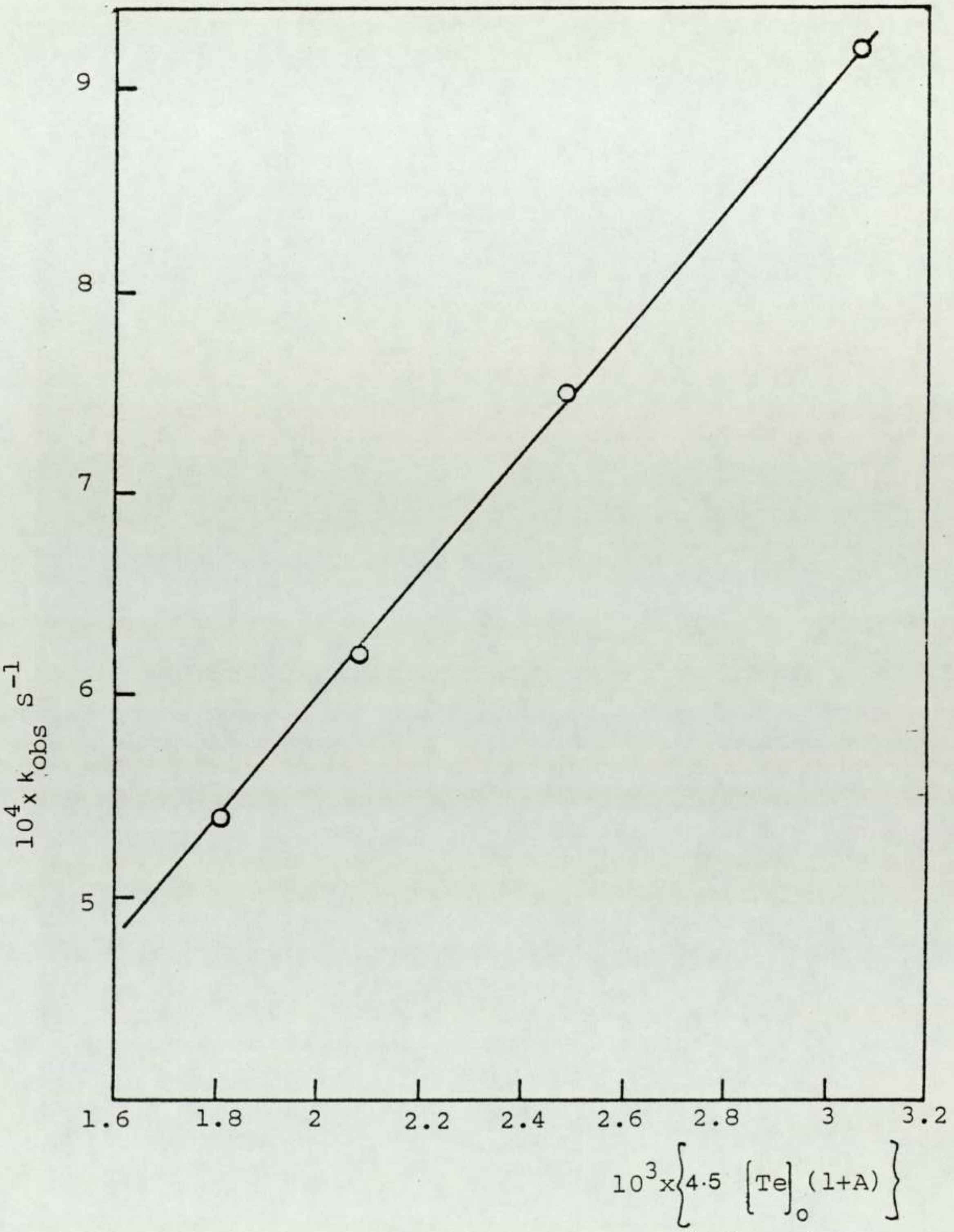


Fig (3:9) Plot of log k_{obs} versus $4 \cdot 5 [Te]_o (1+A)$ for the reaction of p-$EtOPhTeCl_3$ in different concentration with constant concentration of $Na_2S_2O_5$ 5.2×10^{-4}M in mixed solvent of aqueous 1,4 dioxane 93% by volume.

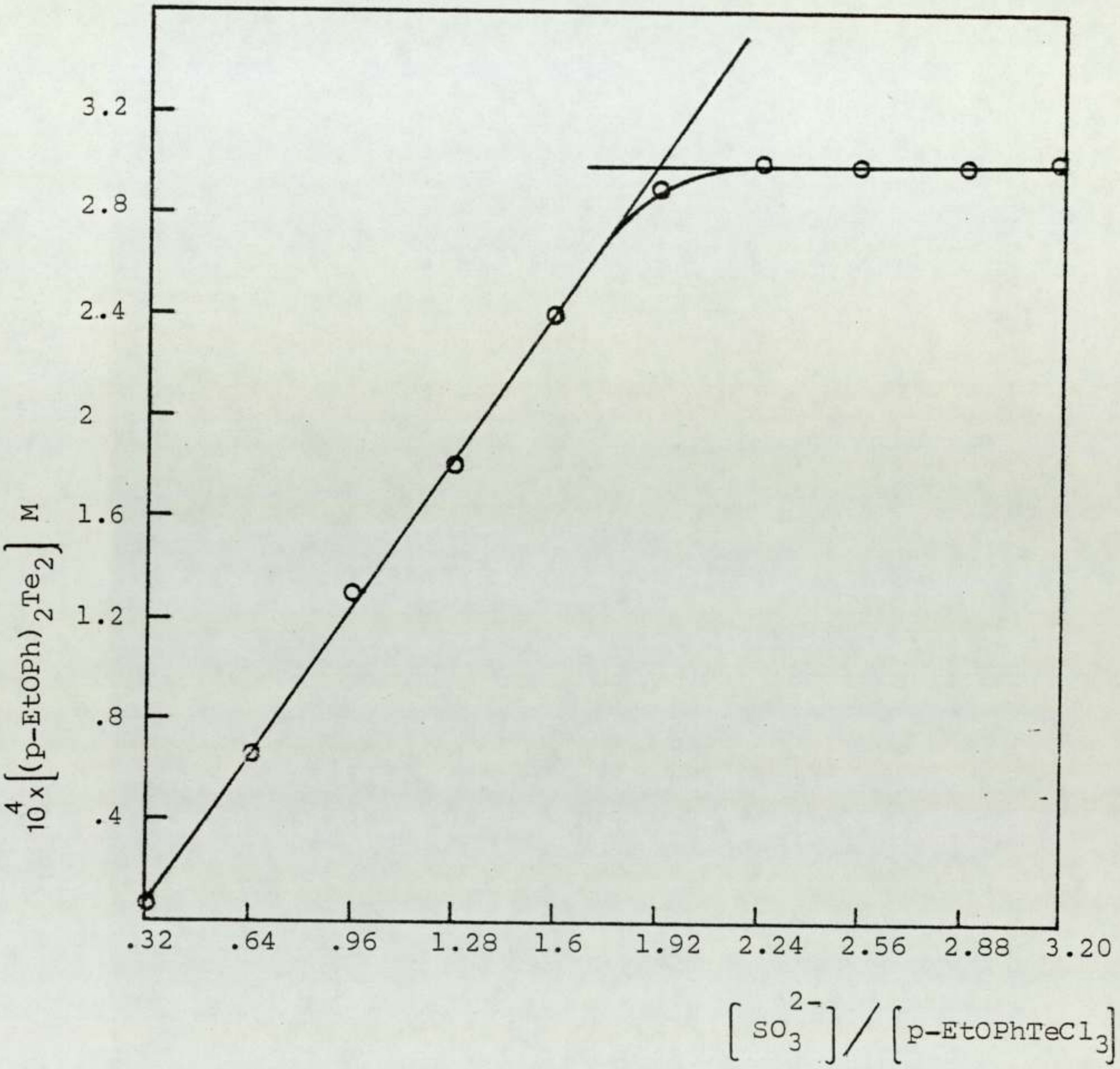
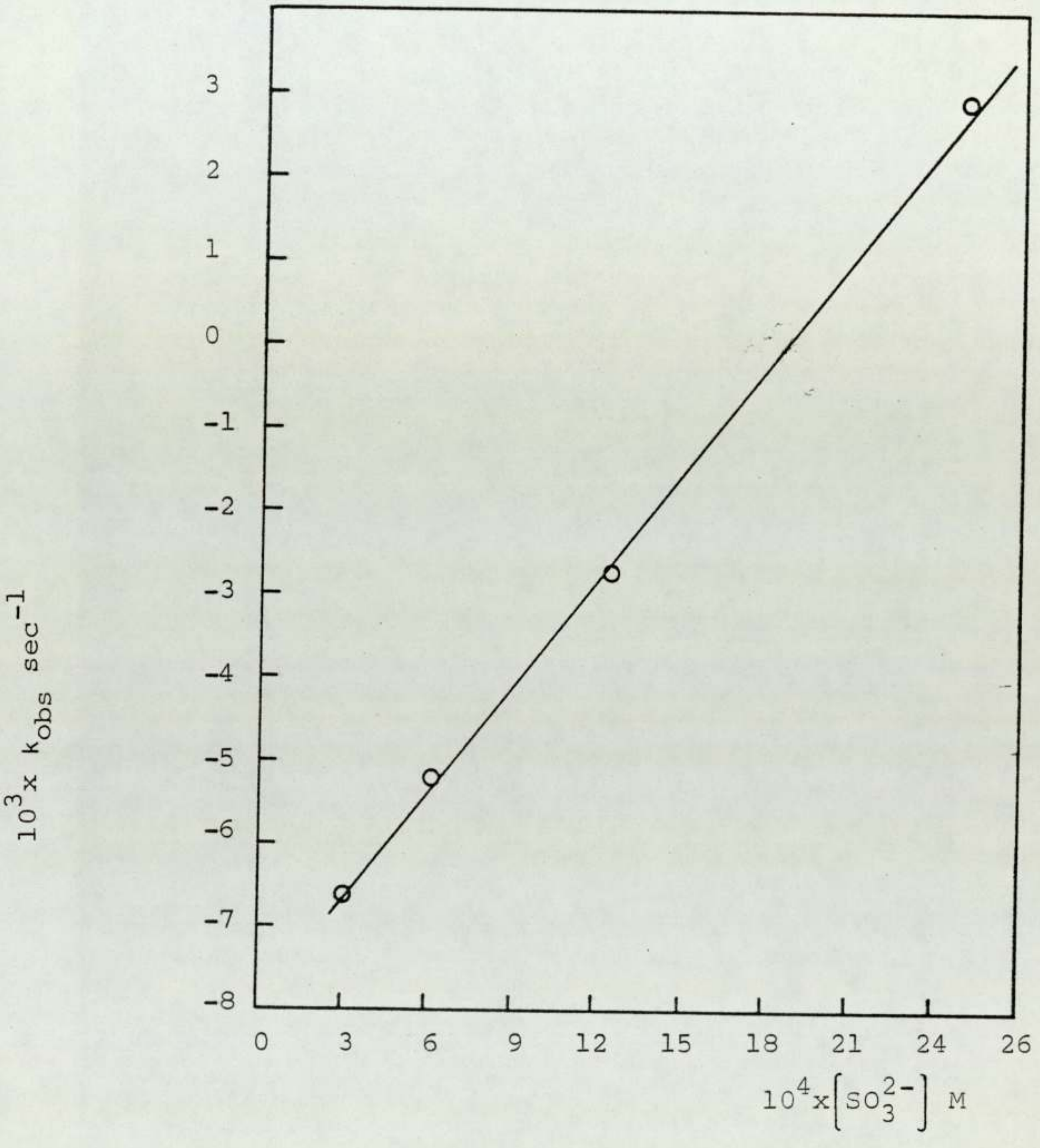


Fig (3:10) plot of molar concentration of $(p\text{-EtOPh})_2Te_2$ in aqueous 1,4 dioxane versus the molar ratio of SO_3^{2-} / $p\text{-EtOPhTeCl}_3$ at 25°C.



Fig(3:11) Plot of k_{obs} versus molar concentration of Na_2SO_3 at 25°C

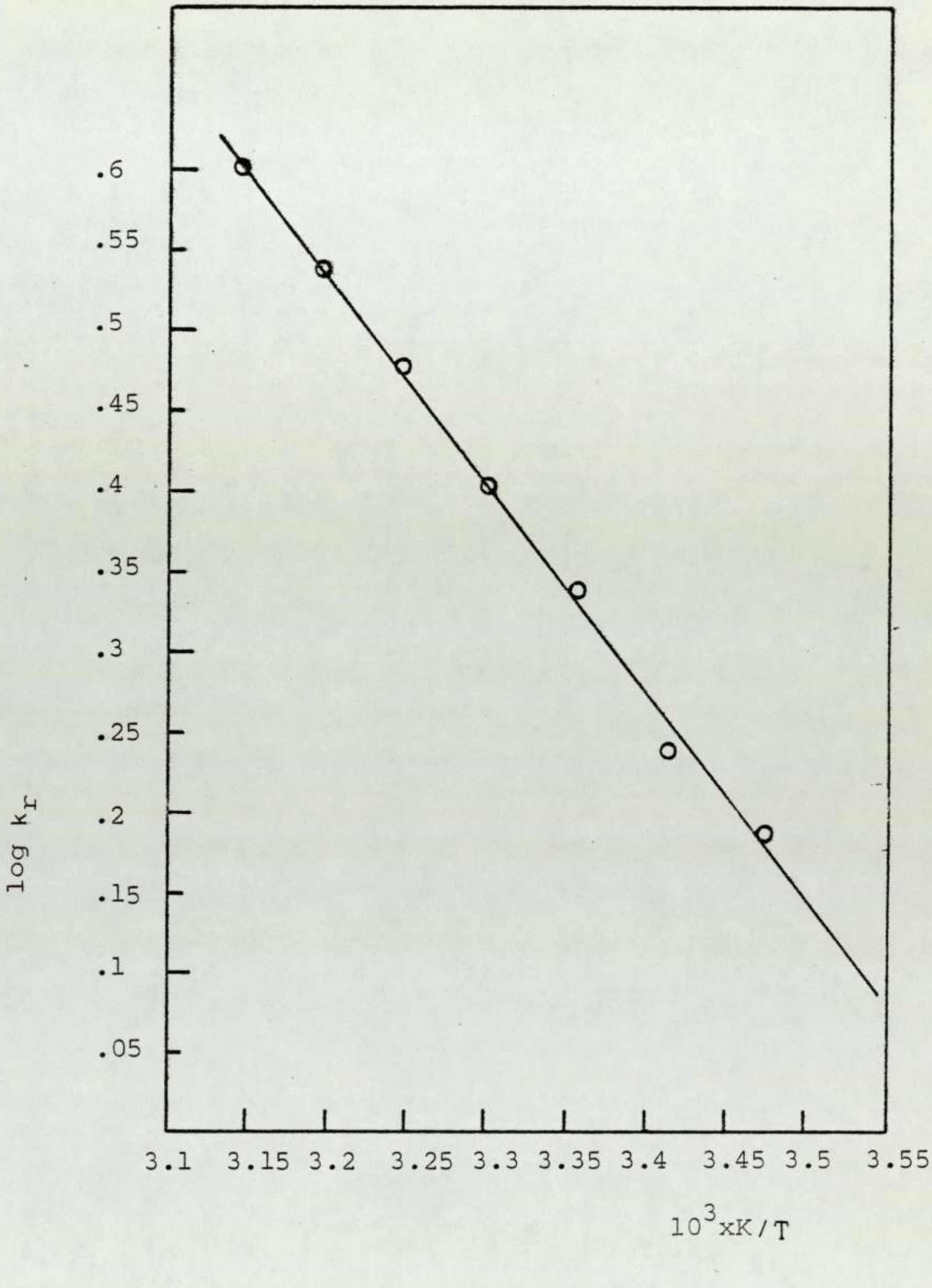


Fig (3:12) Plot of log k_r versus K/T for the reaction of Na_2SO_3 with p-EtOPhTeCl_3 in aqueous 1,4 dioxane.

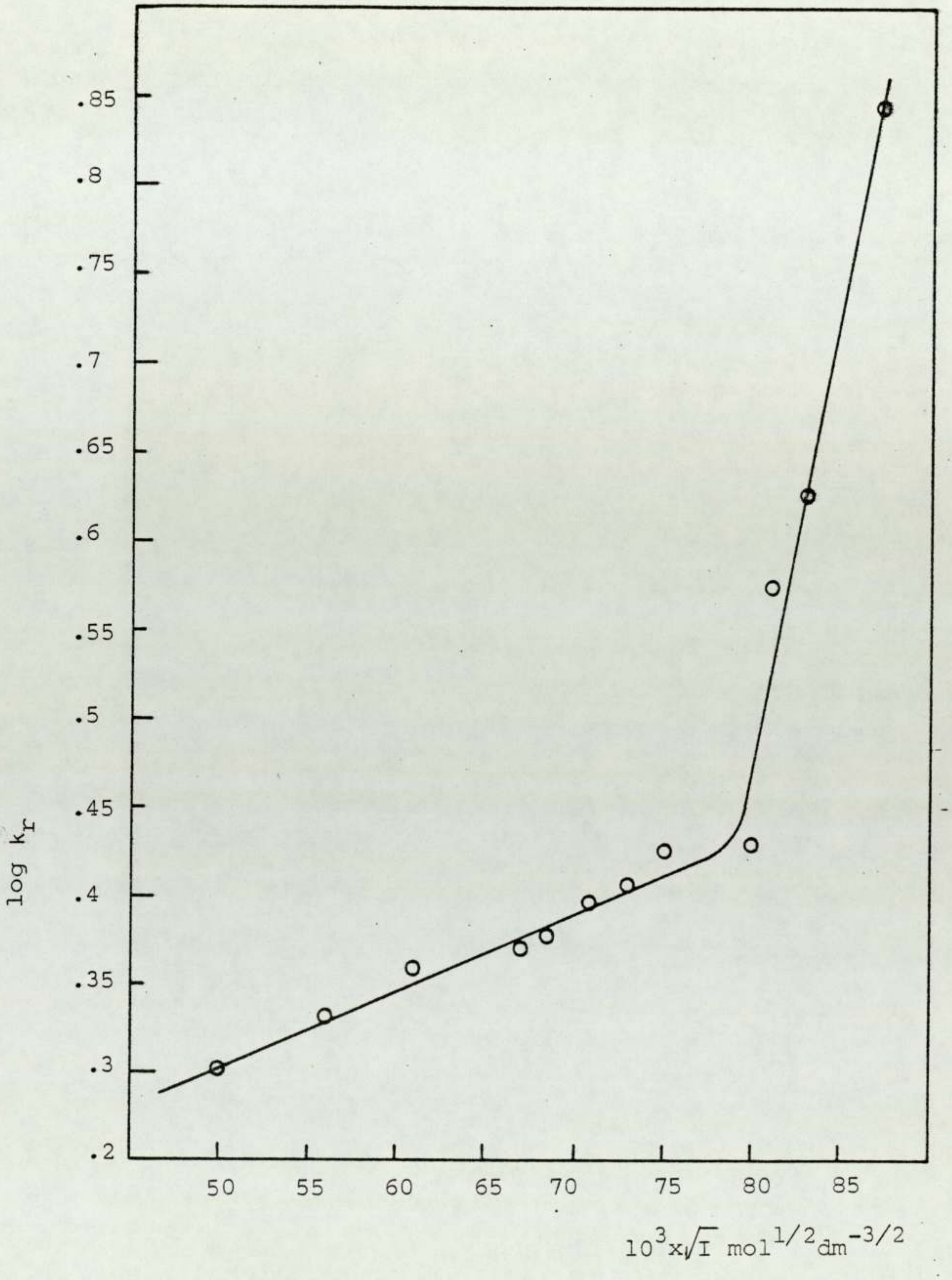
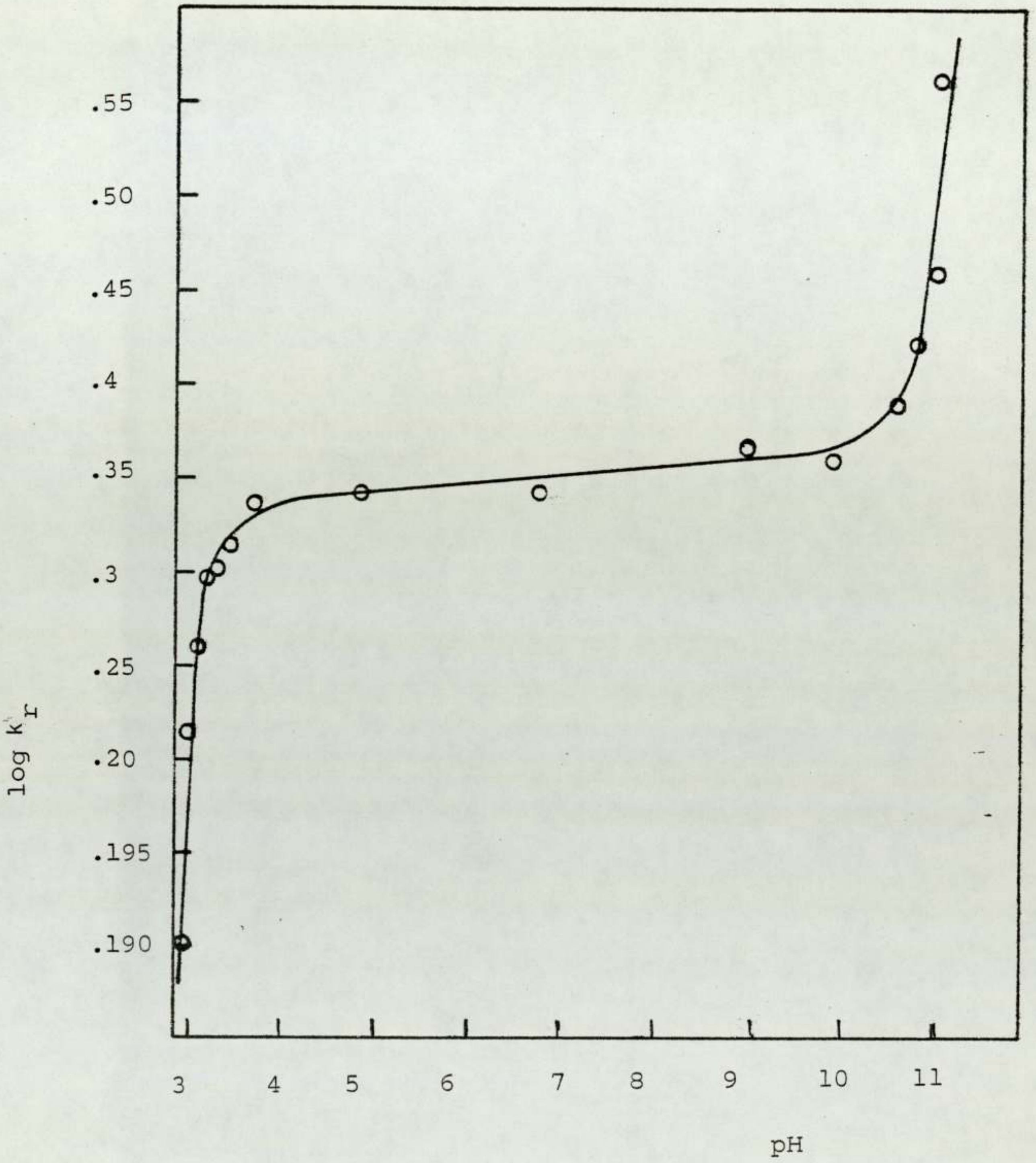


Fig (3:13) Plot of log k_r versus $\sqrt{I}$ for the reaction of p-EtOPhTeCl$_3$ 1.25×10^{-3}M with Na$_2$SO$_3$ 6.25×10^{-4}M at 25°C in aqueous 1,4 dioxane



Fig(3:14) Plot of log k_r versus pH for the reaction of Na_2SO_3 ($6.25x10^{-4}M$) with p-EtOPhTeCl_3($1.25x10^{-3}M$) at 25°C and ionic strength of $2.3x10^{-3}$mol dm^{-3} in aqueous 1,4 dioxane.

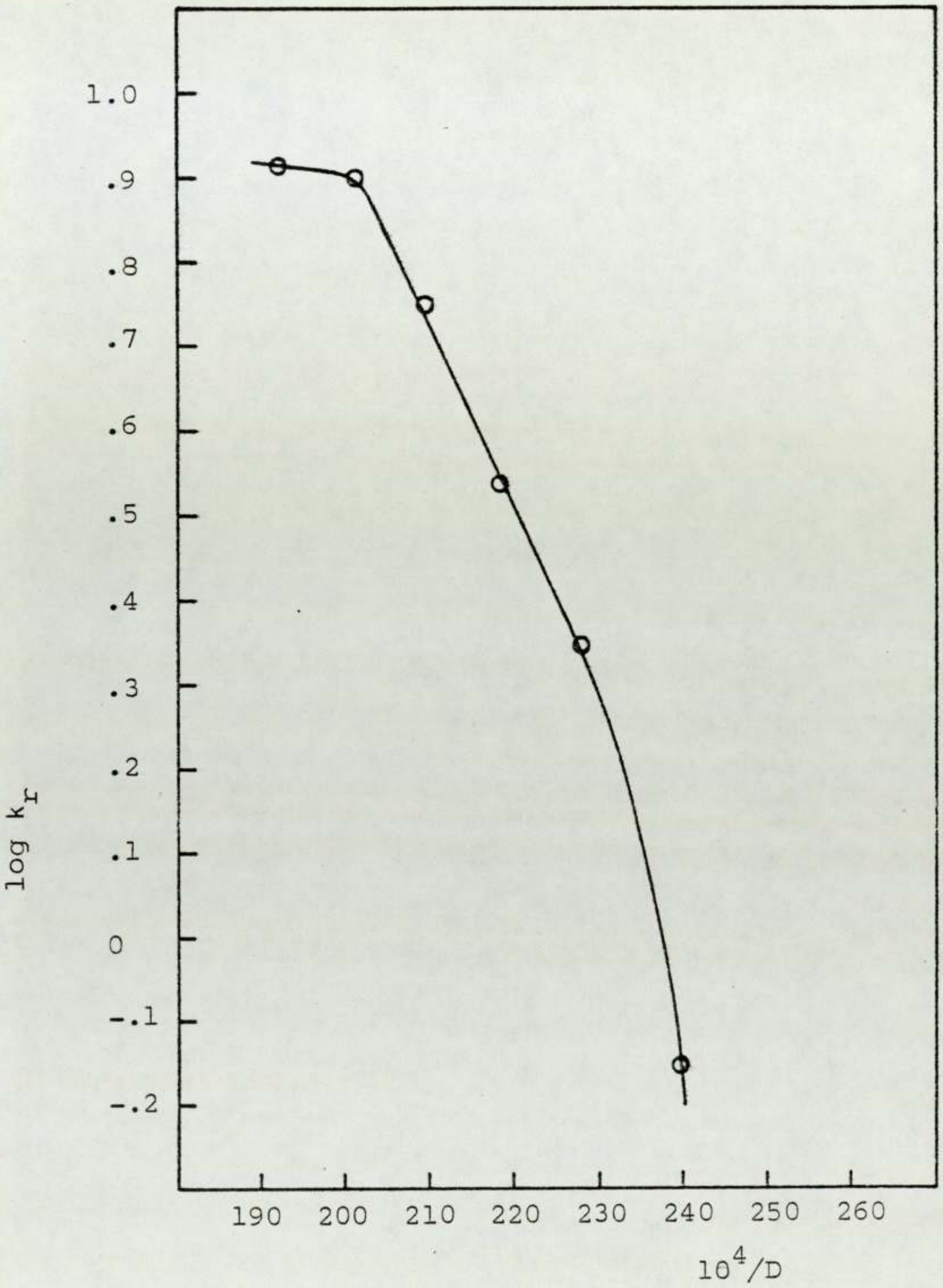


Fig (3:15) Plot of log k_r versus 1/D for the reaction of Na_2SO_3 6.25×10^{-4} M with p-EtOPhTeCl_3 1.25×10^{-3}M at 25°C

3-3 Discussion

The results obtained under different conditions of the reaction of p-EtOPhTeCl$_3$ with $S_2O_5^{2-}$ and SO_3^{2-} were found to be reproducible. In general they are parallel to the previous work reported in the literature.(18,19,20) The visible spectrum of (p-EtOPh)$_2$Te$_2$ shows a maximum absorbance at 400 n m.,. There is no absorbance noticed at this region for the reactants, p-EtOPhTeCl$_3$, $S_2O_5^{2-}$ and SO_3^{2-}. Therefore, the rates of these reactions were followed spectrophotometrically by measuring the absorbance at 400 n m. as a function of time under different reaction conditions.

The solution of (p-EtOPh)$_2$Te$_2$ in aqueous 1,4 dioxane (1:3 by volume) obeys Beer's Law in the range of concentrations studied, as shown in Fig (3:2). It has been observed that p-EtOPhTeCl$_3$ undergoes solvolysis in methanol (studied and discussed in chapter 5) and a condensation reaction with acetone.(35) No such unwanted reaction occurs in 1,4 dioxane.

Stoichiometric measurements of the oxidation of the reducing ions by p-EtOPhTeCl$_3$ show that one mole of p-EtOPhTeCl$_3$ is equivalent to 0.75 mole of $S_2O_5^{2-}$ and 1.5 mole of SO_3^{2-}. Test also indicates that there is no formation of dithionate. This inability to detect any dithionate is to be expected from the overall stoichiometry of the reaction. However, the overall production of ditelluride during the kinetic measurements was sometimes observed to be slightly less than stoichiometric ($\geqslant 90\%$) value. This departure from the theoretical measurements could be attributed to one of two reasons. The oxidation of reducing agents by any residual dissolved air in the reacting solution could occur. The photochemical decomposition of ditellurides(8), i.e. product decomposition, might occur. The measurements show that the following quantitative electron transfer reactions occur:-

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

$$3S^{IV} \longrightarrow 3S^{VI} + 6e^-$$

In more detail the reaction of SO_3^{2-} and $S_2O_5^{2-}$ with $ArTeCl_3$(Ar=p-EtOPh) can be written as:-

$$2ArTeCl_3+3SO_3^{2-} + 3H_2O \longrightarrow Ar_2Te_2+3SO_4^{2-} +6H^++6Cl^-$$

$$4ArTeCl_3+3S_2O_5^{2-} + 9H_2O \longrightarrow 2Ar_2Te_2+6SO_4^{2-} +18H^++12Cl^-$$

From these equations it seems likely that the reaction proceeds primarily via a preferential reaction of 2 - equivalent. Otherwise, if SO_3^{2-} were to react one electron at a time with the tellurium species, the collision of two SO_3^- ions would result in the formation of dithionate, Once formed, dithionate would be unlikely to react further. It has usually been found that oxidation-reduction reactions between simple compounds or ions derived from two non-transition elements, whether metallic or non-metallic, occur in two-equivalent steps.(59) Since the tellurium species prefers the 2-equivalent reaction, the oxidation products, therefore, will depend almost entirely upon the nature of the tellurium species and ultimately be independent of other reaction conditions such as pH, dielectric constant, etc.,.

Further studies were carried out in an effort to verify the stoichiometric measurements. The iodometric determination of excess SO_3^{2-} at the end of the reaction period with p-EtOPhTeCl_3 was found to be unreproducible. This could be attributed to the reaction of iodine with diarylditellurides(8), to the atmospheric oxidation of sulphite during the titration with iodine, to the formation of dithionate(40), or to the presence of organic solvent 1,4 dioxane in the mixed solutions which decreases the sensitivity of the colour for starch.(88)

The main reaction, the reduction of p-EtOPhTeCl_3, was carried out in a mixed solvent of 75% by volume 1,4 dioxane. It was found that the variation of the concentration of each reactant linearly affected the reaction rate. The good agreement found between observed data and the integrated form of equation (3:2) confirms that the reaction is first order in each reactant.

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 (3:5) and (3:11). The activation parameters for the reaction of SO_3^{2-} with p-$EtOPhTeCl_3$ are as follows:-

$k_r = 2.1\ dm^3 mol^{-1}.s^{-1}$

$\Delta E^{\ne} = 24.9 \mp 0.3\ kJ.Mol^{-1}$

$\Delta S^{\ne} = -164 \mp 1.0\ J.K^{-1}mol^{-1}$

$\Delta H^{\ne} = 22.4 \mp 0.3\ kJ.mol^{-1}$

These parameters may be compared to those of the reaction of $S_2O_5^{2-}$ ion with p-$EtOPhTeCl_3$:-

$k_r = 2.1\ dm^3 mol^{-1} s^{-1}$

$\Delta E^{\ne} = 28 \mp 0.4\ kJ.\ mol^{-}$

$\Delta S^{\ne} = -154 \mp 1.0\ J.K^{-1}mol^{-1}$

$\Delta H^{\ne} = 25.5 \mp 0.4\ k.J\ mol^{-1}$

This comparison indicates that the paths in both reducing agents are almost certain to be identical, under all different reaction conditions. This is in agreement with much evidence available in the literature which indicates that the hydrolysis of the $S_2O_5^{2-}$ ion produces a solution of sulphite ions. Therefore, we conclude that the discussion of the results of the reaction of p-$EtOPhTeCl_3$ with the solution of SO_3^{2-} holds for the solution of $S_2O_5^{2-}$ as well.

The addition of an aqueous dioxane solution of SO_3^{2-} or $S_2O_5^{2-}$ to the solution of p-$EtOPhTeCl_3$ in pure dioxane causes a rapid discolouration of the pale yellow colour of the trichloride. The decolourisation, which can be attributed to the hydrolysis of $ArTeCl_3$,(2) becomes slower as the water content of the final mixed solvent decreases. This was observed very clearly when the reduction of p-$EtOPhTeCl_3$ was carried out in a mixed solvent containing 93% by volume of 1,4 dioxane. The reduction of p-$EtOPhTeCl_3$ dissolved, prior to mixing, in pure 1,4 dioxane shows a detectable induction period when the reducing agent in aqueous dioxane is added, see graph (1) in Fig (3:8). This may be attributed to the, now, slow initial reaction of p-$EtOPhTeCl_3$ with (H_3O^+) producing an intermediate (Int). This first step is then followed by a faster reaction of the intermediate (Int) with the reducing agent, that is,

$$H_3O^+ + \text{p-EtOPhTeCl}_3 \xrightarrow[\text{slow}]{k_1} \text{Int} \qquad (3:16)$$

$$\text{Int} + 0.75S_2O_5^{2-} \xrightarrow[\text{fast}]{k_2} 4.5H^+ + \text{product} \qquad (3:17)$$

The second equation (3:17) represents the overall result of several rapid steps. Since the later stages produce more acid, this represents an autocatalytic process. The low value of the rate of reduction of p-$EtOPhTeBr_3$ $0.9dm^3mol^{-1}s^{-1}$ compared to that of p-$EtOPhTeCl_3$ $2.1dm^3mol^{-1}s^{-1}$ could be due to the low rate of the hydrolysis of p-$EtOPhTeBr_3$ compared to p-$EtOPhTeCl_3$.(23) This correlation indicates that the initial stage of the reaction, the hydrolysis reaction, may be rate determining.

Up to 75 to 80% completion, the absorbance time graphs are well fitted by equation (3:11). This indicates that the slow step in the overall reaction of p-EtOPhTeCl$_3$ with $S_2O_5^{2-}$ in a low percentage presence of H_2O (7% by volume) is first order in p-EtOPhTeCl$_3$ and H_3O^+ concentrations. The data in Table (3:6) show that under these conditions the rate of reaction is independent of the $S_2O_5^{2-}$ concentration, i.e. $k_1 \ll k_2$ (equations 3:16 and 3:17). The overall yield of the product is still governed by the reagent concentrations. At higher percentages of water i.e. 25% by volume the relative magnitudes of the rate constants change, k_1 becomes much greater than k_2. Then the reaction becomes first order in each of $S_2O_5^{2-}$ and p-EtOPhTeCl$_3$ as mentioned before.

As a further check on the hypothesis that the first step is an acid catalysed hydrolysis of Te-Cl bonds, the following experiments were carried out. When dilute sulphuric acid (1cm^3 of 1M) is added to the solution of, p-EtOPhTeCl$_3$ in pure 1,4 dioxane (47cm^3), 30 minutes prior to the reduction, the induction period becomes shorter but does not disappear completely, graph (2) in Fig (3:8). This effect could be due to two factors. The addition of acid prior to mixing should start the first step of the reaction, but that step may not be completed within thirty minutes. Either because the water concentration is down to two percent , or because the much higher concentration of $[H^+]$ affects an equilibrium step incorporated into equation (3:17).

The induction period disappears when one cm^3 of water is added in place of sulphuric acid, graph (3) in Fig (3:8). This may be due to the fact that within the waiting time an adequate amount of hydrogen ions were released which makes the reaction in its initial stage fast enough to make the induction period disappear.

The reaction profile is very different when reduction is carried out in higher percentages of water i.e. 25% by volume. Studies under these conditions were again carried out using a solution of p-EtOPhTeCl$_3$ in pure 1,4 dioxane as one of the reagent solutions to be mixed together. The rate of the reaction k_r is faster than at the lower percentage of water (k_r (high)/ k_r (low) $\sim$ 7 at 6.25×10^{-4}M $S_2O_5^{2-}$), This may be explained by the fact that in a higher percentage of water, the reaction represented by equation 3:16 becomes faster than the reaction represented in equation 3:17. Thus, we are now measuring a different slow step, one whose rate depends upon the initial concentration of the reducing agent $S_2O_5^{2-}$ as well as on the oxidizing agent, p-EtOPhTeCl$_3$.

Several rate determinations were made in a dioxane:water mixture (3:1 by volume) while the pH was varied from (3) to (11), at constant ionic strength and temperature.

It was found that the increasing hydrogen ion concentration caused a moderate decrease in the reaction rate. There are three possible causes of such phenomena.

1) Equilibrium incorporated into equation 3:17 as mentioned above.
2) Rapid protonation and deprotonation equilibrium involving the p-EtOPhTeCl$_3$ hydrolysis product.
3) Rapid hydrolysis involving SO_3^{2-} or $S_2O_5^{2-}$.

The effect of the addition of "inert" salt on the rate of the reaction of p-EtOPhTeCl$_3$ with SO_3^{2-} was investigated. Sodium sulphate was added to alter the ionic strength of the reacting solution, since it is inert to both the reactants and the products and it has no effect on the pH of the solution. The rate of the reaction does seem to be a function of the ionic strength, at least partially due to ion pairing. The rest of the dependence may be due to the fact that SO_3^{2-} reacts with an ionized form of tellurium species produced from the hydrolysis of p-EtOPhTeCl$_3$. No reliable measurements are possible to directly estimate the charge on, or the concentration of, the hydrolysed tellurium intermediate in the solution. Also the contribution to the total ionic strength due to small amounts of tellurium containing ions will be slight. Therefore, in the calculation of the final ionic strength, the concentration of p-EtOPhTeCl$_3$ has been neglected. A plot of log k$_r$ versus $\sqrt{I}$ in Fig (3:13), with a positive slope indicates that the reaction is between ions of similar charge. The plot obtained shows two stages of acceleration of the rate constant. In the first stage the slow increase in the rate constant at low ionic strengths, up to 6.3x10^{-3}M, may be due to the primary salt effect. In the second range, a big increment in the rate constant is found at higher ionic strengths. This could be due to either the salt effect's drastically altering the relative ionizing power of the solvent which evidently affects the rate of the reaction (89); or to the onset of ion pairing which offers an alternative path-way for the reaction:-

$$[\mathrm{Int}]^{N-} + SO_3^{2-} \xrightarrow{k_2} \text{products} \qquad (3:18)$$

$$[\mathrm{Int}]^{N-} + N\,M^{+} \longrightarrow \mathrm{IntM_N} \qquad (3:19)$$

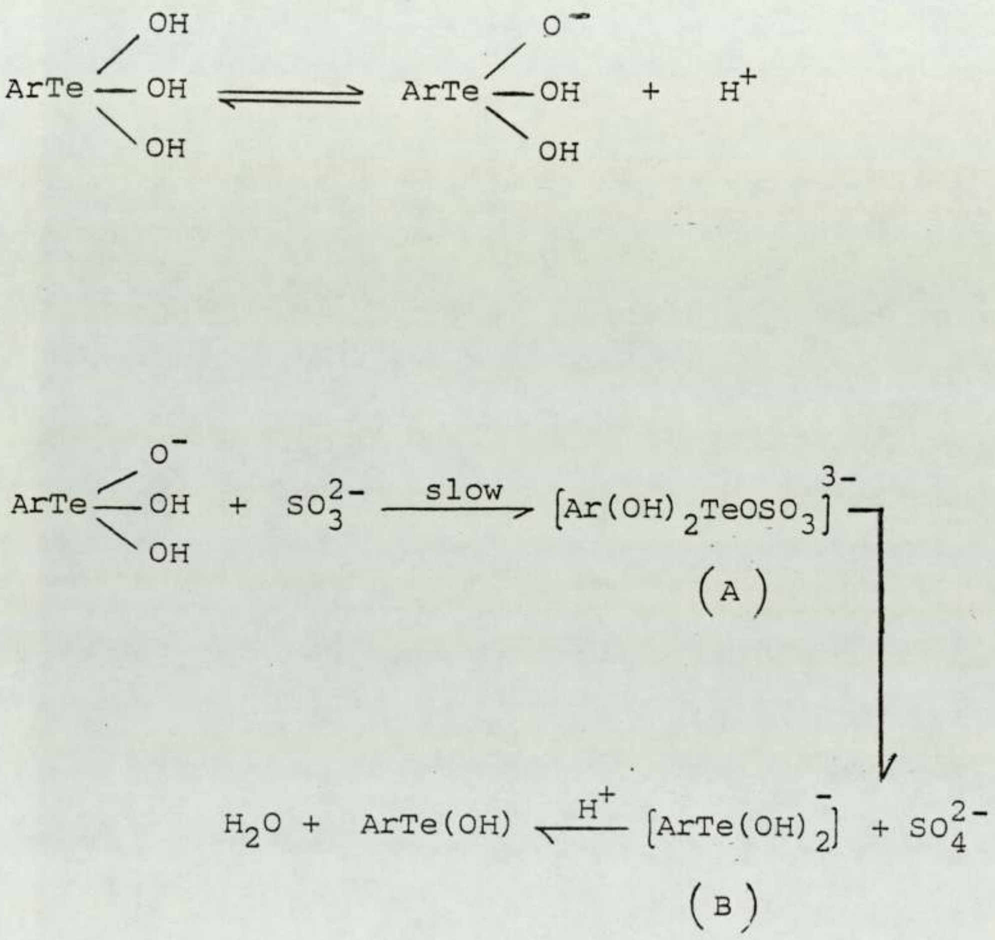
$$\mathrm{IntM_N} + SO_3^{2-} \xrightarrow{k_3} \text{products} + M_NSO_4 \qquad (3:20)$$

Ion pairing is very likely to occur in a mixed solvent of lower dielectric constant and at a relatively high ionic strength, (90) and is, therefore, the more likely to cause the change in rate.

For the reaction of p-EtOPhTeCl$_3$ with either $S_2O_5^{2-}$ or SO_3^{2-}, a plot of log k$_r$ versus 1/D Figs(3:7, 3:15) results in a straight line with a negative slope to a value of (1/D) around 0.023. For this mixed solvent, aqueous 1,4 dioxane, at lower dielectric constant the plot deviated from a straight line. This might be attributed to the preferential path of the reaction in equation (3:16) and to the effective change in the ionization constants of the reactants in the mixed solvents of lower dielectric constant.(91,92) The evidence available in the literature(80,93) indicates that for purely ionic reactions, in which the electrostatic forces are of primary importance, the slope of the curve obtained by plotting log k_r at zero ionic strength against (1/D) for higher dielectric constant is a straight line. If the charges on both the reactants are of the same sign, the slope will be negative. However, when the charges are of the opposite sign the slope will be positive. Therefore, the rate of the reaction between ions of the same sign will increase with an increase in the dielectric constant. It will decrease for opposite signs.(80) The correlation of the effect of the dielectric constant on the reaction rate with the change from higher to lower percentage of water gives a good picture of the role of solvent water. The effect of increasing 1,4 dioxane content is to retard the rate of the reaction. The effect decreases the rate of hydrolysis of p-EtOPhTeCl$_3$ and lowers the dielectric constant of the solvent, so increasing the repulsion between like-charged ions, resulting in a decrease in the rate of reaction.

In conclusion the data discussed above suggest that there are two main stages in the overall reaction of p-EtOPhTeCl_3 with SO_3^{2-} . The initial stage of the reaction is the hydrolysis of p-EtOPhTeCl_3. It has been observed that this stage of the reaction is sensitive to the concentration of H_3O^+, in fact it is acid catalysed. This could be due to the dependence of the predominant hydrolysis product formed upon the conditions of the reaction. The mechanism of the solvolysis of p-EtOPhTeCl_3 is discussed in detail in Chapter Five. According to this mechanism, the product of the hydrolysis of p-EtOPhTeCl_3 in dilute acidic media (pH - 5) is expected to be p-EtO Similar products have indeed been isolated(20). The analogous compounds have also been reported for the hydrolysis of ArSeX_3.(94)

The second stage commences with the nucleophilic attack of SO_3^{2-} on p-EtOPhTe$(OH)_2O^-$, which is produced by the ionization of the hydrolysis product of p-EtOPhTeCl_3 The ionization is more favoured in basic medium than in acidic medium. Also it seems that the oxygen atom of (Te-O^-) is more available for attack by the reducing agent rather than that in (Te-OH). This preference for attack on (Te-O^-) may explain the increase in the rate constant as the pH of the reacting solution increases. Thus the probable scheme is:-



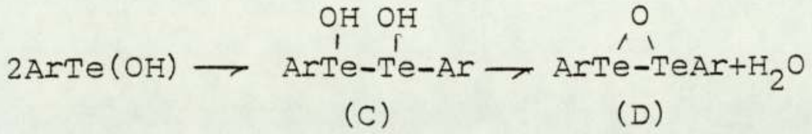
where Ar=p-EtOPh. The analgous compounds of RTeX (X=Cl,Br,I, CNS etc.,) are known for aromatic compounds.(95) They have been prepared from the reduction of aryl tellurium trichloride.

The hydrolysis of ArTeX (X=Cl, Br, I) in basic media produces a mixture of ditellurides and tellurini acid RTe(O)OH derivatives. (102-103) The product of ArTe(OH) is not isolated. This may be due to the fact that ArTe(OH) is too co-ordinatively unsaturated to allow the isolation.

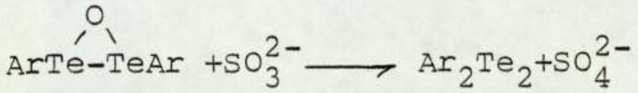
The absence of an ortho group in p-EtOPhTe(OH) which acts as a stabilizing agent (104) by interacting with Te may also increase the overall reactivity of p-EtOPhTe(OH).

From the observations quoted above we can conclude that ArTe(OH) can reasonably be suggested as an intermediate, but an intermediate with a short life-time. Thus it may undergo a fast reaction in one of two alternative pathways, (3:21) or (3:23), to give Ar_2Te_2.

In pathway (3:21) the product ArTe(OH) reacts with another ArTe(OH) to give an intermediate corresponding to (C) which then decomposes to give $(ArTe)_2O$:-



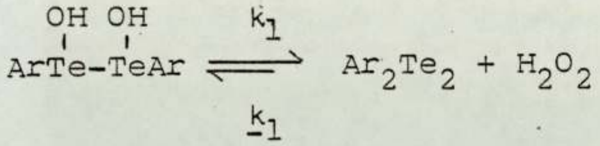
$$2\mathrm{ArTe(OH)} \longrightarrow \underset{(C)}{\mathrm{Ar}\overset{OH}{\mathrm{Te}}-\overset{OH}{\mathrm{Te}}-\mathrm{Ar}} \longrightarrow \underset{(D)}{\mathrm{ArTe}\overset{O}{-}\mathrm{TeAr}}+\mathrm{H_2O}$$



$$\mathrm{ArTe}\overset{O}{-}\mathrm{TeAr} + \mathrm{SO_3^{2-}} \longrightarrow \mathrm{Ar_2Te_2} + \mathrm{SO_4^{2-}} \qquad (3:21)$$

Ar(O)TeTeAr is an alternative possibility for (D).

The possibility of (C) cutting out H_2O_2 as:-



$$\mathrm{Ar}\overset{OH}{\mathrm{Te}}-\overset{OH}{\mathrm{Te}}\mathrm{Ar} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Ar_2Te_2} + \mathrm{H_2O_2} \qquad (3:22)$$

is ruled out because of the oxidation effect of H_2O_2 on Ar_2Te_2. It has been reported that hydrogen peroxide decolourizes an alcoholic solution of diaryl ditellurides.(20) Here the rate of decolourization of diaryl ditellurides with hydrogen peroxide has been briefly investigated under the same conditions as those used in the formation of diaryl ditelluride (Ar_2Te_2) by the reduction of p-EtOPhTeCl$_3$ with SO_3^{2-}. The absorbance-time graph shows a short induction period relative to the time taken for the reaction to go to completion. This induction period becomes shorter upon increasing the concentration of reactants, and disappears when the reacting solution is made slightly acid by adding HCl. This could be due to the fact that the overall reaction becomes so fast that the time of the induction period becomes correspondly small and unobservable. The data obtained from the rest of each run, when once the induction period is past, can be fitted to an equation which is first order with respect to diaryl ditelluride, that is so even when the ditelluride is in excess. The reaction always goes to completion. A plot of log $(A_0 - A_\infty)/(A_t - A_\infty)$ versus time where A_0, A_t, A_∞ is the absorbance at time=0, time intervals and time infinity respectively, is, therefore, a straight line. I have measured a value of the appropriate rate constant of $6.6\text{x}10^{-2}S^{-1}$ for the decolourization of diaryl ditelluride by hydrogen peroxide in mixed solvent of aqueous 1,4 dioxane 1:3 by volume at $25^{o}C$ and a pH of 3. The rate constant for the formation of diarylditelluride is $5.4\text{x}10^{-3}S^{-1}$. The deduction from the above data is that the presence of hydrogen peroxide in the solution catalyzes the destruction of the product, perhaps via a radical chain reaction. The rates of reaction of SO_3^{2-} with H_2O_2 in both basic and acidic media have been reported.(105,64) These results suggest that this reaction is not very rapid. Thus, if H_2O_2 has to be formed in this reaction then it's effect on the final product would be very pronounced.

The prediction from the equation (3:22) is that the formation of H_2O_2 will increase $\underline{k}_1$ relatively. This increment in $\underline{k}_1$ causes a great decrease in the formation of Ar_2Te_2, which is in contrast to the results obtained. Therefore, H_2O_2 cannot be formed in this reaction.

The intermediate $(ArTe)_2O$ could then be reduced in a further reaction with SO_3^{2-} to produce Ar_2Te_2.

Alternatively, by pathway (3:23) the product ArTe(OH) could react with SO_3^{2-} to produce ArTeH. The latter being attacked by ArTe(OH) to produce Ar_2Te_2

$$ArTe(OH) + SO_3^{2-} \longrightarrow ArTeH + SO_4^{2-}$$

$$ArTeH + ArTe(OH) \longrightarrow Ar_2Te_2 + H_2O \qquad (3{:}23)$$

Organyltellurols are often postulated as reaction intermediates, recently they have been isolated under oxygen-free atmosphere.(11,16,95) Tellurols are quite acidic and easily oxidized by mild oxidizing agents. Unfortunately, the results obtained from the kinetic measurements described here do not enable us to decide which of these two routes is the more probable reaction pathway. No indication of any intermediates was seen. It seems almost inevitable that a Te(II) species such as ArTeOH is produced. Therefore, it must react rapidly in its further, final reaction. The kinetic form of the first hydrolysis reaction is such that (A) can be assumed to be derived from a monomeric tellurium containing species and to be formed as a result of the relatively slow approach of similar sign charged ions. When this separates to give its immediate products the complete transfer of the oxygen atom occurs. This is associated with the transfer of 2-electrons to the oxidizing agent which passes from SO_3^{2-} to SO_4^{2-} with no chance of $S_2O_6^{2-}$ production. Such a step is associated with a higher energy of activation perhaps due to the need to overcome the repulsive barrier. Therefore, it is reasonable to expect that this step is the rate determining step in the system under study. The suggested scheme is in agreement with the calculation of the salt and dielectric constant effects and also in agreement with a low negative value of the entropy of activation obtained for these reactions, which can be attributed to the reaction between ions of the similar charge sign(106).

Irgolic(107) has pointed out that tellurinic acids and tellurinic acid anhydrides can be reduced to ditellurides. Also he has suggested, without supporting evidence, that the reduction of $ArTeCl_3$ by SO_3^{2-} and $S_2O_5^{2-}$ might proceed via reduction of tellurinic acid chlorides. Definitely the initial stage of the reaction is the hydrolysis of $ArTeCl_3$ to give a hydrolysed tellurium species, probably $ArTe(OH)_3$, although $ArTe(O)Cl$ and $ArTe(O)OH$ are often possibilities. The nature of the product depends very largely upon the hydrogen ion concentration of the hydrolysis media. All hydrolysis products are reported in the literature to give Ar_2Te_2 on reduction with $S_2O_5^{2-}$ or SO_3^{2-} . Thus, whichever hydrolysis product is in fact formed, it is likely to be subsequently reduced in a way which is consistent with our experimental kinetic findings and could, therefore, be accommodated in an appropriately modified mechanistic scheme.

There is no direct evidence available to show that the reaction of p-EtOPhTeCl$_3$ with $S_2O_5^{2-}$ or SO_3^{2-} has either an inner or an outer sphere mechanism. We strongly favour the former. Outer-sphere, proceeding necessarily one electron at a time, would be expected to produce some $S_2O_6^{2-}$. The reactivity pattern, compared to that of Cr(II) (Chapter 4) also indicates that the reaction probably proceeds via an inner-sphere mechanism.

CHAPTER FOUR

REDUCTION OF p-ETHOXYPHENYLTELLURIUM TRICHLORIDE WITH CHROMOUS AND VANADOUS IONS

4-1 Introduction

A review of the literature shows that no work has been reported dealing with the reduction of aryltellurium trihalides by mechanistically simple reagents such as chromous or vanadous ions. Investigations of the reduction of p-EtOPhTeCl$_3$ with Cr(II) and V(II) ions were carried out on similar lines to the familiar reduction of p-EtOPhTeCl$_3$ with $S_2O_5^{2-}$ and SO_3^{2-}. The choice of Cr(II) and V(II) has been made because they are among the most intensively studied reducing agents, along with such other ions as Eu(II) and Fe(II). The indications from the literature are that Cr(II) almost always prefers an inner-sphere substitution mechanism, while there are many examples of both inner and outer-sphere reactions for V(II). The substitutionally inert character of the Cr(III) products can be used to highlight the nature of the oxidant partner of Cr(II). It was hoped that comparison of the results obtained in these reactions with those of other reducing agents would lead to definite conclusions about the mechanisms of the reduction of aryltellurium trihalides.

The discovery of chromous salts in the middle of the nineteenth century by Moberg(108) has led many scientific researchers(109-114) to investigate different techniques and procedures for the preparation of chromous salts or solutions. Chromium (II) solutions are commonly prepared by three general methods:-

i) The electrolytic reduction of Chromium (III) solutions.

ii) The reduction of Chromium (III) solutions with zinc and mineral acid.

iii) The reaction of Chromium (II) acetate with mineral acid.

Vanadium (II) solutions can be obtained by the reduction of Vanadium (V) oxide or vanadyl (IV) solutions in oxygen free electrolyte cells at a mercury cathode with platinum or carbon anode. The electrolysis of methanolic vanadium (III) solutions is also used to obtain vanadium (II) solutions. Vanadyl (IV) solutions are often reduced by sodium amalgam, zinc or zinc amalgam/acid mixtures. In this study, the reduction of chromic solution by a mixture of pure zinc metal with sulphuric acid in a closed all-glass system has been used. This method has the advantage that the chromic solution has been entirely reduced to the chromous solution. The chromous solution is in contact with the mixture of the pure zinc and dilute sulphuric acid, and the chromous solution may be prepared in accurate concentration. Vanadous solutions were prepared by the same method.

Both chromium (II) and vanadium (II) solutions are highly sensitive to aerial oxidation. Different methods have been used for excluding oxygen. The development of nitrogen and vacuum line useage(115) has greatly facilitated the preparation of Cr(II) and V(II) compounds. It has been found that the oxidation of Cr(II) by the hydrogen ions is very slow(116) especially in the nearly neutral solutions (pH - 5) that remain after the excess acid is neutralized upon completion of the reaction. The oxidation is catalysed in the presence of platinum. It occurs even more rapidly if the Cr(II) solutions are acidified by HCl rather than by H_2SO_4.(113)

Many reactions have been studied mechanistically in which Cr(II) or V(II) ions react with substitution inert oxidants such as Co(III) aquo orammine complexes.(117) A considerable amount of information is now available concerning the alternative mechanistic pathways available to these reagents. Candlin, Halpern and Trimm(118) found that the rates of the reaction of different oxidizing agents with V(II) or $Cr(bipy)_3^{2+}$ as reducing agents are much slower than with Cr(II). They assumed that the reduction by V(II) and $Cr(bipy)_3^{2+}$ are via outer-sphere electron-transfer mechanisms. The reduction by Cr(II) proceeds by an inner-sphere mechanism. They attributed the variation in the rate of the reaction to the inner-sphere bridging roles of ligands originating on the oxidant. The rates of the reactions of Cr(II) and V(II) with $Co(NH_3)_5PO_4$ all exhibited a marked (pH) dependence which is interpreted in terms of the protonation equilibria of the complex.

Zwickel and Taube(119) investigated the rates and mechanisms of the reactions of $Cr(bipy)_3^{2+}$ with Co(III) complexes. They found that $Cr(bipy)_3^{2+}$ reacts with $Co(en)_3^{3+}$ several times less rapidly than it does with $Co(NH_3)_6^{3+}$. The decrease in rate observed with ethylenediamine, as compared to (NH_3), as ligand on the oxidizing agents was attributed to the greater size of the ethylenediamine. This will necessitate a greater tunneling distance and a consequent lowering of the probability of barrier penetration. The comparison of the relative rate of reaction of $\left[Co(NH_3)_5OH\right]^{2+}$ and $\left[Co(NH_3)_5OH_2\right]^{3+}$ with $Cr(bipy)_3^{2+}$ and Cr_{aqu}^{2+} indicated that when Cr_{aqu}^{2+} reacts with both oxidizing agents a bridged activated complex is involved and the hydroxo ion reacts at least 10^6 times more rapidly than does the aquo ligand. But by the "outer-sphere" mechanism, the hydroxy ion reacts less rapidly than the aquo. They concluded that even for the outer-sphere activated complex the rates of reaction are sensitive to the nature of the groups associated with the oxidizing agent.

Taube(120) investigated the rate of the reaction of Cr(II) with Co(III) complexes with organic ligands. It was found that the rates of the reactions are approximately the same with bridging groups of acetate, butyrate, coronate and succinate, but greater with oxalate and maleate as bridging groups. The similarity of the rates of the reactions with bridging groups of acetate, butyrate, coronate and succinate was attributed to the attack by Cr(II) on a common carboxyl group adjacent to the metal ion. With Oxalate and maleate as bridging groups different points of attack are available to the Cr(II) and for these bifunctional ions it could be the carboxyl end away from the metal atom.

The chloride-catalysed oxidation of chromium (II) by iron(III) has been studied by Taube and Myers(121,122). They found that both $[CrCl(OH_2)_5]^{2+}$ and $[Cr(OH_2)_6]^{3+}$ were produced in the oxidation and that their relative amounts depended upon the chloride and hydrogen ion concentration of the solution. They proposed that the $[CrCl(OH_2)_5]^{2+}$ is produced from the reaction of $[FeCl(OH_2)_5]^{2+}$ with $[Cr(OH_2)_6]^{2+}$ and that this reaction proceeds via an inner-sphere activated complex containing a Fe-Cl-Cr bond. This interpretation has been questioned by Ardon, Levitan and Taube,(123) who studied the chloride-catalysed oxidation of $[Cr(OH_2)_6]^{2+}$ by $[Fe(OH_2)_6]^{3+}$ at -50°C, where the formation of $[FeCl(OH_2)_5]^{2+}$ from $[Fe(OH_2)_6]^{3+}$ and Cl^- proceeds relatively slowly. The results obtained from the above study show that $[CrCl(OH_2)_5]^{2+}$ is produced even when $[FeCl(OH_2)_5]^{2+}$ is not present prior to the reaction. However, they did not study the oxidation of $[Cr(OH_2)_6]^{2+}$ by $[FeCl(OH_2)_5]^{2+}$ or identify the products of this reaction. Dulz and Sutin(124) have studied the kinetics of the oxidation of chromium(II) by iron(III) in the presence of chloride ions at 25°C. They found that the chloride catalyzed reaction proceeds via two paths at this temperature. One of these paths involves $[FeCl(OH_2)_5]^{2+}$ as a reactant and the other does not. The former reaction is very rapid and both paths produce $[CrCl(OH_2)_5]^{2+}$.

Espenson and Slocum(125) performed a kinetic study of the reaction of Cr(II) with isomeric $[CrCl_2(OH_2)_4]^+$ ions. They pointed out that the reaction proceed by a chloride-bridged Cr(II)-Cr(III) exchange process. The reduction of the trans-isomer occurs at a slightly higher rate than that of cis. The lower rate of reaction of cis$[CrCl_2(OH_2)_4]^+$ compared to the trans-isomer is consistent with the lower ligand field strength of chloride compared to water. In related chloride - bridged inner-sphere reactions, chromium(II) exchanges with $[CrCl(OH_2)_5]^{2+}$ more rapidly than it does with $[CrCl(NH_3)_5]^{2+}$. Ograd and Taube(126) attributed the lower rate of the ammine complex to the greater ligand field strength of NH_3 compared to H_2O.

Sutin(127) attributed the increase of the rate of the reduction of aqua complexes with the decreasing acidity to displacement of the hydrolysis equilibrium

$$MOH_2^{3+} \rightleftharpoons MOH^{2+} + H^+$$

with MOH^{2+} undergoing more rapid reduction than MOH_2^{3+}. It was found that the reaction of V(II) with Fe(III) is an exception in the V^{2+} does not react much more rapidly with $FeOH^{2+}$ than Fe^{3+}. This was interpreted as showing that the reaction of V^{2+} with Fe^{3+} proceeds by an outer-sphere mechanism, while the reaction of V(II) with $FeOH^{2+}$ involves inner-sphere mechanism, which is limited by the rate of substitutuion on V(II).

Newton et al (128) investigated the oxidation of V(II) by Thallium (III). They found that the Vanadium product is predominantly V(IV) and the rate of the reaction is less than that for the oxidation of V(III). They concluded that the reaction of V(II) proceeds predominantly by a two-electron mechanism. Green and Sykes (129) studied the equivalent paths in the reaction of vanadium(II) with mercury(II). They found that the one-electron path proceeds with the formation of Hg(I) as an intermediate,

$$V(II) + Hg(II) \longrightarrow V(III) + Hg(I) \qquad (4:1)$$

and the subsequent reactions as in (4:2) and (4:3) are rapid

$$V(II) + Hg(I) \xrightarrow{\text{Fast}} V(III) + Hg(0) \qquad (4:2)$$

$$Hg(0) + Hg(II) \xrightarrow{\text{Fast}} 2Hg(I) \qquad (4:3)$$

The two-electron path proceeds with the formation of vanadium(IV) (VO^{2+}) and mercury(0) atoms.

$$V(II) + Hg(II) \longrightarrow V(IV) + Hg(0) \qquad (4:4)$$

Where Hg(0) reacts subsequently as in (4:3). They concluded that the rate constant for the one-electron path is independent of hydrogen ion concentration. The rate constant for the two-electron path is inversely dependent of hydrogen ion concentration. They believe that the two-electron paths in equation (4:4) are inner-sphere while the mechanism of the one-electron path is less certain.

The literature cited indicate that the oxidation of Cr(II) by (H^+) in a nearly neutral solution (pH ~ 5) is negligible. The rates of the reduction of oxidants by Cr(II) and V(II) exhibit a considerable pH dependence. The ligands originally on the oxidant control the rate of the inner-sphere reaction and to some extent the outer-sphere reaction as well. The chloride-catalyzed oxidation of Cr(II) by Fe(III) proceeds via inner-sphere activated complex containing Fe-Cl-Cr bond. The relative amount of $\left[CrCl(OH_2)_5\right]^{2+}$ depends upon the chloride and hydrogen ion concentrations of the solution. The rate of aquation of $\left[CrF(OH_2)_5\right]^{2+}$ increases with increasing (H^+) while the rate of the aquation of $\left[CrX(OH_2)_5\right]^{2+}$, (X=Cl, Br, I), decreases when (H^+) increases.

4:2 RESULTS

4:2:1 The reduction with Cr (II)

The reaction between chromous sulphate and p-EtOPhTeCl$_3$ in an aqueous solvent of 1,4 dioxane, 1:3 by volume has been investigated. The visible spectra of Cr(II) in aqueous 1,4 dioxane (1:3) is shown in Fig (4:1). It is found that the maximum absorbance of Cr(II) is (710-715n.m). The best wavelength to follow the rate of reaction is 400n m., the absorption maximum of product ditelluride, (as was mentioned in section 3:2).

The kinetic runs were followed by monitoring the increase in the concentration of (p-EtOPh)$_2$Te$_2$ with time, usually for a period up to ten minutes. The reactions were monitored by using an SP8-100 UV-visible spectrophotometer. Up to (80) to (90%) completion, the absorbance-time graphs were used to determine the rate constants in different conditions. A computer program written in BASIC (Appendix II) was used to calculate the individual rate constants.

The determination of the stoichiometry of the reaction of Cr(II) with p-EtOPhTeCl$_3$ was made by potentiometric titration . The data are listed in Table (4:1), and a typical plot of ΔE against the volume of added reagent is shown in Fig(4:2). The plot shows that, within experimental error, one mol of p-EtOPhTeCl_3 is equivalent to (3) mols Cr(II). The colour of the chromium product after oxidation is deep green which indicates that the oxidation state is Cr(III). Magnetic and ion exchange measurements, discussed later, confirm this observation.

The data obtained from the curves of absorbance against time for the reaction of p-EtOPhTeCl_3 with Cr(II), can be fitted to a second order equation. The equation, in general is:-

$$aA+bB \longrightarrow cC+\text{other products}$$

where A, B and C represent p-EtOPhTeCl_3, Cr(II) and $(p\text{-EtOPh})_2Te_2$ respectively. The equation derived for this reaction is similar to that of SO_3^{2-} in section (3:2).

The effect of varying the initial concentration of the reducing agents on the rate of the reaction was determined by fitting equations 3:3, 3:4 and 3:5 using a computer program (Appendix II). The determined value of k_{obs} and k_r are listed in Table (4:2). Plots of k_{obs} versus Cr(II) represented in Fig (4:3) give a good straight line. The slope shows that the experimental value of the rate of the reaction k_r is 15.7$dm^3mol^{-1}S^{-1}$ at 25^oC. The intercept is found when the concentration of Cr(II) is three time that of p-EtOPhTeCl_3 concentration, within experimental error. This is in agreement with the data obtained from stoichiometric measurements. The plot shows that the reaction is first order in respect to each reactant.

Table (4:3) shows the variation of the rate constant with temperature over the range 15 to 35°C for the reaction between Cr(II) and p-EtOPhTeCl_3. According to the Arrhenius equation (3:7) a plot of log k_r versus (K/T) is linear as shown in Fig(4:4). The least squares computer program (Appendix III) was used to obtain the slope of the plot. Equation 3:8 and 3:9 were used to determine the values of the activation parameters as:-

$$\Delta E^{\#} = 26.5 \mp 0.4 \text{ kJ. mol}^{-1}$$

Alternatively we can write:-

$$\Delta S^{\#} = -141 \mp 1.4 \text{ J. mol}^{-1}\text{. K}^{-1}\text{.}$$

$$\Delta H^{\#} = 24 \mp 0.4 \text{ kJ.mol}^{-1}$$

The above experiments were repeated under constant temperature but with different solvent ratios of 1,4 dioxane and water. Values of the dielectric constant for the mixed solvents can be found in the work of G. Akerlöf(87). The rate constants are listed in Table (4:4). Plot of log k_r versus 1/D represented in Fig (4:5) shows straight line dependances, whose slopes were calculated using a least squares equation. The intercepts of the plots show the significant effect of the lowering of the dielectric constant of the solution on the rate of the reaction.

The hydrogen ion concentration was varied in this reaction by adding differing amounts of H_2SO_4 to the reaction solution. The rate of the reaction was found to be inhibited by the acid. The data listed in Table (4:5) show that increasing the H_2SO_4 concentration from 0.042 M to 0.625 M at 25°C produces a decrease in the average rate of the reaction of about 40%. A plot of log k_r versus (pH) is shown in Fig (4:6). No effect on this reaction was found by varying the ionic strength of the solution.

The effect of chloride ion concentration, over a range between ($0-9.9\times10^{-3}$M), on the rates of reduction by Cr(II) was also investigated. The effect can be described by an equation in the form:-

$$k_r = \frac{K_R k_3 [\bar{Cl}]^x}{1 + K_R [\bar{Cl}]^x} \qquad (4:5)$$

Where $x=1$, K_R is the equilibrium constant and k_3 is the rate constant at limiting effect of chloride ion concentration on the rate of the reaction, (see section (4:3), equations 4:6, 4:7, 4:8). For further details see Appendix (VI). Values of K_R and k_3 can be determined graphically by plotting $1/k_r$ against $1/[\bar{Cl}]$ as shown in Fig (4:7). From the data for the Cr(II) reduction listed in Table (4:6) one can obtain a value of $K_R=320$ dm^{3}mol^{-1} while $k_3=32$ dm^{3}mol^{-1}s^{-1}.

Curves numbered one and nine in Fig (4:8) represent the spectra obtained by dissolving para-ethoxyphenyl tellurium trichloride (1.5×10^{-4}M) in aqueous dioxane

(75% by volume) and pure dioxane respectively. The curves numbered 2 through to 8 represent the equimolar spectra when a range (0 to 18.3×10^{-3}M) of concentration of KCl are added. The largest change in absorbance is found at 278 n m. where it increases with the KCl concentration. Thus an equilibrium constant for a process between the hydrolysed p-$EtOPhTeCl_3$ and added potassium chloride may be calculated from the increase in the absorbance at this wavelength. The spectra show what may be an isosbestic point at 245 n m., although the measured absorbance is not completely unchanging. If we assume that only two absorbing species are involved represented by:-

$$ArTeCl_n + xCl^- \xrightleftharpoons{K_o} ArTeCl_{(n+x)}$$

with other groups unspecified, then the equilibrium constant K_o can be determined by an equation of the form:-

$$(D_{mix}-D_n) = \frac{(D_B-D_A)\ K_o \left\{Y\left[T\right]+\left[KCl\right]\right\}^x}{1 + K_o \left\{Y\left[T\right]+\left[KCl\right]\right\}^x}$$

where Y=3-n, D_{mix} is the absorbance when both forms of tellurium species present in the solution i.e. $ArTeCl_n$ and $ArTeCl_{(n+x)}$, D_n is the absorbance when all tellurium species present in the solution as $ArTeCl_n$. For further details see Appendix (VII). Assuming D_n=0.467, a plot of $1/(D_{mix}-D_n)$ versus $1/\left\{Y\left[T\right]+\left[KCl\right]\right\}$ is a straight line as shown in Fig (4:9). The values of D_{mix} in different KCl concentrations are listed in Table (4:7). The values of D_n range between 0.467 to 0.560 depending on the values of (n) and (x) assumed. n=0 or 1 and x=1 offered values of K_o range between (32 to 46) dm^3mol^{-1}. That is the value of K_o does not vary much whichever values of (n) and (x) are operational in the solution. It is always close to $40dm^3mol^{-1}$. and never close to $320dm^3mol^{-1}$.

In an attempt to investigate the nature of the chromium containing product, ion exchange was used to determine the total charge on the chromic species. The method is based on the exchange capacity of the cation resin. The equivalent of the charge per species taken up by the resin is equal to the total equivalent of charge displaced from the resin. In general:-

$$M^{n+} + \underline{zH^+} \rightleftharpoons \underline{M}^{n+} + zH^+$$

Where M^{n+} represents the complex species in the solution and $\underline{H}^+$ the hydrogen ion on the resin.

In this experiment a sample of the chromic complex (0.0600gm) was weighed accurately, dissolved in redistilled water and the solution made up to $50cm^3$. The ion exchange column in hydrogen form was prepared as mentioned in Section (2:9) and rinsed free of excess acid. The solution of the chromium complex was added to the column. The acid liberated by the adsorbed chromium complex was washed from the resin. The eluent was titrated against 0.01M sodium hydroxide, under nitrogen to eliminate the effect of atmospheric CO_2 on the titration. Bromomethyl Blue 6-7 pH was used as indicator. It was found that $10cm^3$ of the eluent is equivalent to $8.3cm^3$ of NaOH solution. The nearest integer for the value of the equivalent of chromium complex found is (2+).

Thin layer chromatography on silicagel was used to separate and examine the species in the solution of Cr(II) complex. The complex separated from the reaction of $p\text{-EtOPhTeX}_3$ (X=Cl, Br, I) with chromous sulphate gives only one detectable spot in all cases. It was found that the mixture of 75-80% of aqueous 1,4 dioxane gives a reasonable speed of migration of the solute, while not allowing it to move as fast as does the solvent front.

Conductivity measurements on solutions of the chromium complex $(CrCl(OH_2)_5)SO_4$ were all made at 25°C; using a cell whose cell constant is 1.46 . The equivalent conductance of the complex in water was measured over a concentration range $(1.35x10^{-3})$ to $(4.72x10^{-3})$N. The choice of solvent was determined by the solubility of the complex in the solvent. An increase in conductance is seen for the product solutions from reactions with the chloride, bromide or iodide after their solutions have been refluxed for one hour. The data are listed in Table (4:8). A plot of Λ_e before and after refluxing versus $\sqrt{C_{equi.}}$ is shown in Fig (4:10, 4:11).

The elemental analysis of the chromium complex shows the following percentages of elements to be present:-

element	found %	formula requires %
H	3.75	3.66
Cl	12.25	12.78
Cr	18.90	19.01
S	12.70	11.70

All these results indicate that the chromium product is $(CrCl(OH_2)_5)SO_4$.

The magnetic susceptibility of the chromium complex is also consistant with the formula $(CrCl(OH_2)_5)SO_4$. It was determined at room temperature by the Gouy method. The standard $Hg(Co(NCS)_4)$, an empty weighing glass tube and the powdered solid sample were weighed with and without an applied magnetic field. The glass tube filled with water was also weighed without an applied magnetic field. The data is listed as follows:-

Substance	Weight/gm magnet off	Weight/gm Magnet on
Air	5.0928	5.0922
Water	5.6914	....

Substance	Weight/gm Magnet off	Weight/gm Magnet on
Standard	6.2481	6.3151
Sample	5.7780	5.8305

The calibration constant of β may be calculated:

$$\beta = \frac{(X)(M)-(V)(0.029\times10^{-6})}{\Delta - \delta} \quad \text{reference(130)}$$

$$= \frac{(16.44\times10^{-6})(1.1553)-(0.029\times10^{-6})(0.5998)}{(0.067 + 6\times10^{-4})}$$

$$\beta = 2.8070\times10^{-4}$$

and the susceptibility per mole (Xm) for the sample before correction is 5.956×10^{-3} cgs.

The diamagnetism of ligand, ion, inner core for diamagnetic correction can be determined from the data of reference (131) page 142-143.

H_2O : $5\times13=65\times10^{-6}$

Cl^{-} : $1\times23=23\times10^{-6}$

$\overset{-}{SO_4}$: $1\times40=40\times10^{-6}$

inner core : $=13\times10^{-6}$

Total 0.141×10^{-3} cgs

the susceptibility per mole after corrections is 6.097×10^{-3} cgs. The corrected effective magnetic moment for the sample may be calculated:-

$$\mu_{eff} = 2.83\,(X'_m T)^{\frac{1}{2}}$$

$$\mu_{eff} = 3.8 \mp 0.2 \text{ B.M.}$$

The value of μ_{eff} obtained from the above calculation is very close to the value of μ_{eff} where number of unpaired electrons (n) equal (3) using spin only formula:-

$$\mu_{eff}=(n(n+2))^{\frac{1}{2}}$$

4:2:2 The Reduction with V(II)

The reaction between vanadous sulphate with p-EtOPhTeCl$_3$ in a mixed solvent of 1,4 dioxane and distilled water also has been investigated. The visible spectrum of V(II) in aqueous 1,4 dioxane (1:3) is shown in Fig (4:12). It is found that the maximum absorbance of V(II) is (560-565 n m.). The kinetic runs were followed in the same way of Cr(II) reactions with p-EtOPhTeCl$_3$.

The stoichiometry of the reaction between V(II) and p-EtOPhTeCl$_3$ was measured using a spectrophotometric technique. The final absorbance data of the product (p-EtOPh)$_2$Te$_2$ are listed in Table (4:9). A plot of molar concentration of (p-EtOPh)$_2$Te$_2$ versus molar concentration of V(II)/p-EtOPhTeCl$_3$ is shown in Fig (4:13). The plot shows that within experimental error one mole of p-EtOPhTeCl$_3$ is equivalent to 3 mols V(II). The vanadium product, after oxidation, is pale green which suggests that the product is in the oxidation state (III). This is confirmed by a comparison with the visible spectra of V(II), V(III) and V(IV) as shown in Figs (4:12 , 4:14).

A reaction solution containing p-EtOPhTeCl$_3$, in up to 50% excess, and vanadous ion was kept for 24 hours in the dark under nitrogen. The visible spectra obtained for the product showed no evidence of the formation of V(IV) Fig (4:15). This indicates that V(III) does not undergo further reaction to produce V(IV).

The data obtained from the curves of absorbance against time for the reaction of V(II) with p-EtOPhTeCl$_3$ can be fitted to a second order in the same way of Cr(II). The effect of varying the initial concentration of V(II) was determined. The determined values of k_{obs} and k_r are lisetd in Table (4:10). Plots of k_{obs} versus V(II) concentration represented in Fig (4:16). The slope shows that the experimental value of the rate of the reaction (k_r) is (7.0)dm^{3}mol^{-1}S^{-1}. The intercept is equal to three times that of p-EtOPhTeCl$_3$ concentration within experimental error. This is in agreement with the data obtained from stoichiometric measurements. The plot shows that the reaction is first order in respect to each reactant.

The variation of the rate constant with temperature over the range 15 to 45°C for the reaction of V(II) with p-EtOPhTeCl$_3$ is shown in Table (4:11). A plot of log k_r against (K/T) is linear as shown in Fig (4:17). This gives values for the activation parameters of

$$\Delta E^{\neq} = 21.1 \mp 0.8 \text{ kJ mol}^{-1}$$
$$\Delta S^{\neq} = -166 \mp 2.7 \text{ J mol}^{-1}\text{K}^{-1}$$
$$\Delta H^{\neq} = 18.6 \mp 0.8 \text{ k.J mol}^{-1}$$

Table (4:12) shows the effect of (KCl) concentration on the rate of V(II) reaction with p-EtOPhTeCl_3. KCl was added over a molar concentration range 0-11.5x10^{-3}. According to equation 4:5 a plot of $1/k_r$ versus $1/[Cl^-]$ is a straight line as shown in Fig. (4:18). The equilibrium constant value K_R obtained is 480 $dm^3 mol^{-1}$.

Cr(II) ml 0.116 M	E(mV)
2.0	493
4.0	498
6.0	688
6.1	710
6.2	720
6.3	733
6.4	743
6.5	763
6.6	805
6.7	1053
7.0	1060
7.5	1060
8.0	1060

Table (4:1) Experimental data for determination of the equivalent weight of paraethoxyphenyltellurium trichloride versus chromous ion in aqueous 1,4 dioxane.

$10^3 x \left[Cr\ (II)\right]$ M	$10^3 x k_{obs}$ S^{-1}	k_r $dm^3.mol^{-1}$ S^{-1} (a)
1.93	6.5	15.2
2.06	8.4	15.0
2.50	15.0	15.0
3.18	26.0	15.2
4.00	38.0	15.1

(a) $k_r = k_{obs} / \left[[Cr\ (II)] - 3[p\text{-}EtOPhTeCl_3]\right]$

Table (4:2) Rate constant of the reaction of $p\text{-}EtOPhTeCl_3$ $5x10^{-4}$M with different molar concentrations of Cr(II) in aqueous 1,4 dioxane

T^oC	10^3xK/T	k_r $dm^3 mol^{-1}$ s^{-1}	log k_r
15	3.472	12.4	1.093
20	3.413	14.7	1.167
25	3.356	17.9	1.253
30	3.300	21.2	1.326
35	3.247	25.3	1.403

Table (4:3) Rate constants of the reaction of p-EtOPhTeCl_3 $5x10^{-4}$M with Cr(II) $2x10^{-3}$M at different temperature in aqueous 1,4 dioxane.

1,4 dioxane vol%	D	$10^3/D$	$k_r\,dm^3.mol.^{-1}S^{-1}$	$\log k_r$
50.0	49.7	20.1	29.4	1.468
55.2	48.1	20.8	29.1	1.463
59.4	47.1	21.2	22.6	1.354
63.4	46.1	21.7	20.5	1.311
67.7	45.0	22.2	18.8	1.274
71.9	44.0	22.7	15.9	1.201
75.0	43.7	22.9	15.4	1.188
76.0	43.1	23.2	14.2	1.152
80.2	42.1	23.8	13.9	1.143

Table (4:4) Rate constant of the reaction of p-$EtOPhTeCl_3$ $5x10^{-4}M$ with Cr(II) $2x10^{-3}M$ in aqueous 1,4 dioxane solution of different dielectric constant.

$[H^+]$ M	pH	k_r.dm^3.mol^{-1} S^{-1}	log k_r
0.042	1.38	32.4	1.51
0.052	1.28	30.2	1.48
0.073	1.14	24.0	1.38
0.157	0.80	22.7	1.36
0.209	0.68	19.1	1.28
0.260	0.59	17.0	1.23
0.469	0.33	15.2	1.18
0.521	0.28	14.9	1.17
0.625	0.21	13.4	1.13

Table (4:5) Rate constant of the reaction of p-EtOPhTeCl$_3$ 5x10^{-4}M with Cr(II) 2x10^{-3}M in aqueous 1,4 dioxane solution of different hydrogen ion concentrations.

k_r $dm^3 mol^{-1} s^{-1}$	$10^3/k_r$	10^3 [KCl] M	10^3x [Cl^-] M total	1/[Cl^-] M^{-1} total
17.5	57.1	1.56	3.06	327
20.1	49.8	3.65	5.15	194
22.6	44.3	5.73	7.23	138
24.7	40.5	7.81	9.31	107
25.9	38.6	9.38	11.40	88

Table (4:6) Rate constant of the reaction of p-EtOPhTeCl_3 $5x10^{-4}$M with Cr(II) $2x10^{-3}$M in aqueous 1,4 dioxane solution of different KCl concentrations.

$10^3 x [\bar{Cl}]$ added M	$1/[\bar{Cl}]$ total M^{-1} (a)	D_{mix}	$\frac{1}{D_{mix}-D_n}$
1.02	682	0.653	5.37
2.03	403	0.773	3.27
6.09	153	1.160	1.44
10.2	94	1.507	0.96
14.2	68	1.613	0.87
18.3	53	1.746	0.78

(a)n=o

Table (4:7) Variation of the absorbance (D_{mix}) at wave length 278 nm. with KCl concentration for the U.V. spectrum of p-EtOPhTeCl$_3$ 1.5x10^{-4}M solution in aqueous 1,4 dioxane at constant hydrogen ion concentration of 0.469 M.

Wt.mg	Normality	$N^{\frac{1}{2}}$	Λeq. ohm^{-1}cm^{2}Eq^{-1} before reflux	Λeq. ohm^{-1}cm^{2}Eq^{-1} after reflux
18.5	$1.35\text{x}10^{-3}$	0.037	131.7	345.4
20.3	$1.49\text{x}10^{-3}$	0.039	122.9	336.4
24.1	$1.76\text{x}10^{-3}$	0.042	117.6	326.0
34.2	$2.50\text{x}10^{-3}$	0.050	115.6	297.7
43.5	$3.18\text{x}10^{-3}$	0.056	113.8	277.6
64.5	$4.72\text{x}10^{-3}$	0.069	110.8	232.2

Table (4:8) Equivalent conductance of chromium (III) complex solution in different normalities at 25°C before and after refluxing.

[V(II)] M	[(p-EtOPh)$_2$Te$_2$] M	V(II)/ p-EtOPhTeCl$_3$	Final absor. of (p-EtOPh)$_2$Te$_2$
0.85x10^{-3}	0.80x10^{-4}	1.7	0.096
1.10x10^{-3}	1.21x10^{-4}	2.2	0.145
1.40x10^{-3}	1.76x10^{-4}	2.8	0.210
1.70x10^{-3}	2.16x10^{-4}	3.4	0.260
2.01x10^{-3}	2.33x10^{-4}	4.0	0.280
2.3 x10^{-3}	2.33x10^{-4}	4.6	0.280
2.6 x10^{-3}	2.33x10^{-4}	5.2	0.280

Table (4:9) Experimental data for determination of the equivalent weight of p-EtoPhTeCl$_3$ 5x10^{-4}M versus vanadous ion concentrations in aqueous 1,4 dioxane.

$[V(II)]$ M	k_{obs} s^{-1}	$k_r^{(a)}$ dm^3 mol^{-1} s^{-1}
1.72×10^{-3}	1.52×10^{-3}	6.93
2.00×10^{-3}	3.49×10^{-3}	6.99
2.30×10^{-3}	5.56×10^{-3}	6.95
2.60×10^{-3}	7.65×10^{-3}	6.96

(a) $k_r=k_{obs}/\left[V(II)-3\{p\text{-EtOPhTeCl}_3\}\right]$

Table (4:10) Rate constant of the reaction of $p\text{-EtOPhTeCl}_3$ 5×10^{-4}M with different molar concentrations of V(II) in aqueous 1,4 dioxane.

T^oC	$10^3 xK/T$	$k_r dm^3 mol^{-1} S^{-1}$	$\log k_r$
15	3.472	4.9	0.694
20	3.413	6.1	0.788
25	3.356	6.8	0.835
30	3.300	7.9	0.895
35	3.247	8.7	0.939
40	3.195	10.5	1.020
45	3.145	11.6	1.066

Table (4:11) Rate constant of the reaction of $p\text{-EtOPhTeCl}_3$ $5x10^{-4}M$ with V(II) $2.3x10^{-3}M$ at different temperatures in aqueous 1,4 dioxane.

$k_r dm^3 mol^{-1} s^{-1}$	$1/k_r$ $d\bar{m}^3.mol.S$	$10^3 [KCl]$ M added	$1/[Cl^-]$ $\bar{M}^1$ total
8.1	0.123	0.31	552.5
8.9	0.112	0.73	454.6
9.5	0.105	1.04	393.7
12.1	0.083	3.13	216.0
13.2	0.076	5.21	149.0
14.3	0.070	7.29	113.8
15.1	0.066	9.38	91.9
15.2	0.066	11.46	77.2

Table (4:12) Rate constant of the reaction of p-EtOPhTeCl$_3$ 5x10^{-4}M with V(II) 2.3x10^{-3}M in aqueous 1,4 dioxane solution of different KCl concentrations.

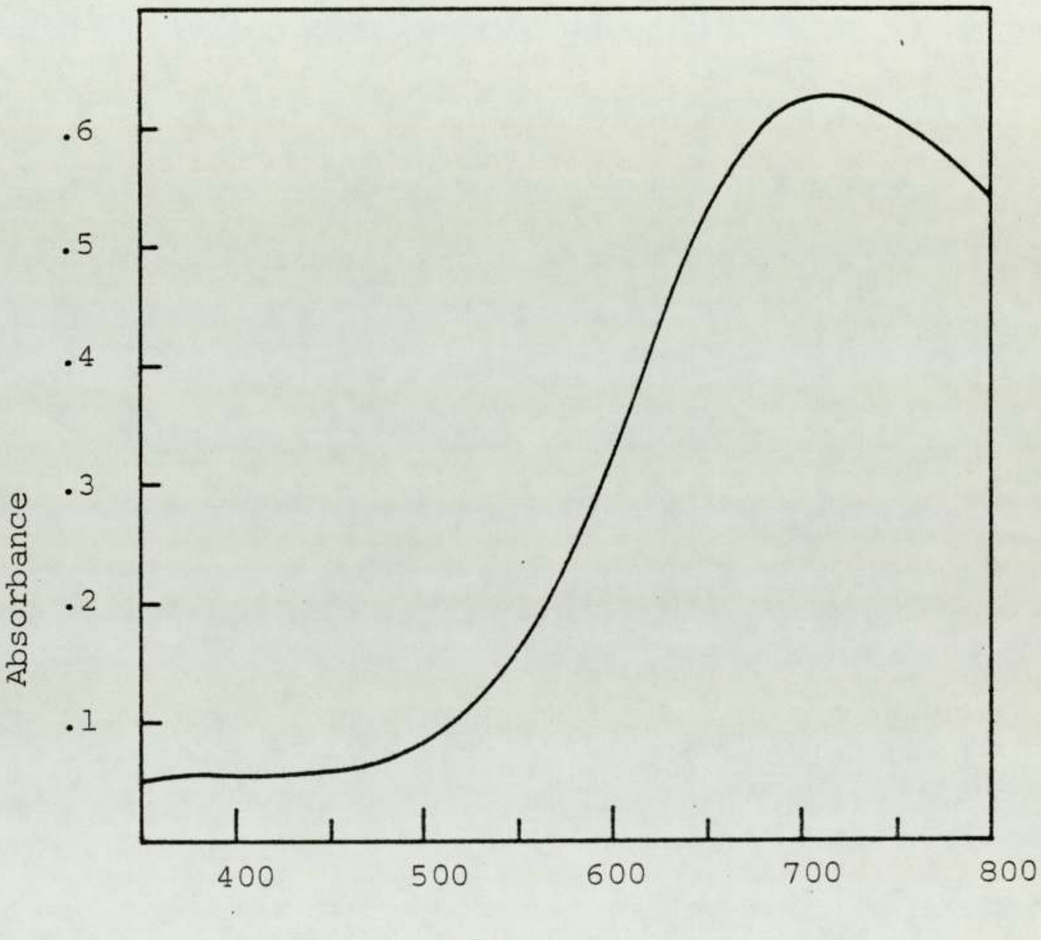
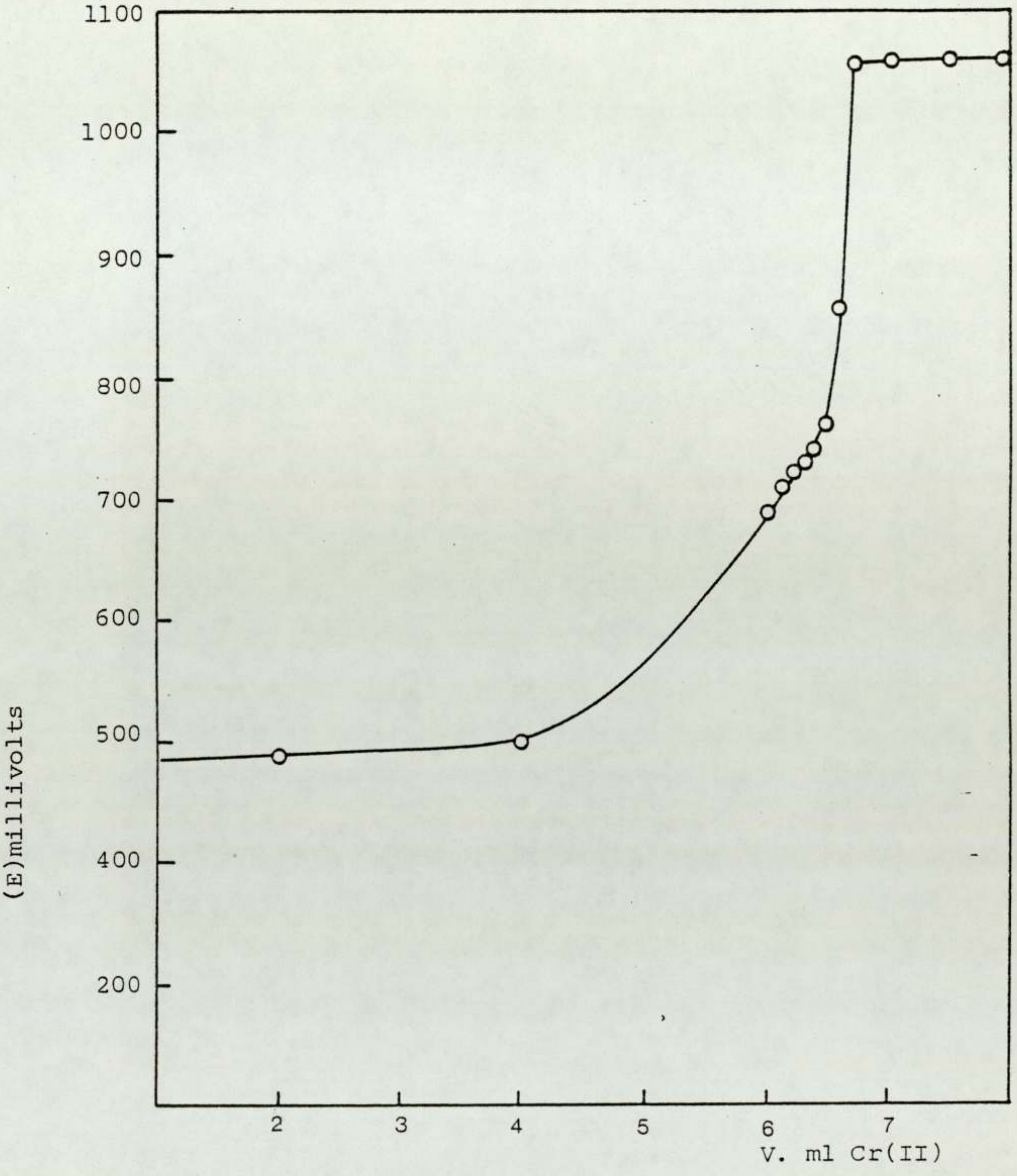


Fig (4:1) Visible spectrum of chromous sulphate solution in mixed 1,4 dioxane-water 3:1.



$$\text{Ratio} = \frac{0.116 \times 6.7}{0.01 \times 25} = 3.1$$

Fig (4:2)Plot of (E)millivolts versus Cr (II) volume for potentiometric titration of Cr(II) 0.116M versus 25ml of p-EtOPhTeCl_3 0.01M.

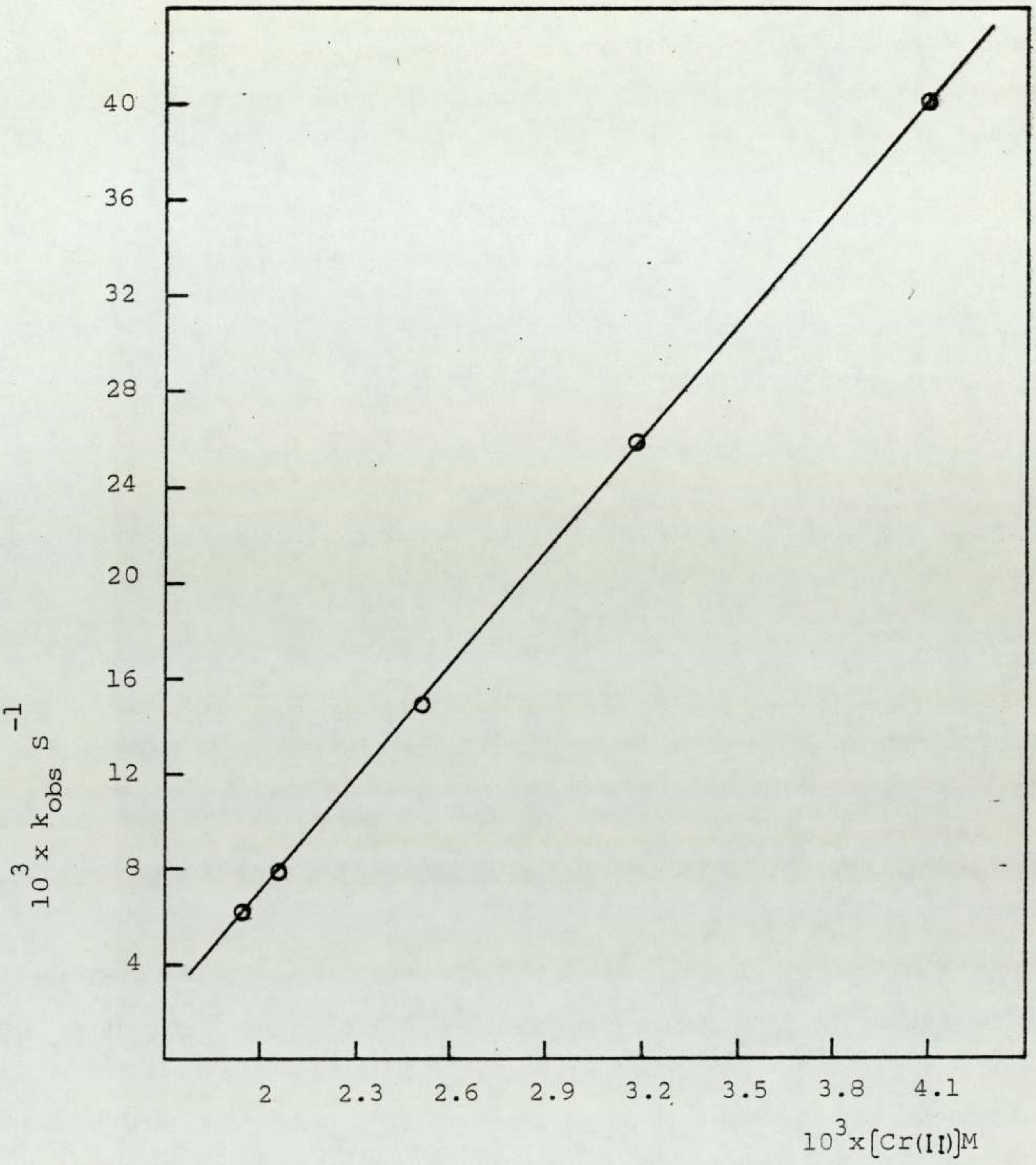


Fig (4:3) Plot of k_{obs} versus [Cr(II)] concentration for the reaction of p-EtOPhTeCl$_3$ with Cr(II) in aqueous 1,4 dioxane

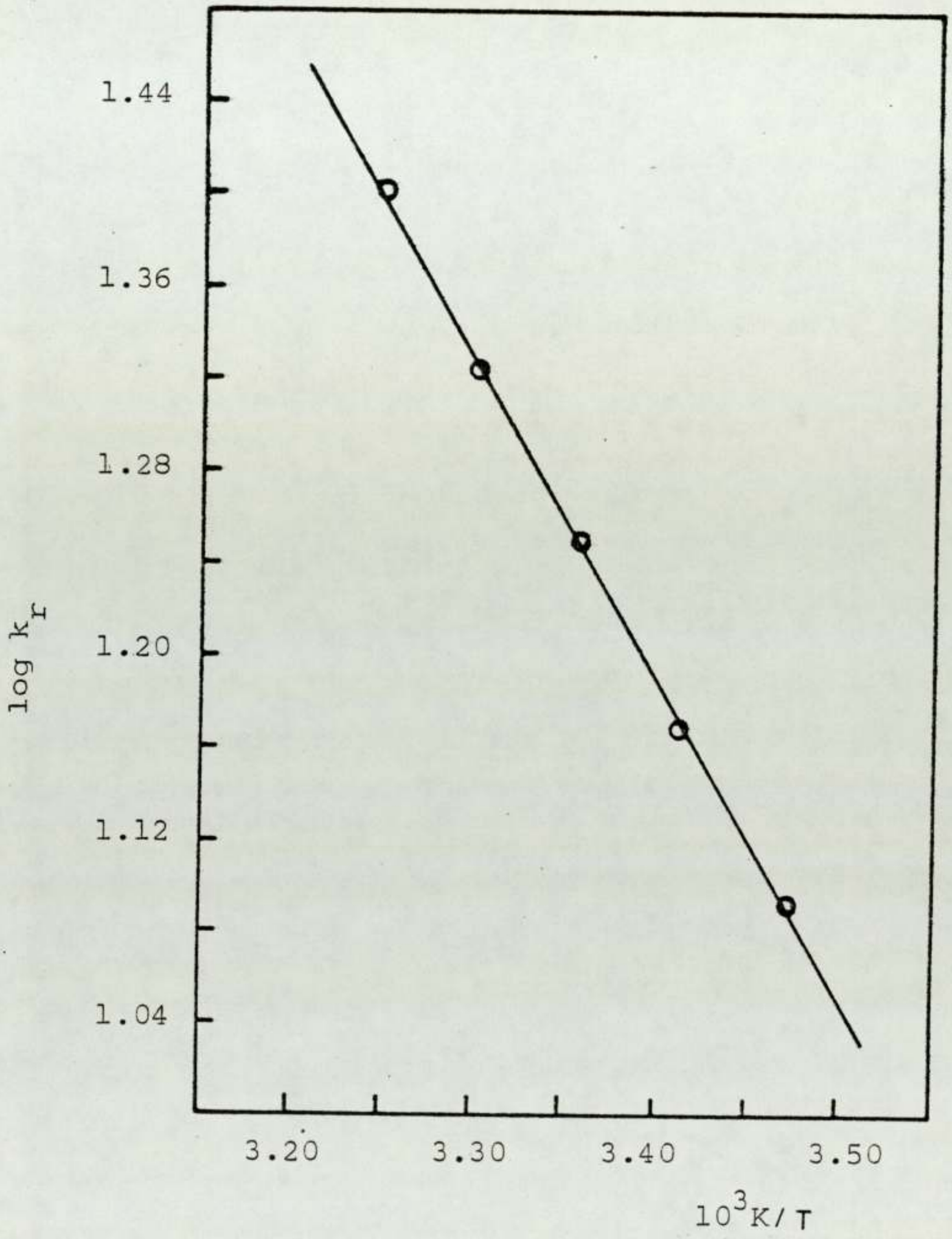


Fig (4:4)Plot of log k_r versus K/T for the reaction of p-EtOPhTeCl_3 with Cr(II) in aqueous 1,4 dioxane.

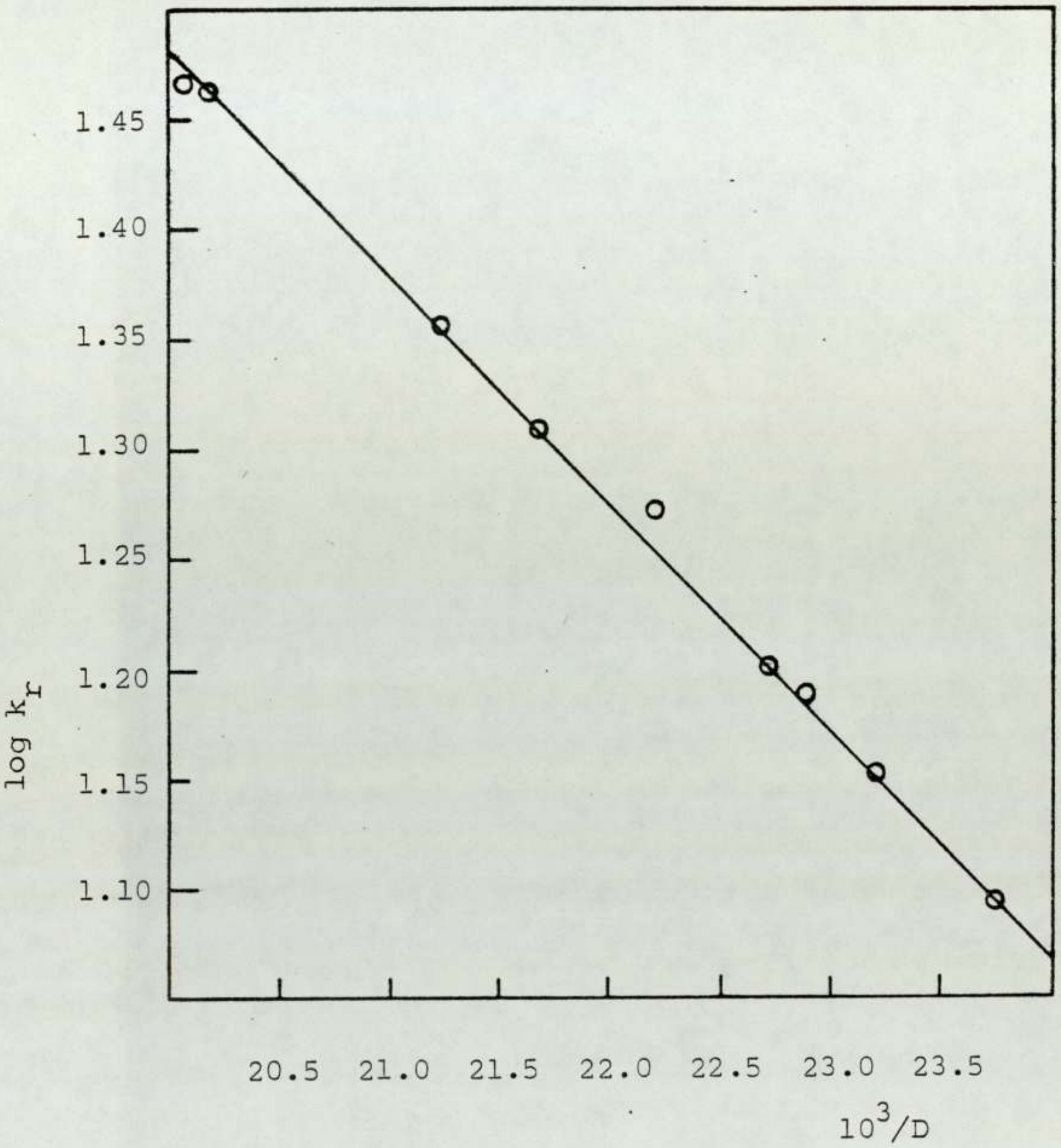
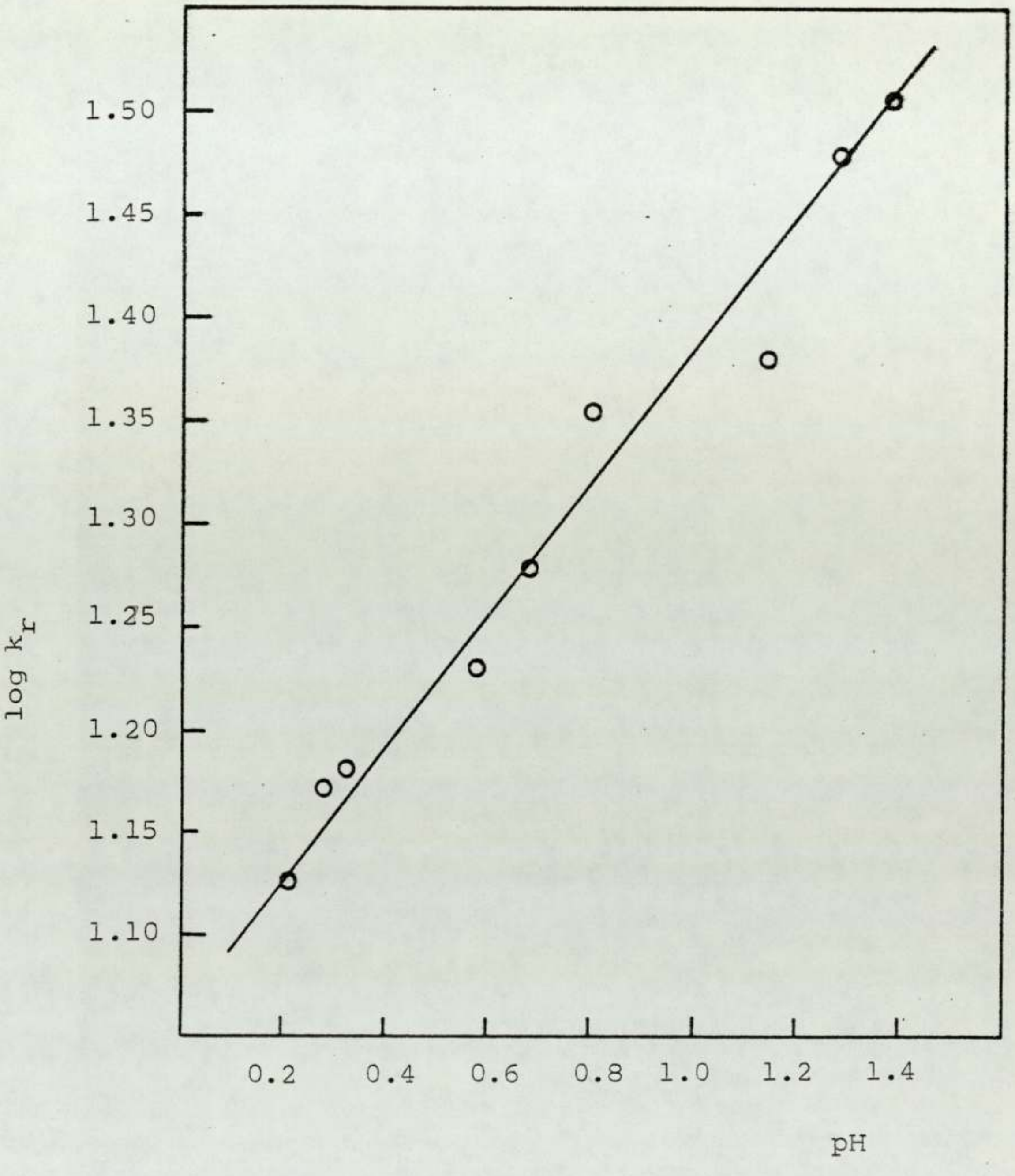
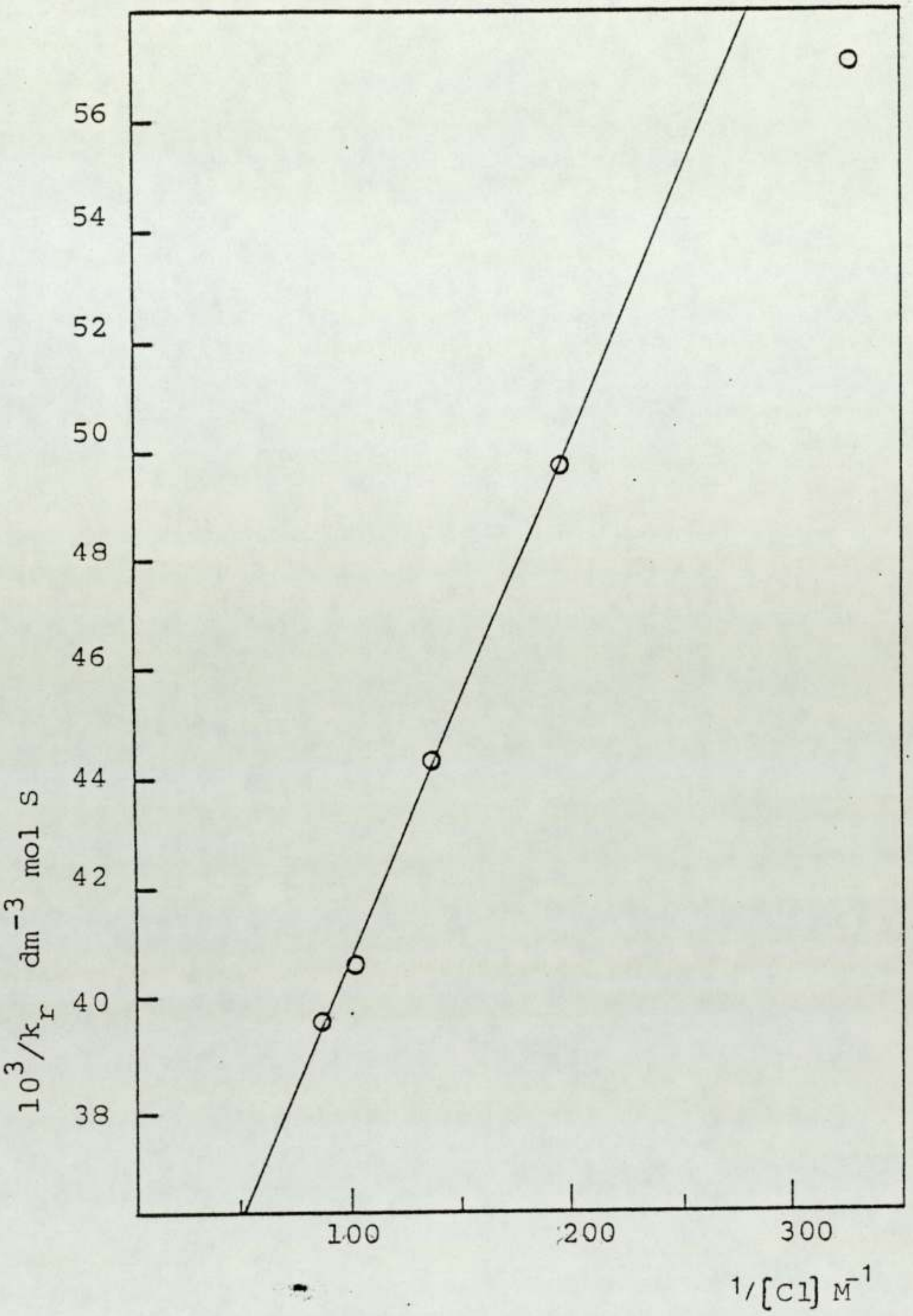


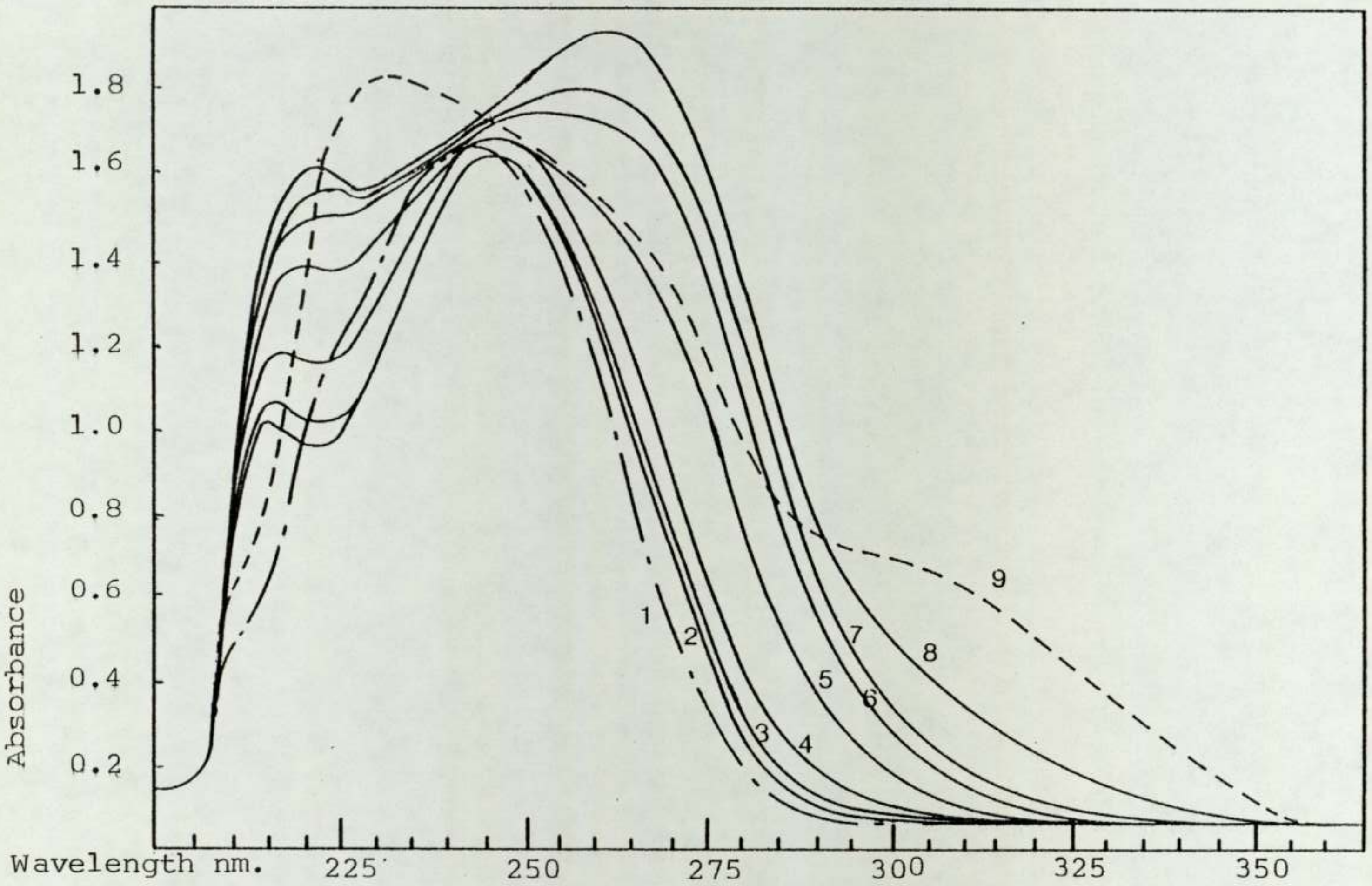
Fig (4:5) Plot of log k_r versus 1/D for the reaction of p-EtOPhTeCl$_3$ with Cr(II) in aqueous 1,4 dioxane.



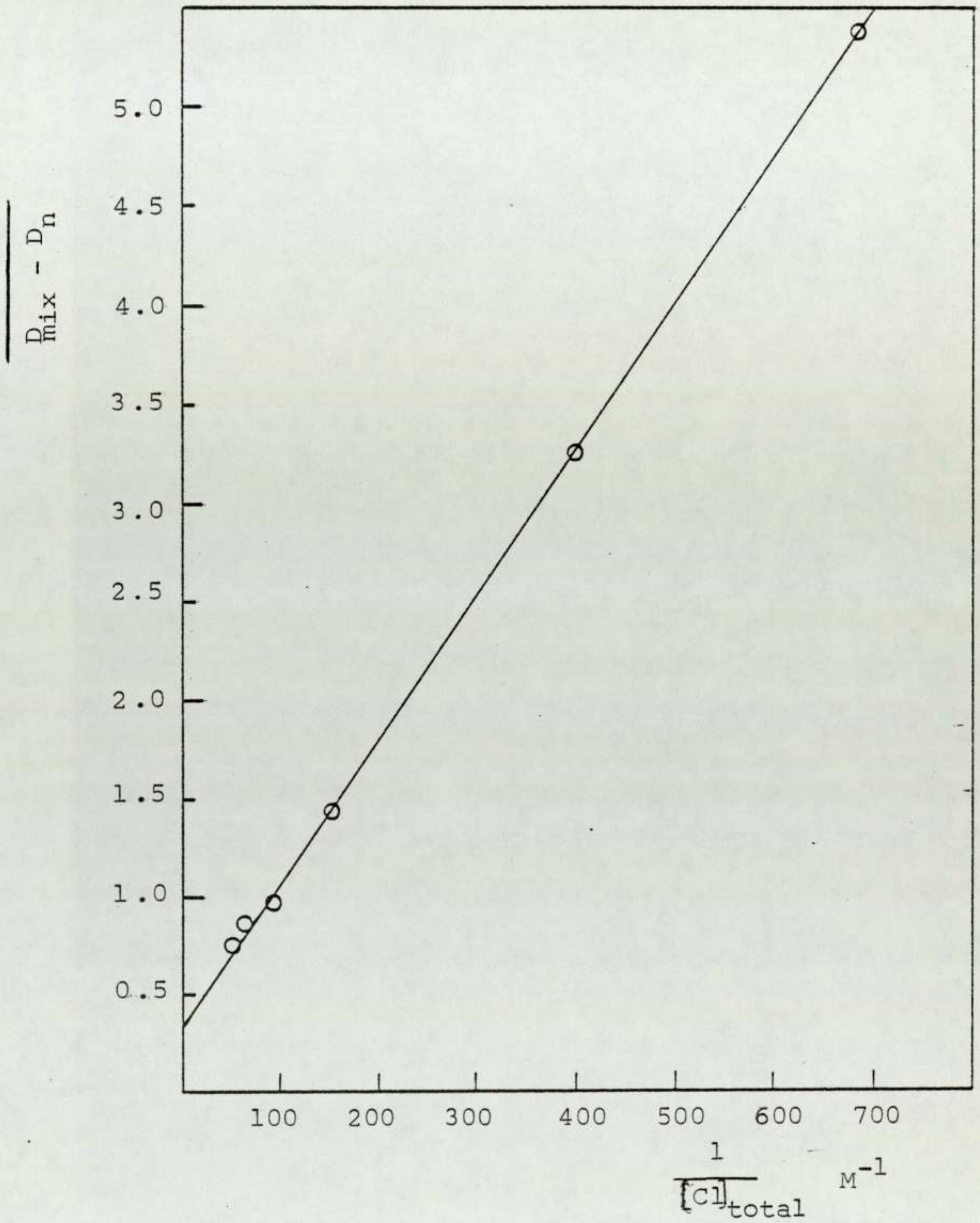
Fig(4:6) Plot of log k_r versus pH for the reaction of p-$EtOPhTeCl_3$ with Cr(II) in aqueous 1,4 dioxane.



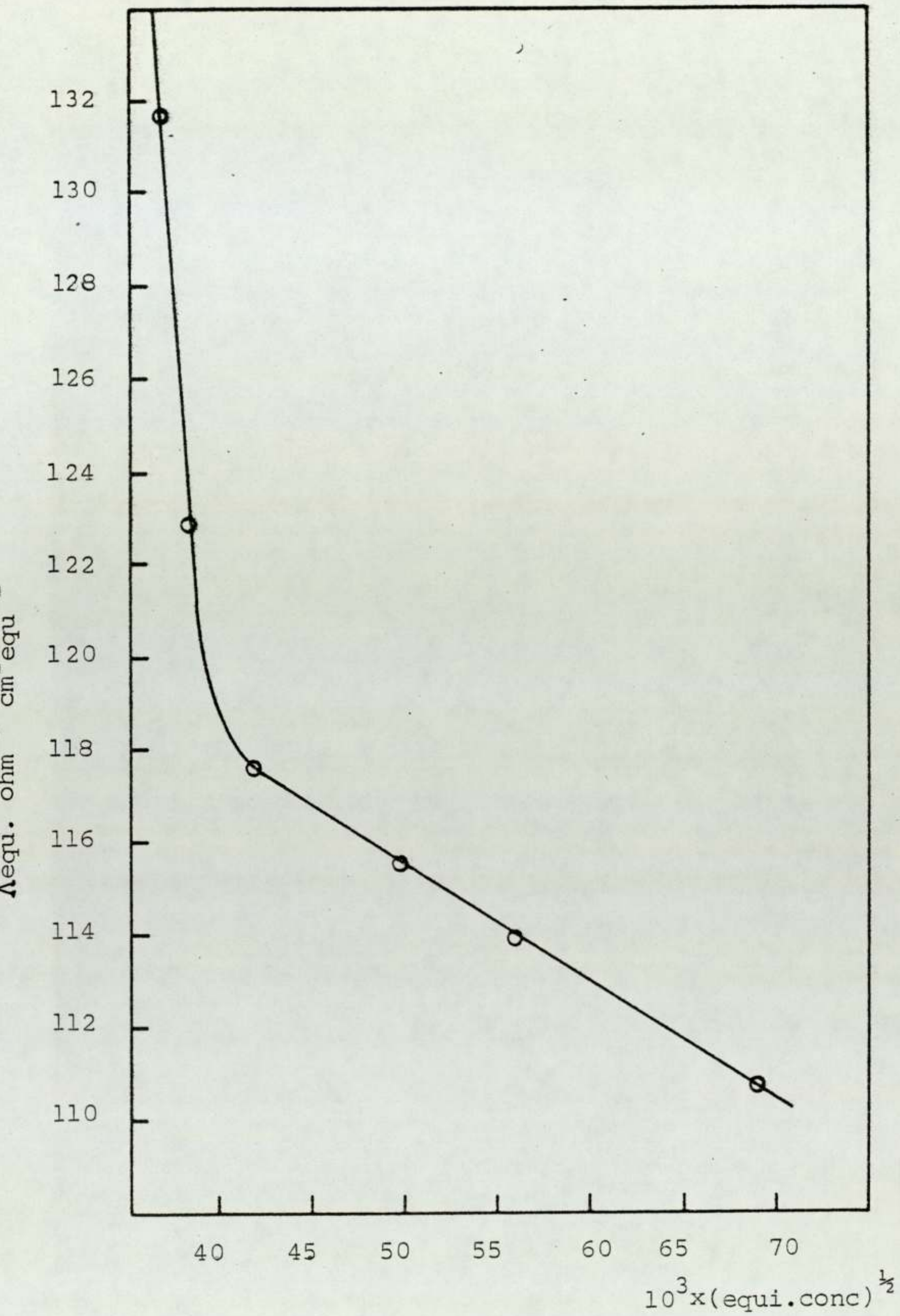
Fig(4:7) Plot of reciprocal rate constant k_r versus the reciprocal of chloride ion concentration for the reaction of p-EtOPhTeCl$_3$ 5×10^{-4}M with Cr (II) 2×10^{-3}M at 25°C in aqueous 1,4 dioxane.



Fig(4:8) U.V. spectra of p-EtOPhTeCl$_3$ 1.5x10^{-4}M in equilibrium with different KCl solution of aqueous 1,4 dioxane.



Fig(4:9) Plot of $1/(D_{mix} - D_n)$ versus the reciprocal of the total chloride ion concentration in aqueous 1,4 dioxane solution.



Fig(4:10) Plot of Λ versus $N^{\frac{1}{2}}$ for Cr(III) complex solution before refluxing in distilled water.

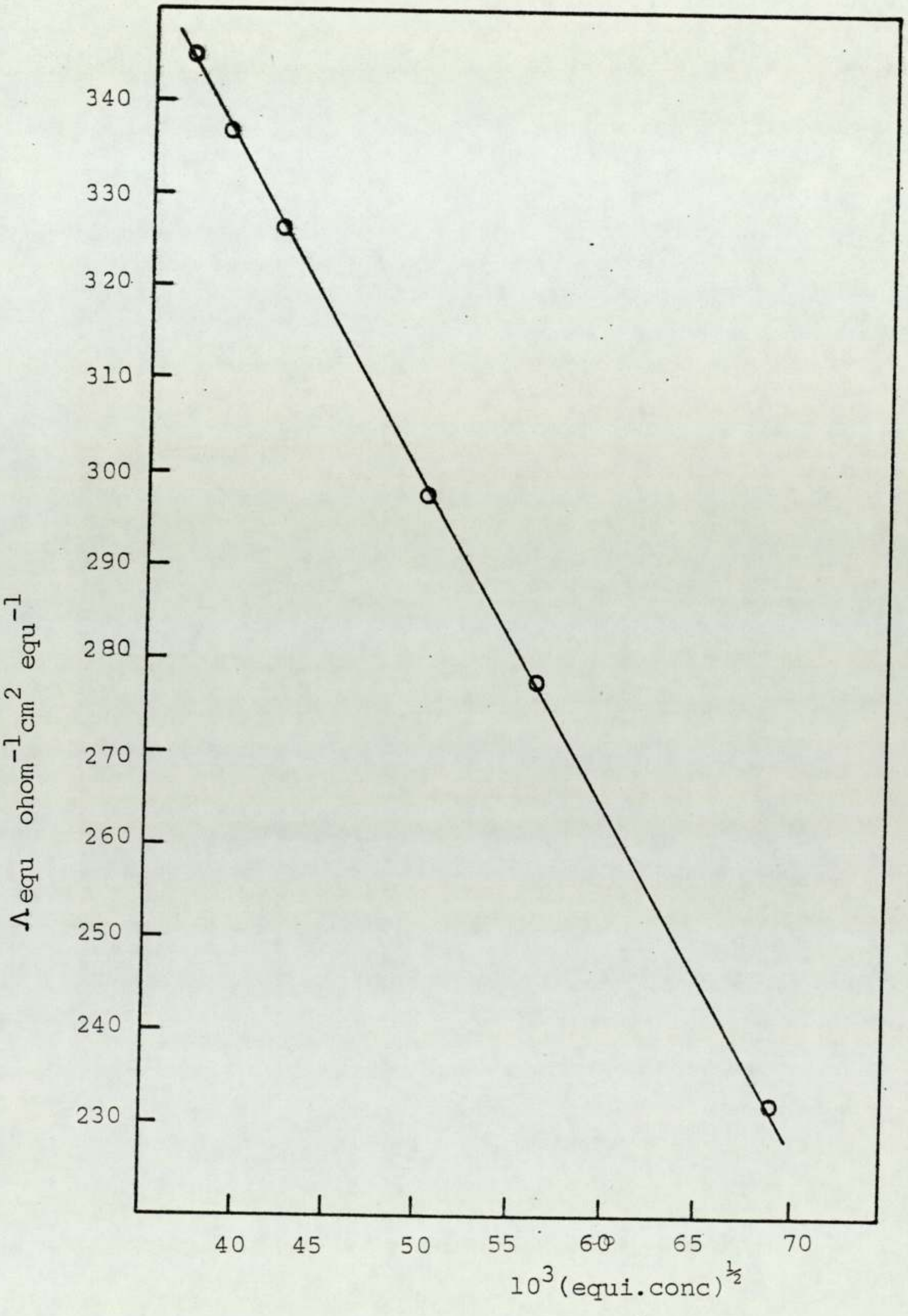


Fig (4:11) Plot of Λ versus $N^{\frac{1}{2}}$ for Cr(III) complex solution after refluxing in distilled water.

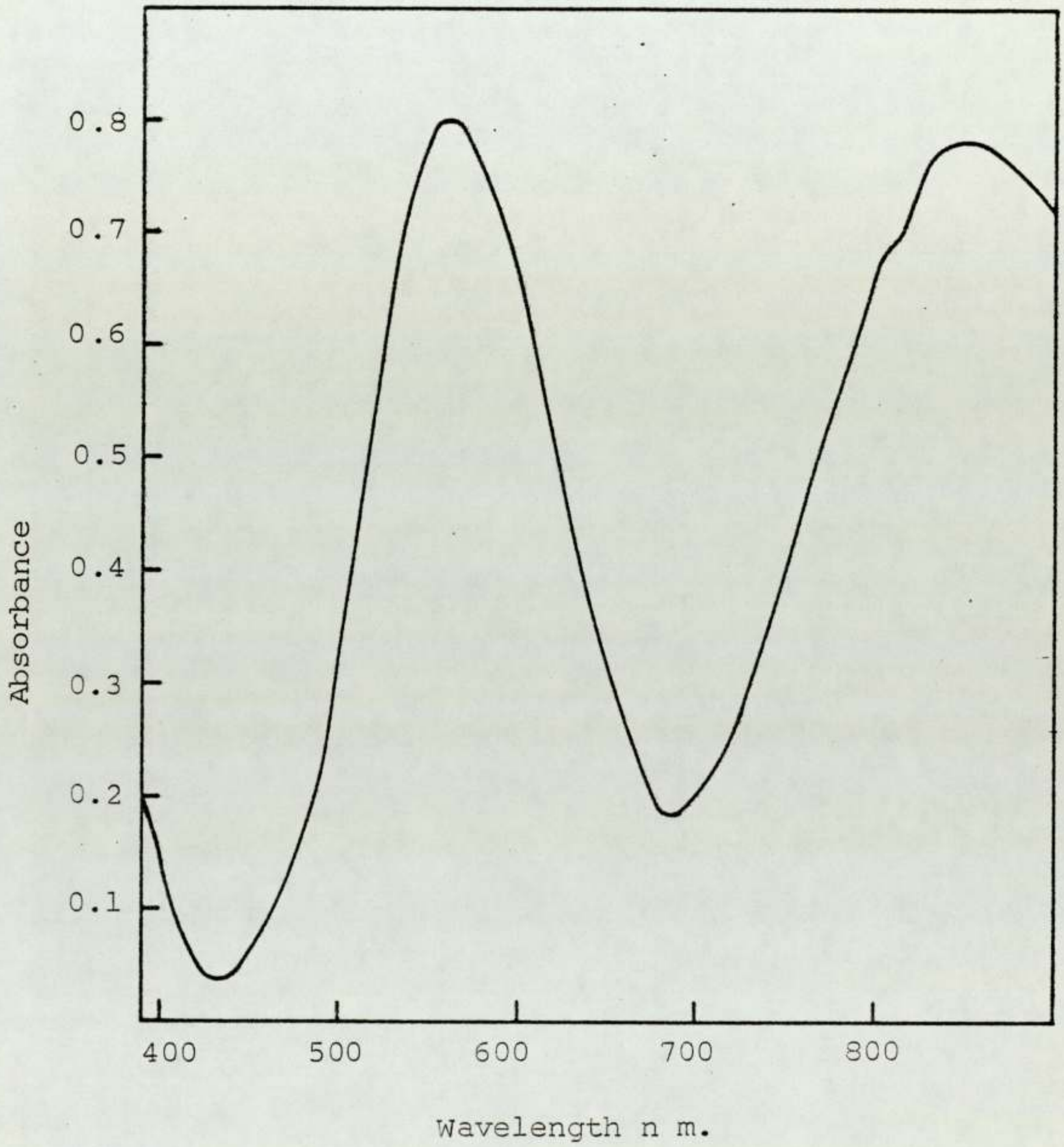


Fig (4:12) Visible spectrumof V(II) solution in aqueous 1,4 dioxane, 1:3 by volume.

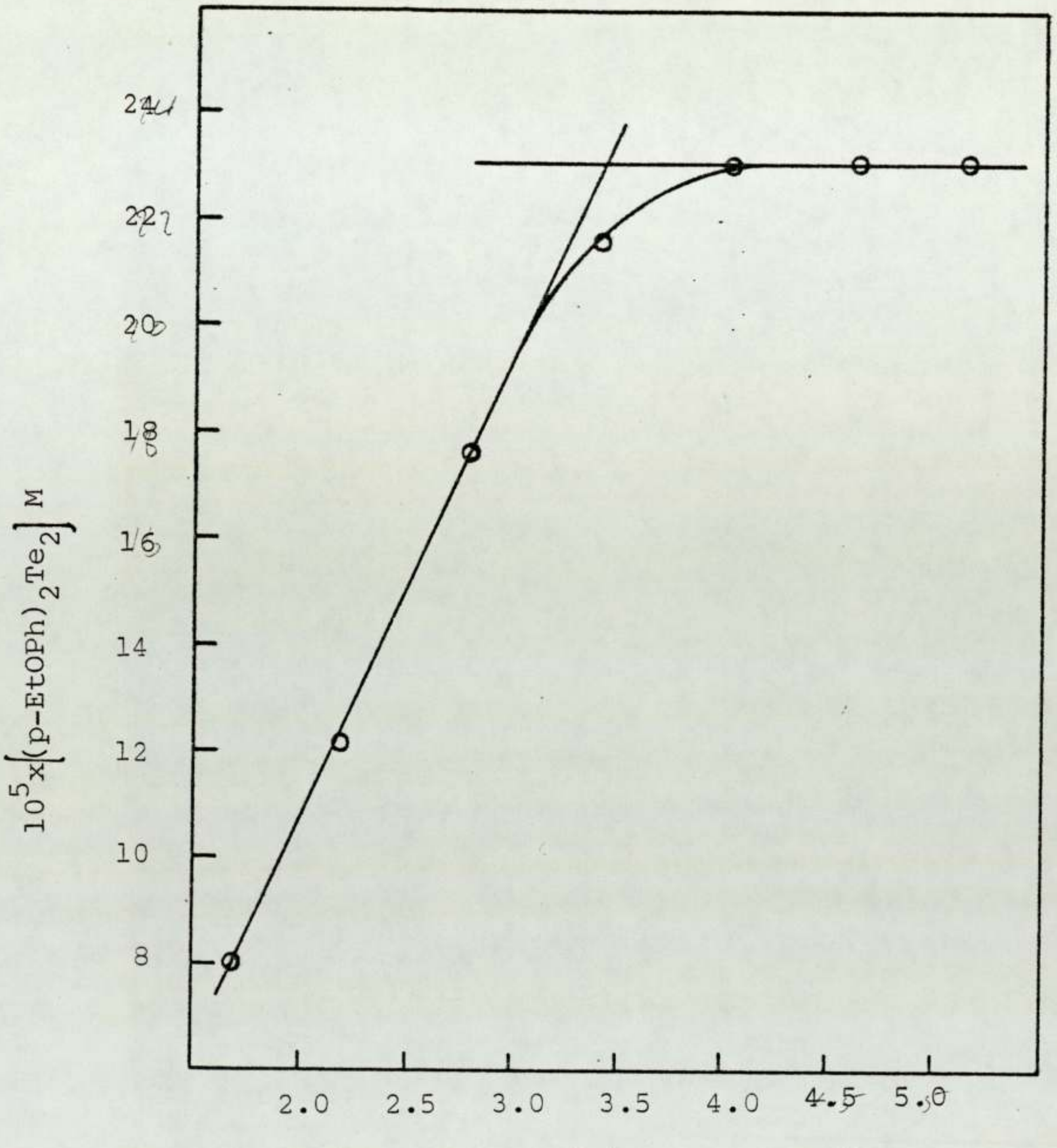


Fig. (4:13) Plot of molar concentration of $(p\text{-EtOPh})_2Te_2$ in aqueous 1,4 dioxane versus the molar ration of $[V(II)]/[p\text{-EtOPhTeCl}_3]$ at 25°C.

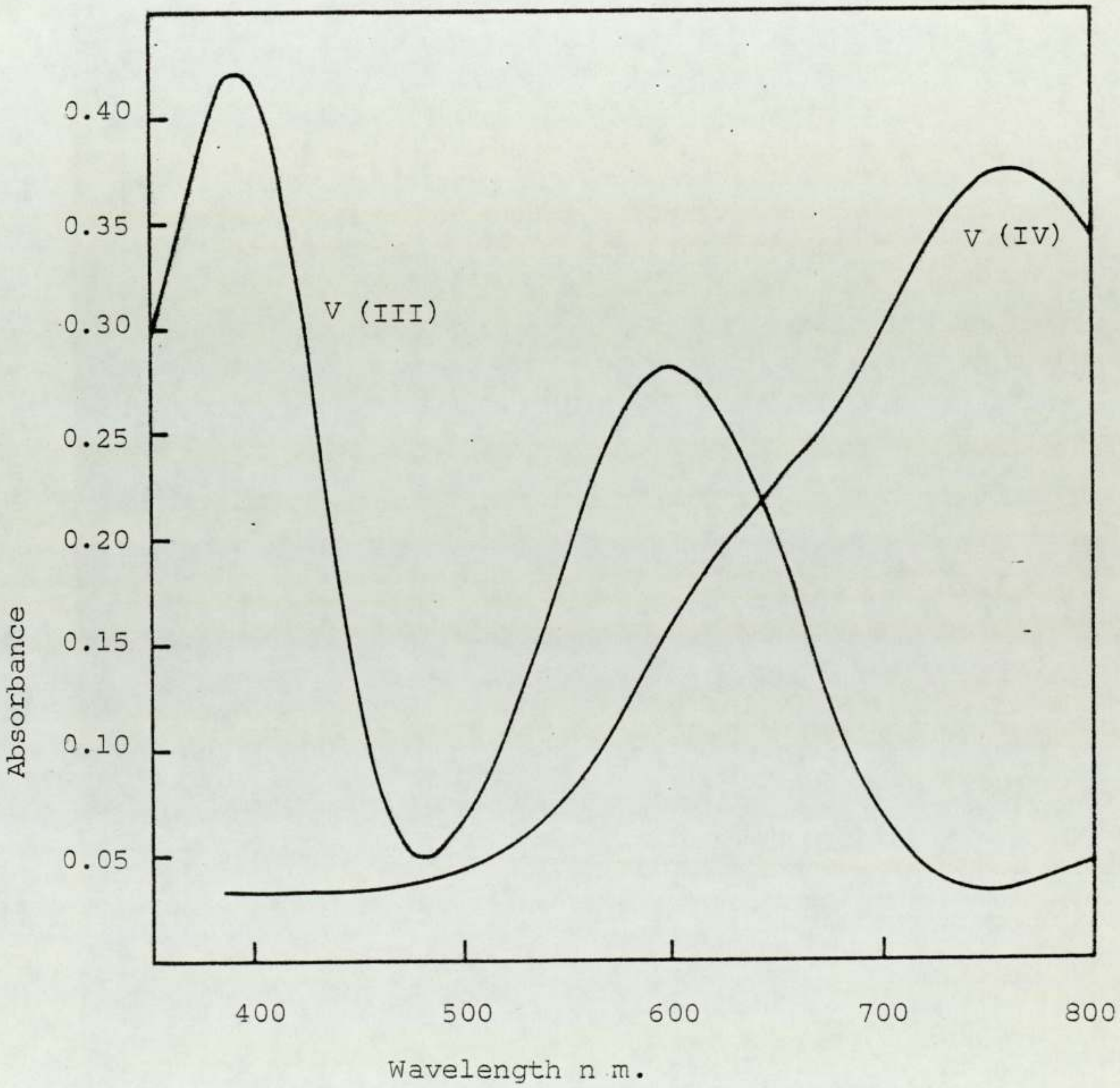


Fig (4:14) Visible spectra of V(III) and V(IV) solutions in aqueous 1,4 dioxane, 1:3 by volume.

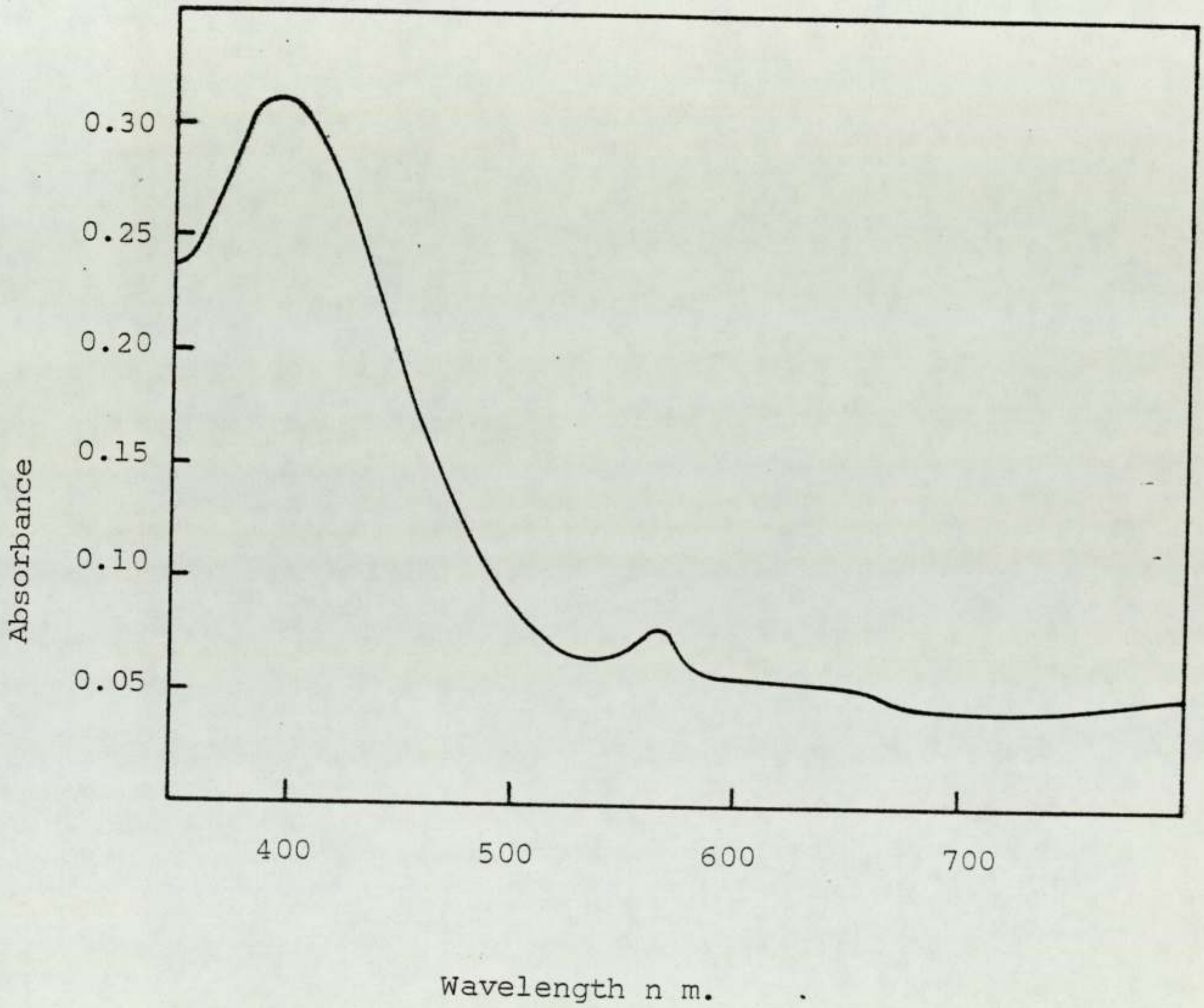


Fig (4:15) Visible spectrumof the products for the reaction of p-EtOPhTeCl_3+V(II), in aqueous 1,4 dioxane.

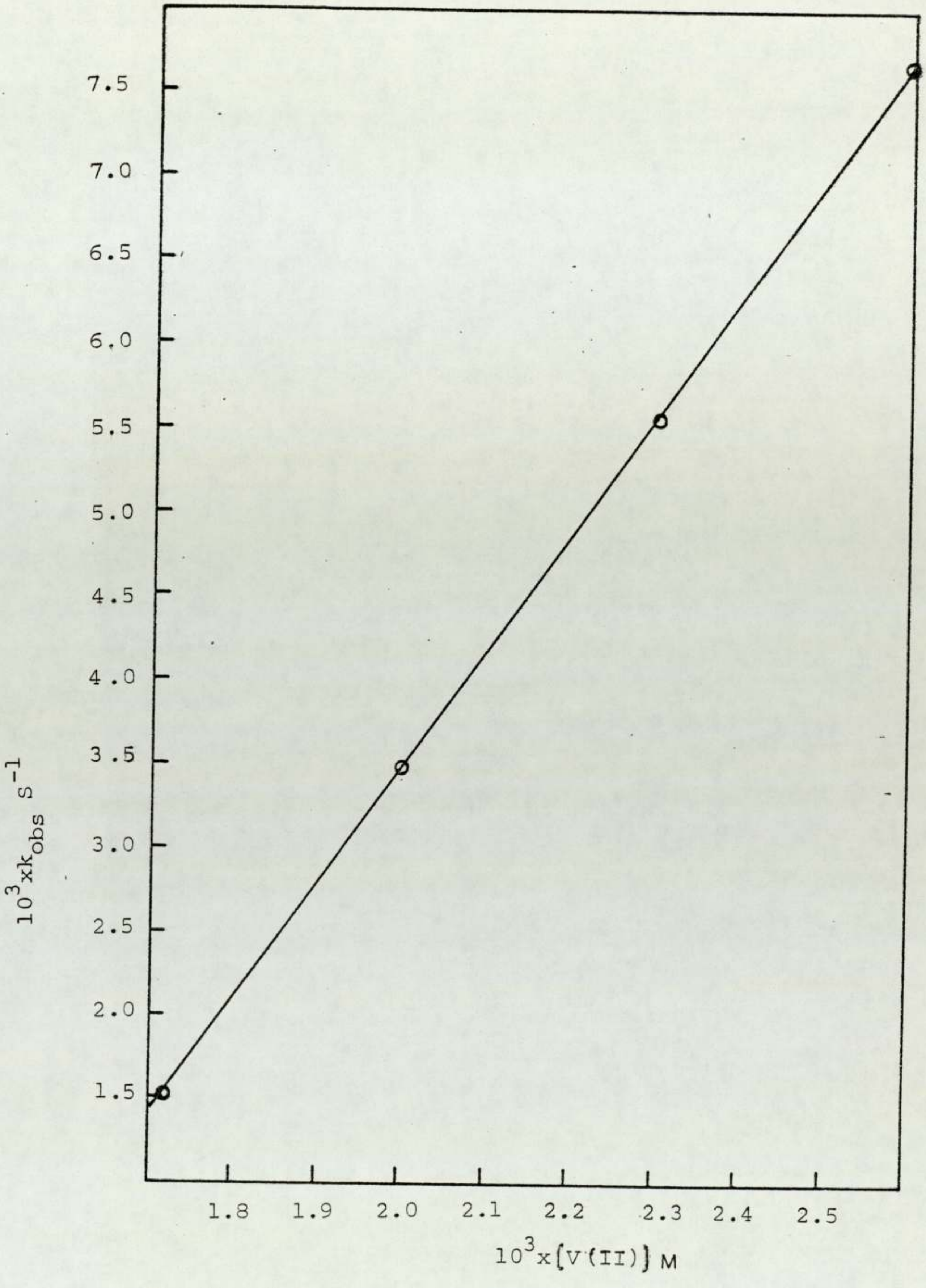
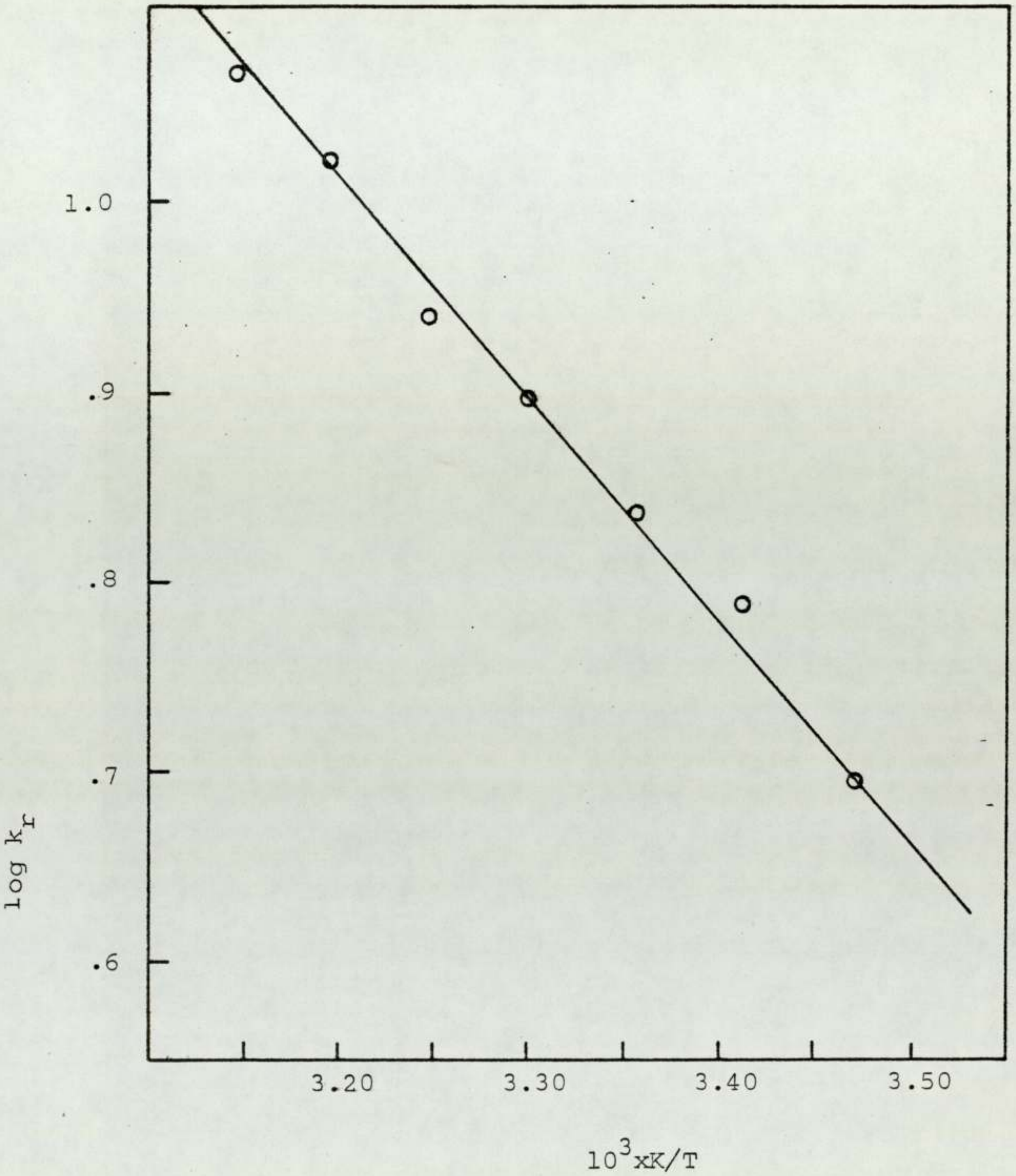


Fig (4:16) Plot of k_{obs} versus [V(II)] for the reaction of p-EtOPhTeCl$_3$ with V(II) in aqueous 1,4 dioxane.



Fig(4:17) Plot of log k_r versus K/T for the reaction of p-EtOPhTeCl$_3$ with V(II) in aqueous 1,4 dioxane.

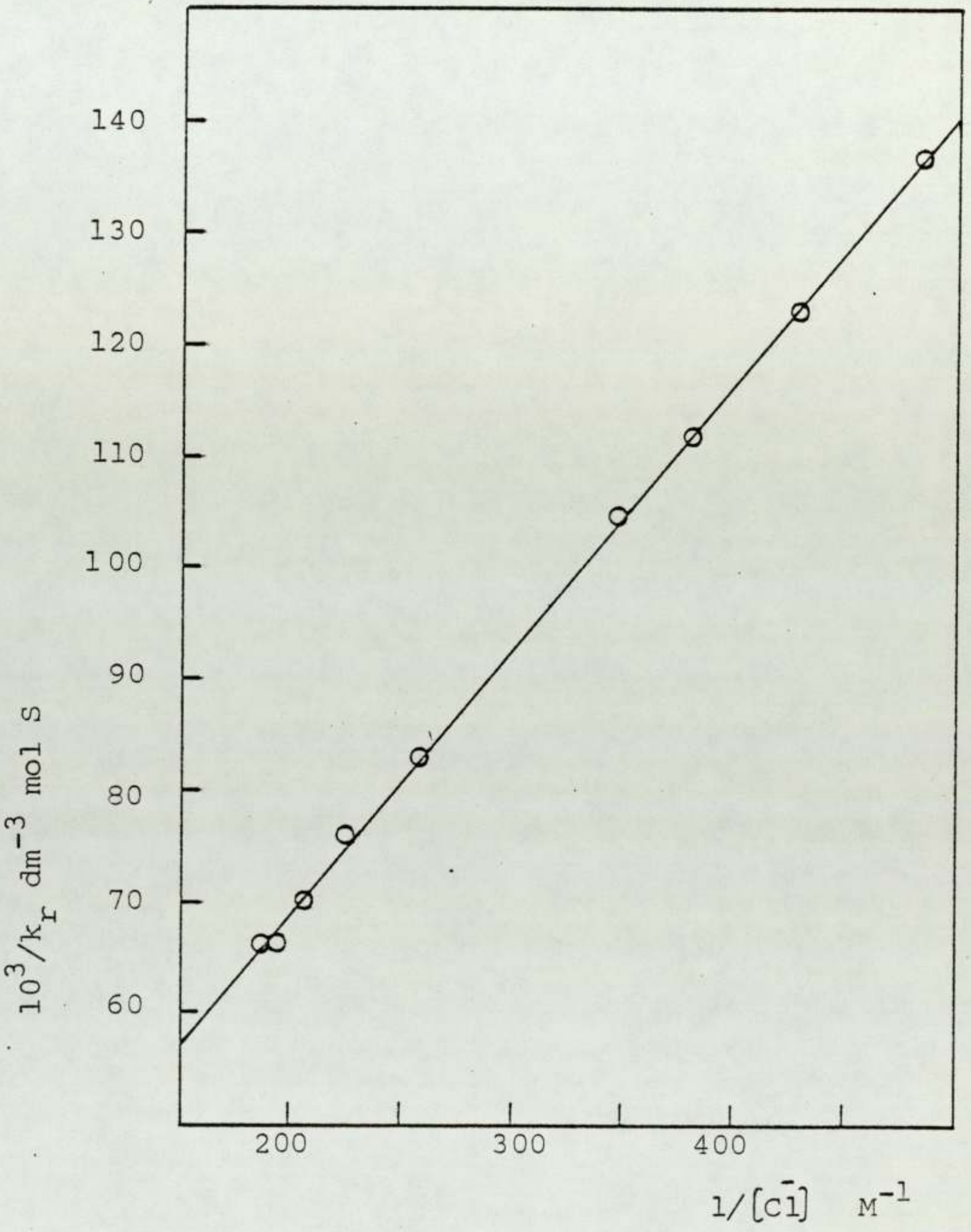
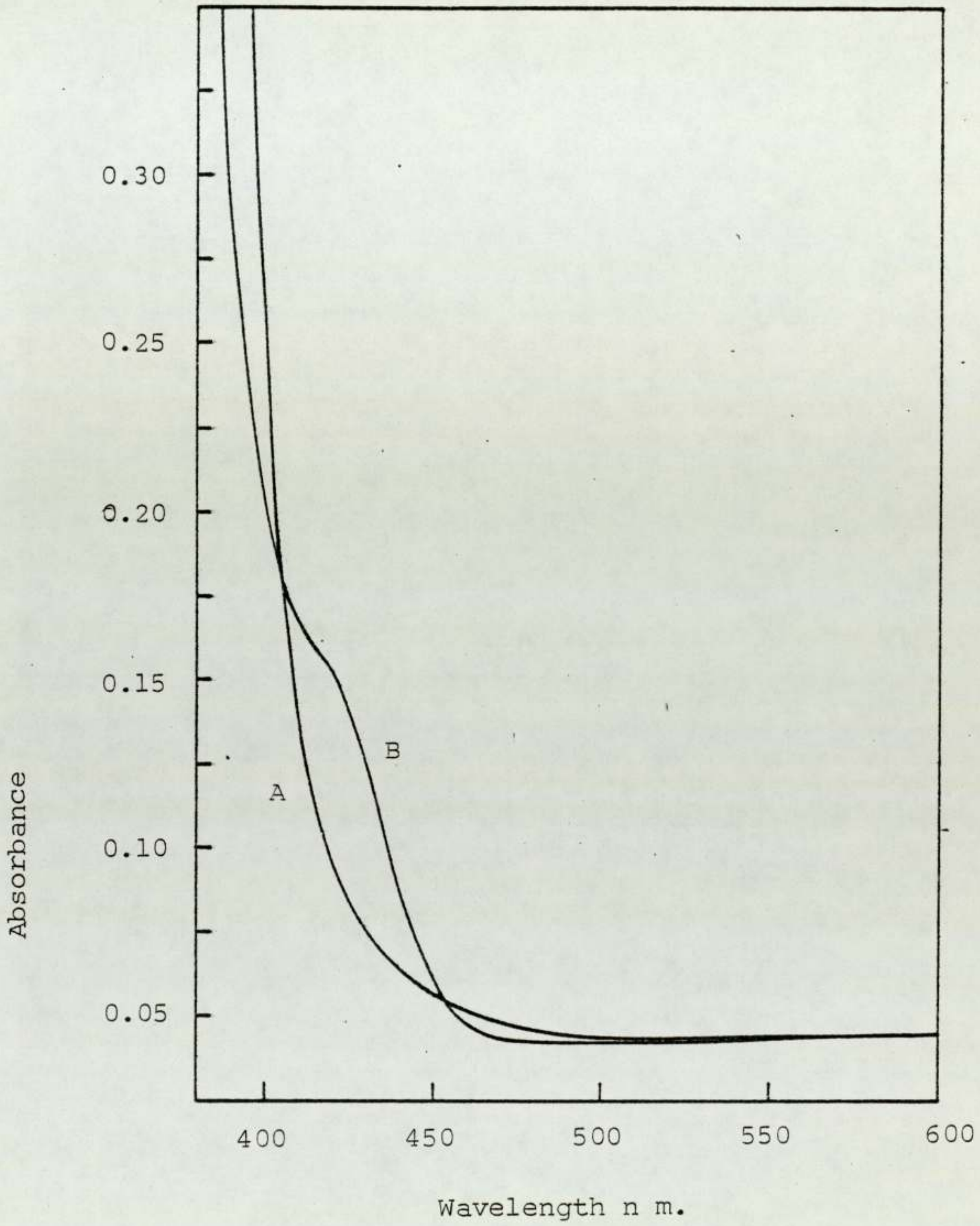


Fig. (4:18) Plot of reciprocal rate constant k_r versus the reciprocal of chloride ion concentration for the reaction of p-EtOPhTeCl$_3$ 5x10^{-4}M with V(II) 2.3x10^{-3}M at 25^{o}C in aqueous 1,4 dioxane.



Fig(4:19) Visible spectra of $K_4Fe(CN)_6$. A new solution, B one week old solution.

4:3 Discussion

The reduction of p-EtOPhTeCl_3 by chromium (II) has been investigated over a range of concentration, temperature, ionic strength, solvent composition, hydrogen ion concentration and chloride ion concentration.

The reduction of p-EtOPhTeCl_3 by V(II) was carried out in several selected kinetic studies to parallel the reduction of p-EtOPhTeCl_3 by Cr(II). The results for V(II) as reducing agents compared with those obtained from Cr(II) might ultimately help to provide a better understanding of the effect of Te(IV) on steering these type of reactions. This is so since V(II) can proceed via inner or outer-sphere mechanisms which are readily distinguishable.

The results obtained by me in this investigation were reproducible. The visible spectra of Cr(II) and V(II) Fig(4:1) and (4:12) show no absorbance in the region of 400 n m. Therefore, the kinetic investigations on the above reactions were carried out by following the increase in absorbance of the reaction mixture at 400 n m., where the product (p-EtOPh)$_2$Te$_2$ shows a maximum absorbance as shown in Fig (3:1)

The stoichiometry of the reaction between p-EtOPhTeCl_3

and Cr(II) was determined potentiometrically. Unfortunately, the potentiometric titration of p-EtOPhTeCl$_3$ with V(II) does not give a precise end point. Therefore, the stoichiometry of that reaction was determined spectrophotometrically. The results obtained in Fig (4:2) shows (3.1) moles of Cr(II) were consumed, while Fig (4:13) shows (3.4) moles of V(II) were consumed. However, the absence of any chromium or vanadium product with an oxidation state other than (III), and also the complete conversion of the tellurium reagent to the ditellurides indicates that three moles of Cr(II) or V(II) are equivalent to one mole of p-EtOPhTeCl$_3$. Hence, the excess consum tion of more than three moles might be due to several reasons. The oxidation of the reducing agent by any residual oxygen dissolved in the reacting solutions, the presence of organic solvent in the potentiometric titration, or due to the effect of light on the product (p-EtOPh)$_2$Te$_2$ during the spectrophotometric determination. This effect is more pronounced in acidic media as shown in Graph (2), Fig (3:8). The stoichiometric measurement indicates that the reaction of Cr(II) or V(II) is in accordance with the electron transfer reaction shown in the equation below:-

$$\text{Te(IV)} + 3\text{M(II)} \longrightarrow \text{Te(I)} + 3\text{M (III)}$$

Where Te(IV) represents p-EtOPhTeCl$_3$ and M represents Cr(II) or V(II).

The reduction of p-EtOPhTeCl$_3$ with Cr(II) or V(II) was carried out in aqueous 1,4 dioxane with a hydrogen ion concentration of 0.469M. It was found that the reduction of p-EtOPhTeCl$_3$ at low hydrogen ion concentration is so fast that the equipment in use is not suitable for following the rate of the reaction. The simple mixing device used here together with the application of a pen-recorder rather than a storage oscilloscope, sets lower limits of several seconds for the half life of any reaction to be studied.

The reduction of p-EtOPhTeCl$_3$ with Cr(II) was carried out at different hydrogen ion concentrations. A plot of log k_r versus pH, Fig (4:6), for the reaction, shows a linear relationship. The rate constant, k_r increases with the pH of the solution. This pronounced effect, combined with the result obtained from the dielectric effect on the rate of the reaction as discussed later on, indicates that the hydrolysis product of p-EtOPhTeCl$_3$ is protonated, e.g. an equation such as:-

$$\text{Ar-TeCl}_3 + 2\text{H}_2\text{O} \rightleftharpoons (\text{ArTeCl(OH)(OH}_2))^+ + \text{H}^+ + 2\text{Cl}^-$$

might represent the phenomenon. The reaction may be completely stopped by adding more concentrated acid to the reacting solutions. The additional proton could be attached either to oxygen, as shown in the equation above, or to the tellurium itself i.e. $(ArTeCl(H)(OH)_2)^+$. It is reasonable to suggest that the hydrogen ion as an electrophilic reagent may bond to the spare electron pair of the tellurium in aryltellurium (IV) species. The effect of the protonation on the rate of the reaction may be related to the electrostatic force which exists between approaching similarly charged ions. In general the rates of the reduction of aqua complexes decrease with increasing acidity. This decrease is ascribed to the displacement of the hydrolysis equilibrium.

The kinetic studies which involved varying the initial concentration of the reducing agents established that the reaction is first order in both reagent. Over the 80-85% of the reactions studied, it was found that the absorbance-time curve that the above reaction follows, has the same differential rate equation as the reaction of p-EtOPhTeCl_3 with SO_3^{2-} (Section 3:2), i.e.

$$\text{rate} = k\left[\text{Oxid}\right]\left[\text{Red}\right]$$

Suitable concentrations of p-EtOPhTeCl_3, Cr(II) and V(II) of ($5\text{x}10^{-4}$M), ($2\text{x}10^{-3}$M) and ($2.3\text{x}10^{-3}$M) respectively, were used under the different conditions of the reactions.

The variation in the rate of the reaction caused by varying the temperatures is in agreement with the Arrhenius equation. This enabled us to determine the activation parameters of the reaction which were found to be almost the same for both the reducing agents Cr(II) and V(II).

The reaction with Cr(II) was investigated at a constant temperature over a range of different solvent compositions. It was found that the rate of the reaction decreases as the dielectric constant of the mixed solvent decreases. This is shown in the plot of log k_r versus 1/D, Fig (4:5) which is a straight line with a negative slope. The sign of the slope indicates that the reaction proceeds between charged species of similar sign.(93) This supports the suggestion that the addition of $[H^+]$ causes protonation of the hydrolysis product of p-EtOPhTeCl$_3$. No deviation of the plot from linearity was observed in the region of lower dielectric constant as seen in the previous experiments (Chapter 3). The linearity of the plot could be due to the fact that the hydrolysed tellurium species becomes more soluble at lower pH media. This leads to the conclusion that in acidic media the attachment of water to the reacting ions become more favourable. Hence, the increase in dioxane percentage in the composition of the mixed solvent of low pH has no significant effect on the rate of the reaction as it has with the solution of higher pH.

The investigation of the salt effect shows the addition of sodium sulphate has no effect on the rate of the reaction of para-ethoxyphenyltellurium trichloride with chromous ions. Since the reaction involves a high hydrogen ion concentration, this may affect the activity of the reactants more than does the added salt. Therefore, any salt effect on the rate of the reaction might be hidden by the pH effect. On the other hand, if the salt effect arises from ion pairing, then the cation Na^+ added to the reaction is unable to lower the electrostatic repulsion force which exists between the positively charged ions in this reaction, as predicted from dielectric effect measurements.

The identification of the initial chromium product, which is obtained from the oxidation of Cr(II) by $p\text{-EtOPhTeCl}_3$ is important in determining the mechanism of the reaction. Then the first step towards elucidation of the structure of the chromium product was to determine whether it is a single compound or a mixture of several species. The results obtained from T.L.C. measurements for the chromium product obtained indicate that the complex is a single species.

The formula of the aqueous species of the chromium(III) product was first indicated by an ion exchange method, where the equilibrium between Cr(III) aqueous species and H^+ on the resin was established.

This showed the total charge per species of Cr(III) to be (2+). The only single charged ion present in the solution of the reaction is Cl^-, therefore, it was concluded that the 2+ species is probably a Cr(III) chloride complex of $[CrCl(OH_2)_5]^{2+}$.

It has also been found that the effective magnetic moment of the product is in agreement with the expected value for Cr(III) with the appropriate molecular weight. Chromium in oxidation state (III), has three 3d electrons all unpaired leading to an expected "spin-only" magnetic moment value of 3.87 B.M..

Elemental analysis for Cr, Cl, H, and S in the Cr(III) complex product were carried out. The results obtained were identical with those expected for $[CrCl(OH_2)_5]SO_4$. The literature method of Shirai(38) for the spectrophotometric determination of Cr(III) in Cr(III) complexes was attempted unsuccessfully. I found that the absorbance at room temperature of the product obtained from the reaction of Cr(III) complex with $K_4Fe(CN)_6$ increased continuously over a whole week. This may be due to the slow change in $K_4Fe(CN)_6$ composition which is present in excess in the solution as shown in Fig (4:19)

Conductivity measurements were carried out as an aid for the detrmination of the structure of the Cr(III) product. A plot of the equivalent conductivity (Λ_e) of the complex versus the square root of the concentration gives a non-linear graph as shown in Fig (4:10).

After refluxing the above solution for one hour, a similar plot gave a straight line, Fig (4:11). The results obtained from conductivity measurements before and after refluxing indicate that water molecules replace the anion in the co-ordination sphere of the Cr(III) complex on refluxing. Assuming the formula $\left[CrCl(OH_2)_5\right] SO_4$ inferred from other data (i.e. elemental analysis, magnetic measurements) for the Cr(III) co-ordinated complex, gives an equivalent conductance which is in the range expected for such an electrolyte (118-131) ohm^{-1}, cm^2. $equi.^{-1}$ This result substantiates our postulate of the formula of $\left[CrCl(OH_2)_5\right] SO_4$ for the Cr(III) co-ordinated complex.

The addition of potassium chloride has a considerable effect on the rates of the reaction of p-EtOPhTeCl_3 with Cr(II) and V(II). This effect is presumably due to the chloride ion. Either it is effective by lowering the repulsion force between ions of positive charges, or it takes the bridging position in an inner-sphere activated complex.

It is difficult to distinguish between these two alternative explanations, I have no evidence that the effect of the chloride ion on these reactions is merely electrostatic. The presence of chloride on the chromium (III) product may supply evidence about the nature of the activated complex. The substitution reactions on Cr(III) are sufficiently slow that the entry of any group after completion of the oxidation can be ruled out. Thus, any group found in the co-ordination sphere of Cr(III) which has been formed from Cr(II) will very likely have been present in the activated complex. Hence a transition state:-

$$\left[\mathrm{ArTe{-}Cl{-}Cr(OH_2)_5}\right]^{*}$$

may be suggested with chloride acting as a bridge during electron transition. The addition of chloride ions may drive the reaction in one of two alternative pathways:-

$$\mathrm{A + xCl^- \underset{}{\overset{K_R}{\rightleftharpoons}} ACl_x} \qquad (4:6)$$

$$\mathrm{A + B \xrightarrow{k_2} AB \longrightarrow products} \qquad (4:7)$$

$$\mathrm{ACl_x + B \xrightarrow{k_3} A{-}Cl{-}B + (x-1)Cl^- \longrightarrow products} \qquad (4:8)$$

where A and B represent the reductant and the oxidant or vice versa. Assuming the reaction proceeds via a chlorine atom bridge as shown in equation (4:8), the contribution of k_2 in equation (4:7) to the overall reaction will be negligible, Hence:-

$$k_r = \frac{K_R k_3 \left[Cl^-\right]^x}{1+K_R\left[Cl^-\right]^x}$$

The similarity of the corresponding values of K_R for the reduction of para-ethoxyphenyltellurium trichloride by both chromous and vanadous (320 and 480 dm^3mol^{-1} for Cr(II) and V(II) respectively) ions suggest that this equilibrium constant refers to a tellurium-chloro species. To check that possibility, a series of solutions were produced by mixing together solutions of p-EtOPhTeCl_3 in pure dioxane with aqueous solutions of KCl in sulphuric acid. These reproduce the conditions of the kinetic experiments, except for the absence of any reducing agent. Spectra of these solutions were measured in the ultra-violet range. The results obtained can most reasonably be ascribed to the equilibrium

$$ArTe(OH)_3 + Cl^- + 2H^+ \overset{K_o}{\rightleftharpoons} \left[ArTeCl(OH)(OH_2)\right]^+ + H_2O$$

This addition of Cl^- to tellurium will be favoured in acidic media by the removal of (OH^-) as H_2O. The tendency towards the co-ordination of Te-Cl is also favoured by the higher chloride ion concentration present in the solution. The values of K_o (range between 32 to 46 dm^3mol^{-1})

determined from these equilibrium studies is significantly smaller than the equilibrium constant K_R (range 320 to 480 dm^3mol^{-1} for Cr(II) and V(II) respectively) determined from the kinetic measurement. Therefore, the two constants must describe different equilibria. Since the kinetically determined constant must precede the slow step in the overall reaction, it follows that the slow step is described by the steps,

$$Te^N + Cl^- \overset{K_R}{\rightleftharpoons} Te^N\text{-}Cl$$

$$Te^N\text{-}Cl + M^{II} \xrightarrow[\text{slow}]{k_r} Te^{N-1} + M^{II}\text{-}Cl$$

Where the oxidation state of tellurium N= III or II. Since there is more evidence for the existance of Te(II) compounds than Te (III), a reasonable overall mechanism would be:-

$$ArTeCl_3 + 3H_2O \xrightarrow{\text{Fast}} ArTe(OH)_3 + 3H^+ + 3Cl^- \qquad (4{:}9)$$

$$ArTe(OH)_3 + Cl^- + 2H^+ \overset{K_o}{\rightleftharpoons} [ArTeCl(OH)(OH_2)]^+ + H_2O \qquad (4.10)$$

$$[ArTeCl(OH)(OH_2)]^+ + M \xrightarrow{\text{Fast}} [ArTe(OH)(OH_2)]^+ + MCl \qquad (4{:}11)$$

$$[ArTe(OH)(OH_2)]^+ + Cl^- + H^+ \overset{K_1}{\rightleftharpoons} [ArTeCl(OH_2)]^+ + H_2O \qquad (4{:}12)$$

$$[ArTeCl(OH_2)]^+ + M \xrightarrow{\text{Fast}} [ArTe(OH_2)]^+ + MCl \qquad (4{:}13)$$

$$[\mathrm{ArTe(OH_2)}]^+ + \mathrm{Cl}^- + \mathrm{H}^+ \overset{K_R}{\rightleftharpoons} [\mathrm{ArTeCl(H)}]^+ + \mathrm{H_2O} \qquad (4:14)$$

$$[\mathrm{ArTeCl(H)}]^+ + \mathrm{M} \xrightarrow[\text{slow}]{k_r} [\mathrm{ArTe(H)}]^+ + \mathrm{MCl} \qquad (4:15)$$

$$2[\mathrm{ArTe(H)}]^+ \xrightarrow{\text{Fast}} \mathrm{Ar_2Te_2} + 2\mathrm{H}^+ \qquad (4:16)$$

Where M= Cr(II) or V(II)

The incorporation of an acid dependent equilibrium, equation (4:14) in the mechanism above requires that the presence of more acid will increase the rate of the reaction until a limiting condition is reached. This is certainly true for the rapid early stages of the overall reaction, which are acid catalysed. Such an increase in the rate of the reaction with an increase of hydrogen ion concentration is observed in the reduction of p-EtOPhTeCl$_3$ by $S_2O_5^{2-}$, when the reaction is performed in nearly neat dioxane (93% by volume, see Chapter 3) There the initial catalytic effect of hydrogen ion concentration has only a limited effect on the rate of the reaction.

When the limit of initial effect of hydrogen ion is reached, other parameters such as rapid protonation and deprotonation equilibrium involving the hydrolysis product, or the repulsion between positively charged ions, may exhibit a greater influence on the overall reaction.

Whatever effect acid has on the reductions by Cr (II) and V(II) must relate to the processes of equation (4:14) to (4:16). Equation (4:14) is written in such a way as to involve H^+, this is to take account of the variation of the overall rate constant with the dielectric constant of the medium. At first sight that contradicts the qualitative observation that the overall reaction was much faster in more dilute acidic conditions. Perhaps a different reaction pathway becomes possible at lower acidities. The alternative explanation, which I have considered , but rejected, is that the variation with the dielectric constant does not prove that the tellurium reagent in equation (4:14) carries a positive charge. If that were really the case, equation (4:14) to (4:16) would need to be re-written with ArTeCl and ArTe taking the place of $(ArTeClH)^+$ and $(ArTeH)^+$ respectively.

The conclusion from the results obtained in this investigation of the reduction by metal ions is that the reaction is first order in each reactant and overall second order. The reacting tellurium species are partially hydrolysed derivatives of the aryltellurium trihalides rather than the trihalides themselves. The reaction of p-EtOPhTeCl_3 with Cr(II) and V(II) proceeds via inner-sphere processes with chloride ions provided by the tellurium atom acting as a bridging group. These results combined with those in Chapter 3, indicate that Te(IV) in these sorts of reactions normally react via an inner-sphere mechanism rather than by outer-sphere. Hence, it exerts a steering influence on the pathway of the reaction.

CHAPTER FIVE

SOLVOLYSIS OF p-ETHOXYPHENYLTELLURIUM TRICHLORIDE

5:1 INTRODUCTION

Several investigations have been made of the hydrolysis of aryltellurium trihalides in moist air, neutral, acidic or basic aqueous media.(6,20,132) No work has been reported concerning the mechanism of the solvolysis of aryltellurium trihalides in non-aqueous or mixed aqueous media. In this study, the solvolysis of p-EtOPhTeX_3 (X=Cl, Br, I) has been investigated in mixed aqueous and mixed non-aqueous solvents, under different conditions of solvent composition and temperature.

I have used methanol as the active, solvolytic component in binary solvent mixtures. The choice of methanol was made because its miscibility properties are more suitable than those of water, while it retains some close structural and chemical similarities to water. Two other features helped to make methanol an appropriate choice. The rate of methanolysis in non-aqueous media is slower than that of hydrolysis in aqueous media, while both p-EtOPhTeCl_3 and its solvolysis product are more soluble in non-aqueous media than in aqueous media.

A mechanism of the hydrolysis of aryltellurium trihalides with water under different conditions has been suggested.(23) The argument is based solely upon the structure of the isolated product of the hydrolysis process, and is, therefore, not very reliable.

The hydrolysis product from an aryltellurium trihalide depends upon the pH of the medium. It has been found that hydrolysis in an acidic medium yields ArTe(O)X, whereas in a basic medium the hydrolysis product is mainly ArTe(O)OH or $(ArTeO)_2O$.(23) In this study a possible scheme for the solvolysis reaction of p-$EtOPhTeCl_3$ has been suggested.

The behaviour of $ArTeCl_3$ in an acidic medium differs from that in a basic medium. This difference may be attributed to its donor and acceptor properties.(133) In the solid state, $ArTeX_3$ molecules are known to have one Te-X bond longer than the other two Te-X bonds.(31) The presence of a Lewis acid in the medium might 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 and probably 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 its vacant 4f orbitals(134) and, therefore, behave as a Lewis acid. So the hydrolysis of aryltellurium trihalides may be ascribed to the increase in the polarity of Te-X bond in the presence of a Lewis acid and the ability of the tellurium atom to accept a pair of oxygen electrons in the vacant 4f orbital. Thus there are easy hydrolysis routes under both sets of conditions, although they may be routes with very different mechanisms.

Petragnani(35) has related, with no evidence, the easy hydrolysis of $ArTeCl_3$, as compared with that of the corresponding tribromides and triiodides, to a decrease in the electrophilic character of the positive fragment $ArTeX_2^+$ on passing from X=Cl to Br and I. However, it has been pointed out that $ArTeCl_3$ is present in a molecular form in organic solutions.(32)

Since the pathway of the reduction of aryltellurium trihalides to diaryl ditelluride starts with the hydrolysis of trihalides, the aim of this chapter's investigation is to gain a better understanding of that early stage of the reduction mechanism of trihalides.

5:2 RESULTS

The effect of the temperature on the solvolysis of p-EtOPhTeX_3(X=Cl, Br, I) in a mixed benzene-methanol solvent was investigated. Whereas the solvent composition's effect on the solvolysis of p-EtOPhTeCl_3 in mixed benzene-methanol, dioxane-methanol and dioxane-water were investigated. It was established that all results obtained in this investigation are reproducible.

The kinetic runs used to study the solvolysis reaction were followed by making pH measurements on the solution. The decrease of the pH is due to the production of HX and typically continues for an overall reaction time of up to ten minutes.

The values of the observed rate of solvolysis, k_{obs}, were obtained from the graphs of pH versus time, by fitting the experimental data to the integrated equation appropriate to the following scheme:-

$$ArTeX_3 + H^+ \xrightleftharpoons{K_N} Int \qquad (5:1)$$

$$ArTeX_3 \xrightarrow{k_4} Prod. + n\ H^+ \qquad (5:2)$$

$$Int \xrightarrow{k_5} Prod. + (n+1)\ H^+ \qquad (5:3)$$

Where Ar=p-EtOPh, Int represents an intermediate and (Prod.) is the final hydrolysis product. According to equations (5:2) and (5:3) the increase in hydrogen ion concentration can be expressed as:-

$$\frac{d[H^+]}{dt} = n(k_4[\text{ArTeX}_3] + k_5[\text{Int}]) \quad (5:4)$$

and $[\text{Int}] = K_N[\text{ArTeX}_3][H^+]$

If $[\text{Int}]$ is small compared to $[\text{ArTeX}_3]$ then the integration of equation (5:4) leads to the final form of:-

$$k_4(1+[H^+]_\infty X)t = \ln\left\{\frac{(1/X+[H^+]_t)([H^+]_\infty - [H^+]_0)}{(1/X+[H^+]_0)([H^+]_\infty - [H^+]_t)}\right\} \quad (5:5)$$

Where $[H^+]_0$, $[H^+]_t$ and $[H^+]_\infty$ are respectively the hydrogen ion concentrations at time = 0, t and infinity, and

$$1/X = \frac{k_4}{K_N\ k_5}$$

The values of the constant 1/X which give the best least squares fit for the plot of

$$\ln\left\{\frac{(1/X + [H^+]_t)([H^+]_\infty - [H^+]_0)}{(1/X + [H^+]_0)([H^+]_\infty - [H^+]_t)}\right\} \text{ versus (t) were}$$

determined by employing BASIC computer program reproduced in appendix VIII. It should be noted that the sum of squared differences between observed and calculated pH readings was minimised and not the equivalent function for $[H^+]$. That was due to two reasons. Firstly, the experimentally determined parameters was pH and not $[H^+]$.

Secondly, a change of (say) 3 units in pH corresponds to a change of 1000 in $[H^+]$. Thus minimising for $[H^+]$ would ignore all but the higher acid concentration, the final points in an experiment.

The program was written to chose upper and lower values of 1/X which gives the best fit for the above plot. It was found that the values of the constant 1/X range between 10^{-8} to 10^{-6} gave the best fit. This indicates that the value of k_4 is relatively very small and, therefore, its contribution to the overall reaction in the above scheme is negligible. Thus the scheme can be simplified, leading to an overall rate equation of:-

$$k_{obs}\, t = \ln\left\{\frac{[H^+]_t\ ([H^+]_\infty - [H^+]_o\ )}{[H^+]_o\ ([H^+]_\infty - [H^+]_t\ )}\right\} \qquad (5:6)$$

where $$k_{obs} = K_N\, k_5\, [H^+]_\infty \qquad (5:7)$$

For further details see (appendix IX). Plots of pH against time for 70% to 80% completion can be fitted to equation (5:6) which used in a BASIC computer program (appendix X) to determine the values of k_{obs} under different solvolysis conditions. The best fit was obtained using a least squares method applied to the difference between observed and calculated pH.

The observed rate of the solvolysis (k_{obs}) of p-EtOPhTeCl$_3$

in a mixed solvent of benzene-methanol in a solvent composition range between 8.3 to 83.3% by volume of methanol at 25°C was studied. The results are shown in Table (5:1). The plot of k_{obs} versus the percentage of methanol (by volume) is shown in Fig (5:1). A plot of k_{obs} versus the molar ratio of benzene/methanol is shown in Fig (5:2) and the data are listed in Table (5:2). A plot of final pH- meter readings versus molar concentration of methanol component is shown in Fig (5:3).

The same experiments were repeated for the solvolysis of p-EtOPhTeX_3 at a constant solvent composition of 2:1 benzene-methanol by volume over a temperature range from 5 to 30°C with runs being carried out at 5°C intervals. The results are listed in Table (5:3). Arrhenius equation (3:7) was used to determine the observed energy of activation, $\Delta E^{\#}$, of the solvolysis reaction, whereas equations (3:8) and (3:9) were used to determine the observed enthalpy ($\Delta H^{\#}$) and the entropy ($\Delta S^{\#}$) of activation. The values of the observed parameters are listed in Table (5:4). In passing, it can be noted that these experiments also show that the values of k_{obs} for the solvolysis of p-EtOPhTeCl_3 in benzene-methanol mixed solvent at different temperatures are less than those for the tribromide, which in turn are less than for the triiodide, as shown in Table (5:4).

Runs to investigate the solvolysis of p-EtOPhTeCl_3 in mixed dioxane-methanol were carried out at 25°C, with different solvent ratios. The data are listed in Table (5:5). A plot of k_{obs} versus the percentage of methanol (by volume) is shown in Fig (5:4). A plot of k_{obs} versus the molar ratio of dioxane/ methanol is shown in Fig (5:5). The data are listed in Table (5:6). A plot of the final pH-meter readings versus molar concentration of methanol is shown in Fig (5:6). Plot of the densities of mixed dioxane-methanol and benzene-methanol versus the mole percent of methanol is shown in Fig (5:7).

The above experiment was repeated in a mixed dioxane-water solvent in different composition at 25°C. The data are listed in Table (5:7).

The identification of the products of a chemical reaction may help to provide an understanding of the reaction mechanism that governs the reaction. Therefore, an attempt was made to isolate the products of the solvolysis of p-EtOPhTeCl_3 with methanol in the hope that they would provide an insight into the mechanism of the solvolysis reaction. A solution of p-EtOPhTeCl_3 in pure methanol was evaporated under vacuum. The vapours, on passing through $AgNO_3$ solution gave a white precipitate of AgCl. Despite several attempts under different conditions, I was unable to find conditions which gave a reproducible value for the weight of the chloride precipitate. Under apparently identical conditions, values ranging between

2 and 10% of the total chloride in the p-EtOPhTeCl$_3$ used in the experiments were obtained.

The solution gains a yellow colour during the course of the evaporation and eventually gives a yellow solid product. The elemental analysis for this solid product is different from that of the reagent p-EtOPhTeCl$_3$ as listed below:-

	%C	%H	%Cl
Found before experiment	27.0	2.8	30.1
Found after experiment	28.4	2.9	25.0
p-EtOPhTeCl$_3$ requires	27.0	2.5	30·0

The addition of pure methanol decolourizes the yellow solution of aryltellurium tribromide dissolved in benzene solution. It was found that a higher concentration of methanol is needed to decolourize a solution of tribromide that is required by the same concentration and volume of trichloride. The yellow colour returns after the evaporation of the solvents. The elemental analysis gave identical results for both the tribromide and the product obtained after evaporation of the mixed solvent of benzene-methanol. There is only a slight visible change on the addition of methanol to a triiodide solution in benzene.

The effect of methanol on p-EtOPhTeX$_3$ in benzene solution is illustrated in the U.V spectra Figs(5:8),(5:9),(5:10).

No precipitate was obtained when the gaseous materials above the solutions of the tribromide or triiodide were passed through solutions of $AgNO_3$.

The reaction between p-$EtOPhTeCl_3$ and $NaOCH_3$ in pure methanol affords a white product. The product was recrystallized from glacial acetic acid. The solution of this product in methanol gives a white precipitate when mixed with water. It shows a colourless solution in acetone changing to yellow in almost five hours at room temperature. The recrystallized product is insoluble in common organic solvents such as benzene, dioxane and nitrobenzene. No melting point can be determined but it decomposes at 185°C to a brown product.

The elemental analysis of the product yielded the following values for carbon, hydrogen and chlorine respectively:- 32.3%, 4.2% and 10.4%. The I.R spectra for the isolated product and p-$EtOPhTeCl_3$ is shown in Figs (5:11) and (5:12).

MeOH Vol%	k_{obs}/s^{-1}	Final pH-meter readings	[MeOH] $Mol.dm^{-3}$
8.3	0.109	0.60	2.0
16.7	0.111	1.00	4.2
25.0	0.110	1.28	6.2
33.3	0.107	1.80	7.5
41.7	0.110	1.80	10.3
50.0	0.103	1.90	12.3
58.3	0.096	1.94	14.5
66.7	0.077	2.40	16.5
75.0	0.068	2.70	18.7
83.3	0.060	3.98	20.7

Fig (5:1) Values of the observed rate constant of the solvolysis of $p\text{-}EtOPhTeCl_3$ 8.3×10^{-5} M in mixed solevnt of benzene-methanol with different solvent composition.

k_{obs} S^{-1}	Molar ratio benzene/methanol
0.109	5.15
0.111	2.21
0.110	1.37
0.107	1.00
0.110	0.63
0.103	0.46
0.096	0.32
0.077	0.22
0.068	0.15
0.060	0.09

Table (5:2) The variation of observed rate constant with the molar ratio of mixed solvent of benzene/methanol for the solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5}M

T/C^o	$10^3 xK/T$	$k_{obs}\ S^{-1}$		
		X=Cl	X=Br	X=I
5	3.597	0.183	0.158	0.120
10	3.534	0.195	0.199	0.128
15	3.472	0.210	0.205	0.141
20	3.413	0.220	0.210	0.151
25	3.356	0.230	0.217	0.169
30	3.300	0.240	0.225	0.171

Table (5:3) Observed rate constant of solvolysis of p-EtOPhTeCl$_3$ 1.7x10^{-4}M in mixed solvent of benzene/methanol 2:1 by volume at different temperatures.

p-EtOPhTeX$_3$	$\Delta E^{\#}$ kJmol^{-1}	$\Delta H^{\#}$ kJmol^{-1}	$\Delta S^{\#}$ J.K.$^{-1}$mol^{-1}
X = Cl	7.6∓0.4	5.1∓ .4	-216.6∓2.3
X = Br	8.3∓2.2	5.8∓2.2	-212.8∓18
X = I	10.7∓0.8	8.2∓0.8	-194.3∓2.7

Table (5:4) Observed activation parameters for the solvolysis of p-EtOPhTeX$_3$ (X=Cl, Br, I) 1.7x10^{-4}M in mixed solvents of benzene-methanol 2:1 by volume at 25°C.

MeOH Vol%	k_{obs}/S^{-1}	Final pH-meter reading	[MeOH] $mol.dm^{-3}$
16.7	0.115	1.98	4.2
25.0	0.108	2.24	6.2
33.3	0.110	2.38	7.5
41.7	0.125	2.65	10.3
50.0	0.169	2.87	12.3
58.3	0.284	3.08	14.5
66.7	0.310	3.19	16.5
75.0	0.393	3.30	18.7
83.3	0.507	3.45	20.7

Table (5:5) The observed rate constant of the solvolysis of p-$EtOPhTeCl_3$ (8.3×10^{-5}M) in mixed dioxane-methanol with different solvent composition.

k_{obs}/s^{-1}	Molar ratio dioxane/methanol
0.115	2.33
0.108	1.42
0.110	1.04
0.125	0.66
0.169	0.47
0.284	0.33
0.310	0.24
0.393	0.16
0.507	0.10

Table (5:6) The variation of observed rate constant with the molar ratio of mixed solvent of dioxane/methanol for the solvolysis reaction of p-EtOPhTeCl$_3$ (8.3x10^{-5}M).

H_2O/Vol %	k_{obs}/s^{-1}
8	0.10
12	0.13
16	0.15

Table (5:7) The observed rate of solvolysis of p-EtOPhTeCl$_3$ 1x10^{-4}M in mixed dioxane-water with different solvent composition.

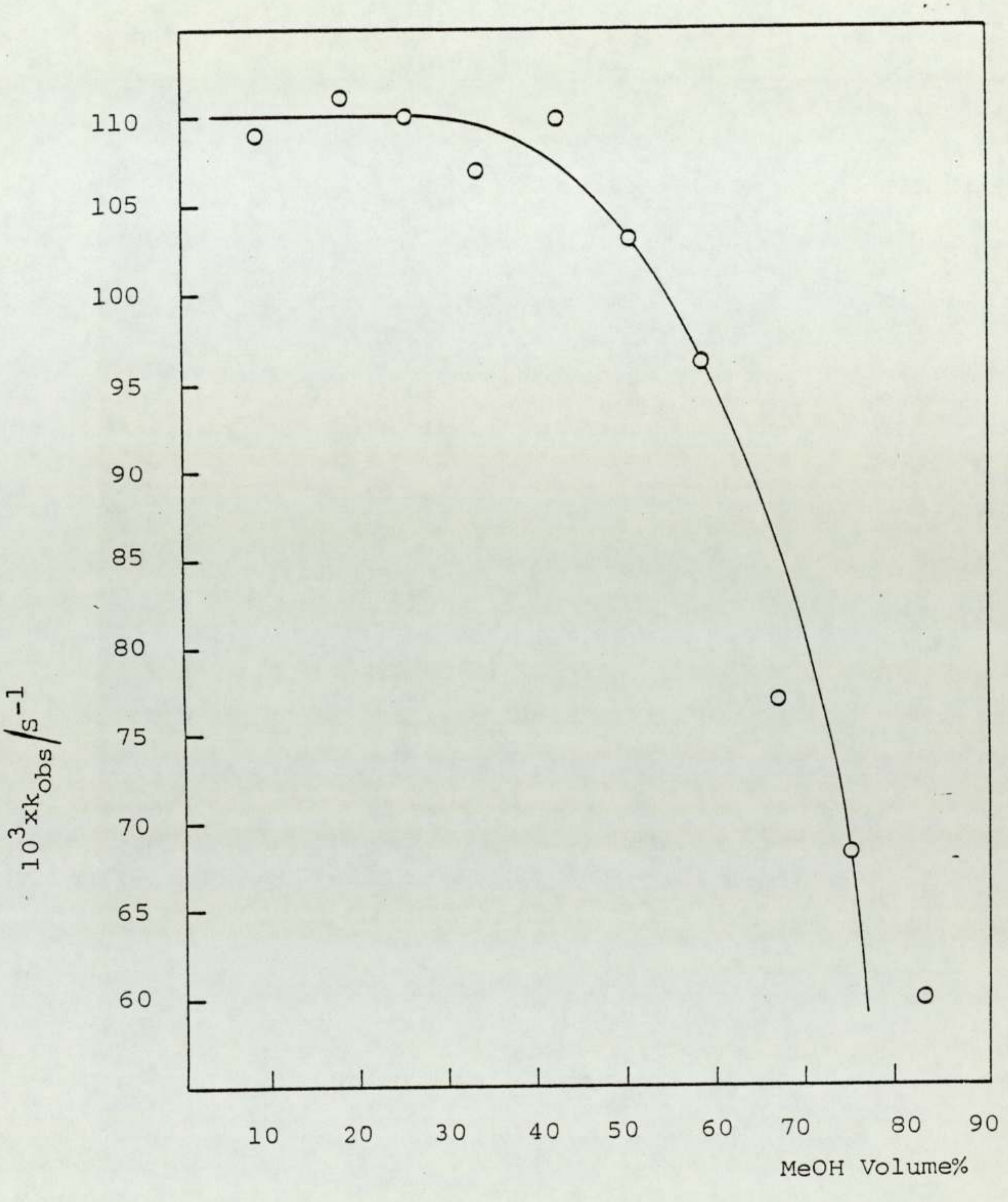


Fig (5.1) Plot of the observed rate constant of the solvolysis reaction of p-$EtOPhTeCl_3$ $8.3x10^{-5}M$ versus the volume percentage of methanol in mixed solvent of benzene metahnol.

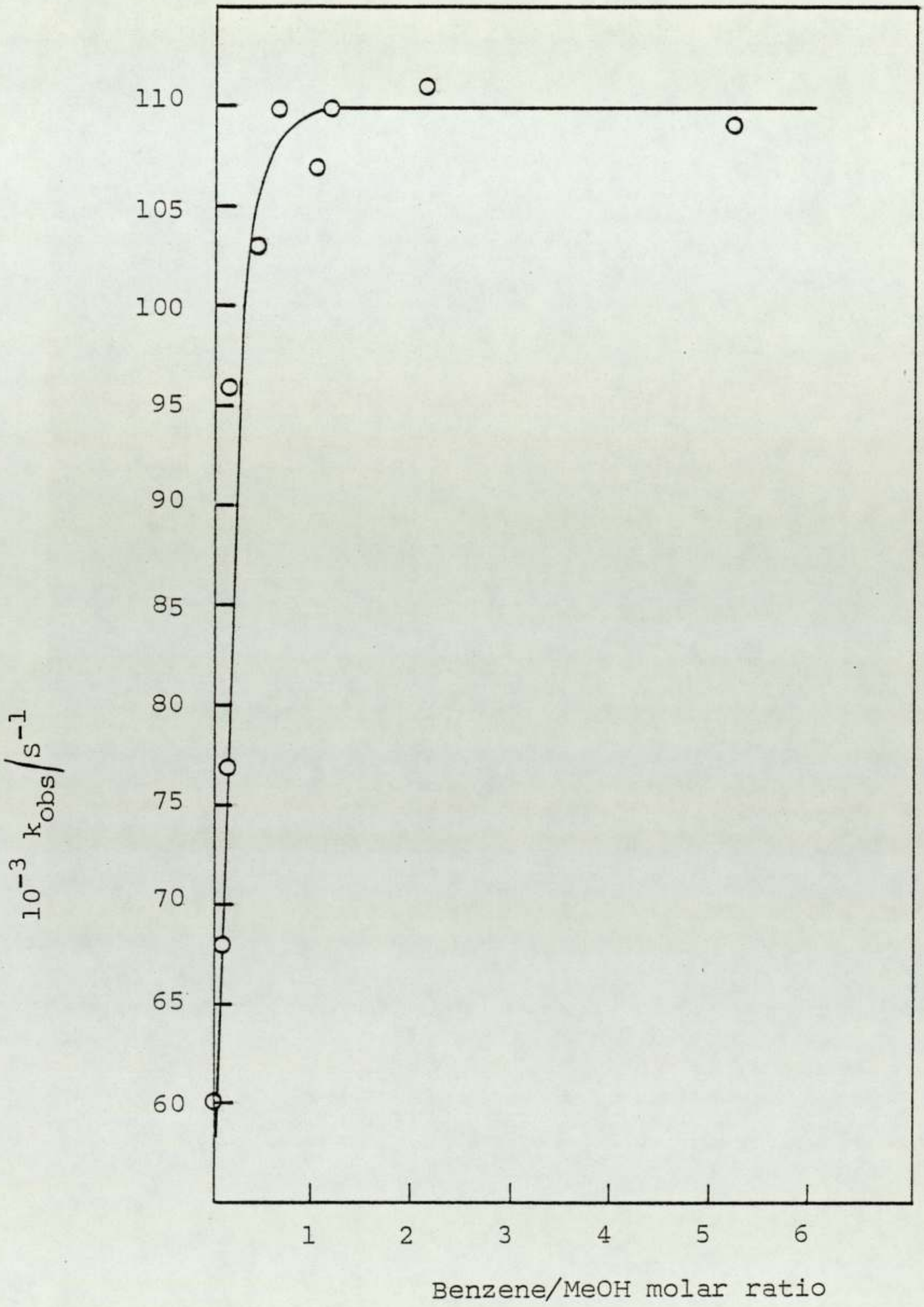


Fig (5:2) Plot of the observed rate constant of solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5}M versus the molar ratio of benzene/methanol in the solution.

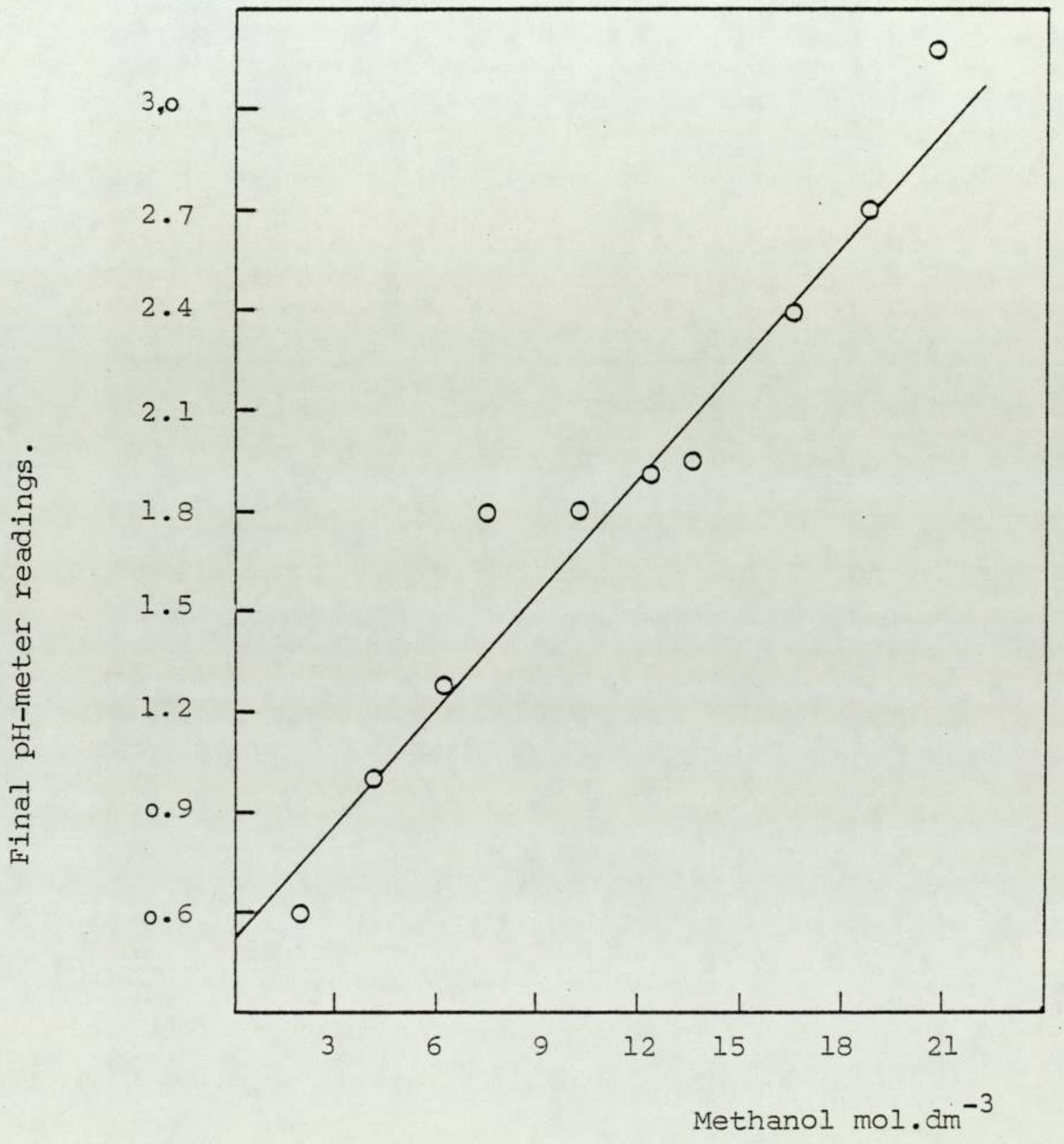


Fig (5:3) Plot of the final pH-meter readings for the solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5} in benzene-methanol solution versus the molar concentration of methanol in the solution.

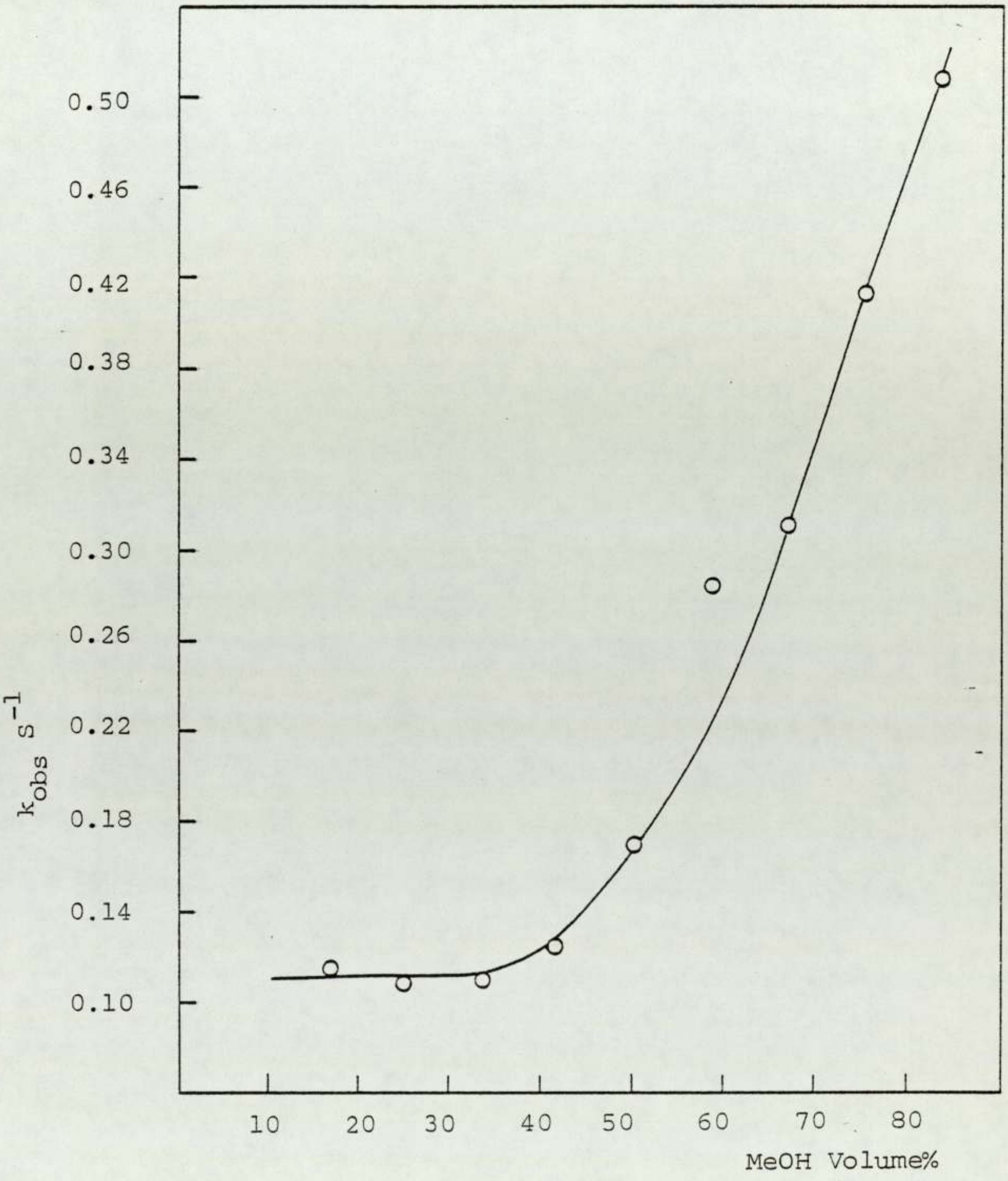


Fig (5:4) Plot of the observed rate constant of the solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5}M in mixed solvent of dioxane-methanol versus the volume percentage of methanol in the solution.

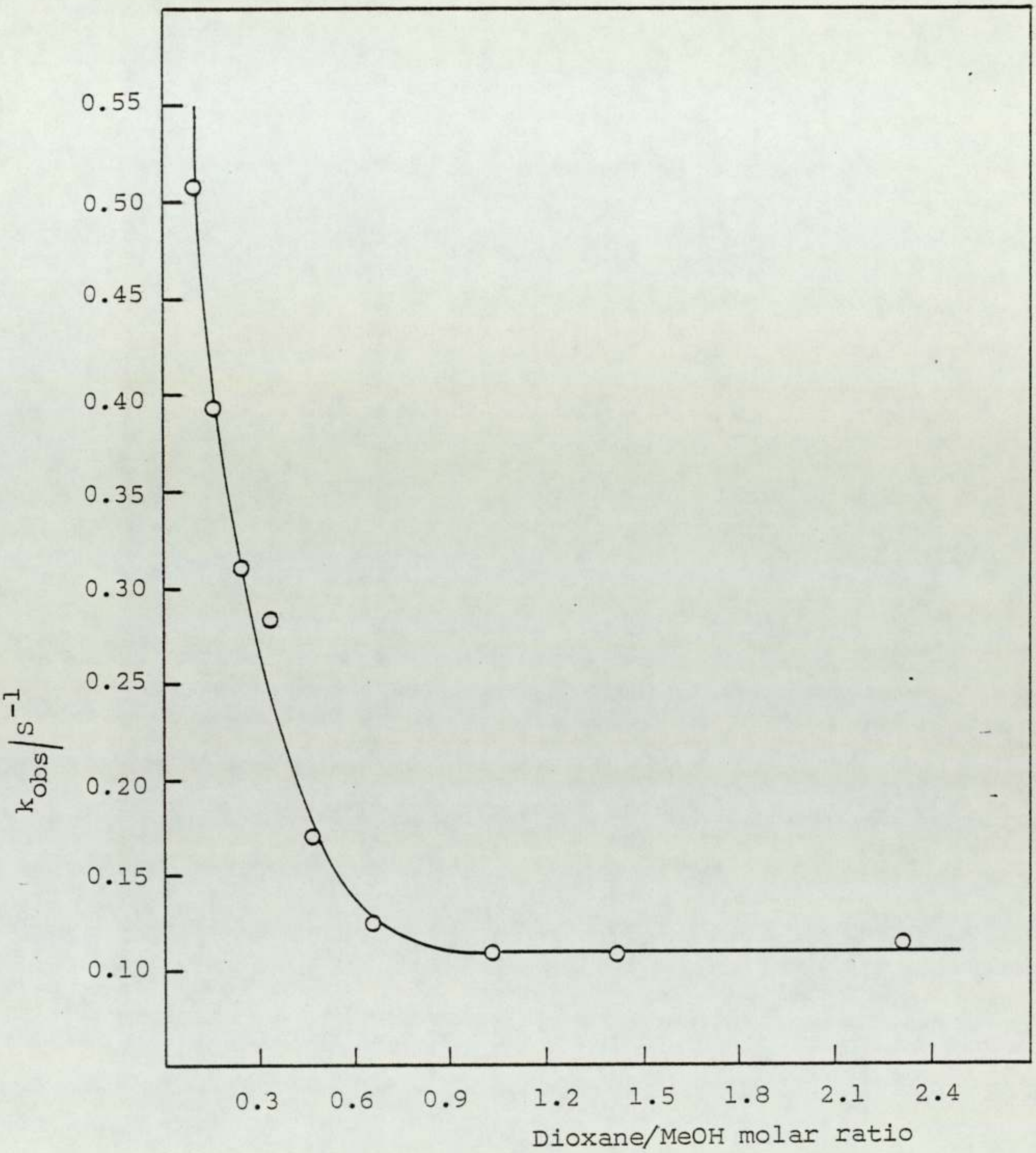
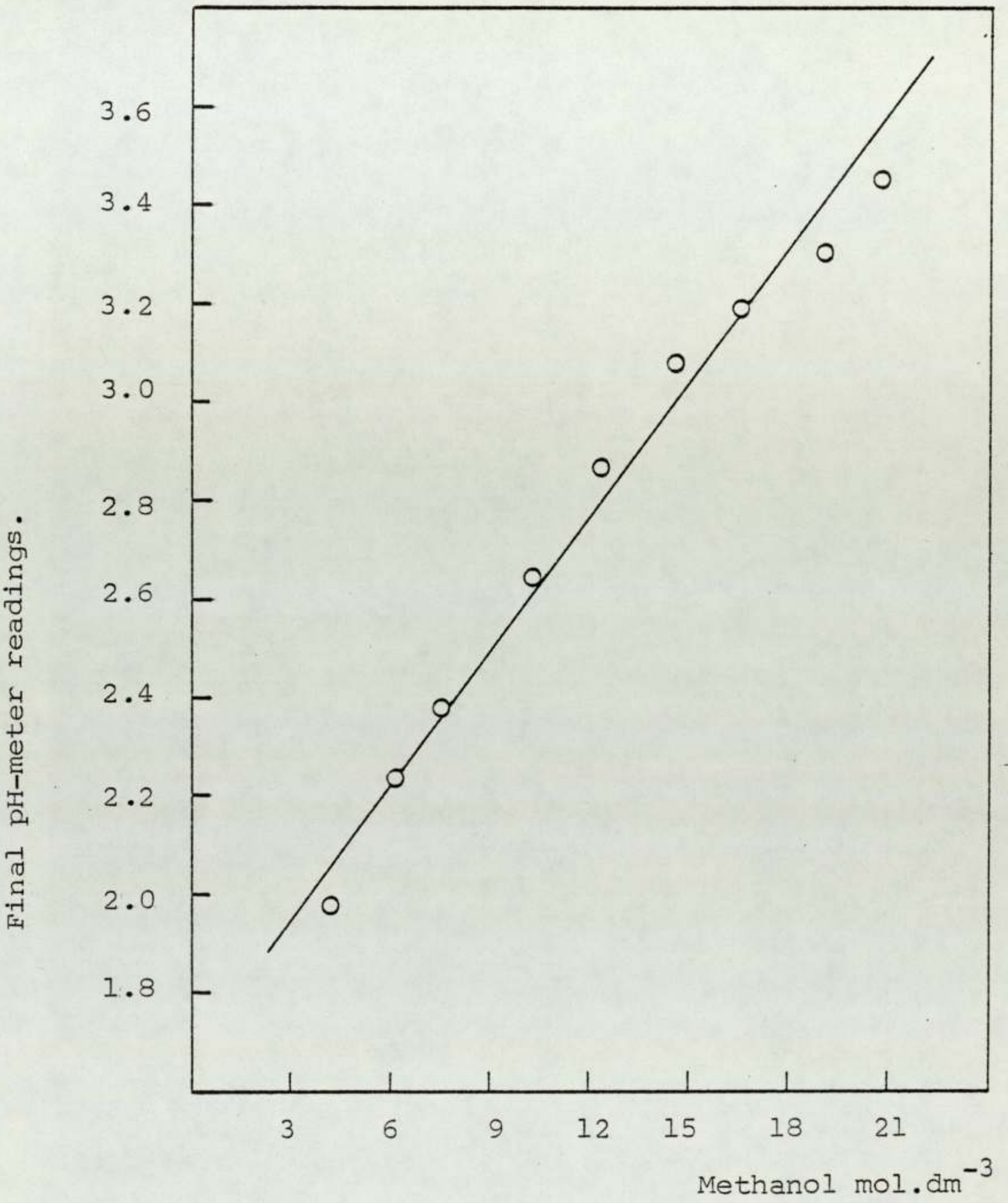
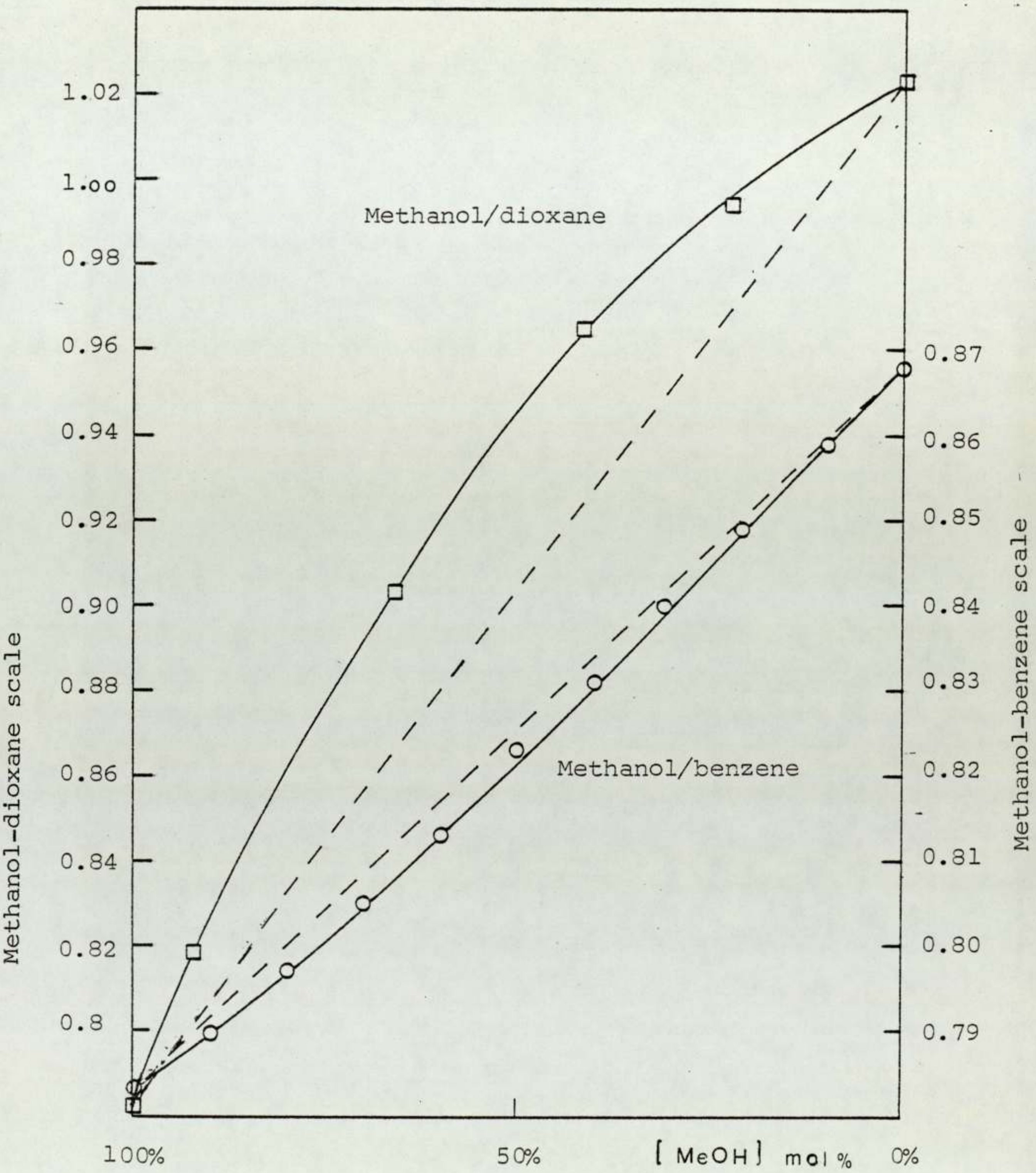


Fig (5:5) Plot of the observed rate constant of the solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5}M versus the molar ratio of dioxane/methanol in the solution.



Fig(5:6) Plot of the final pH-meter readings for the solvolysis reaction of p-EtOPhTeCl$_3$ 8.3x10^{-5}M in dioxane-methanol solution versus the molar concentration of methanol in the solution.



Fig(5:7) Plot of the density of mixed solvent of methanol-dioxane and methanol-benzene versus molar percentage of methanol at 25°C.

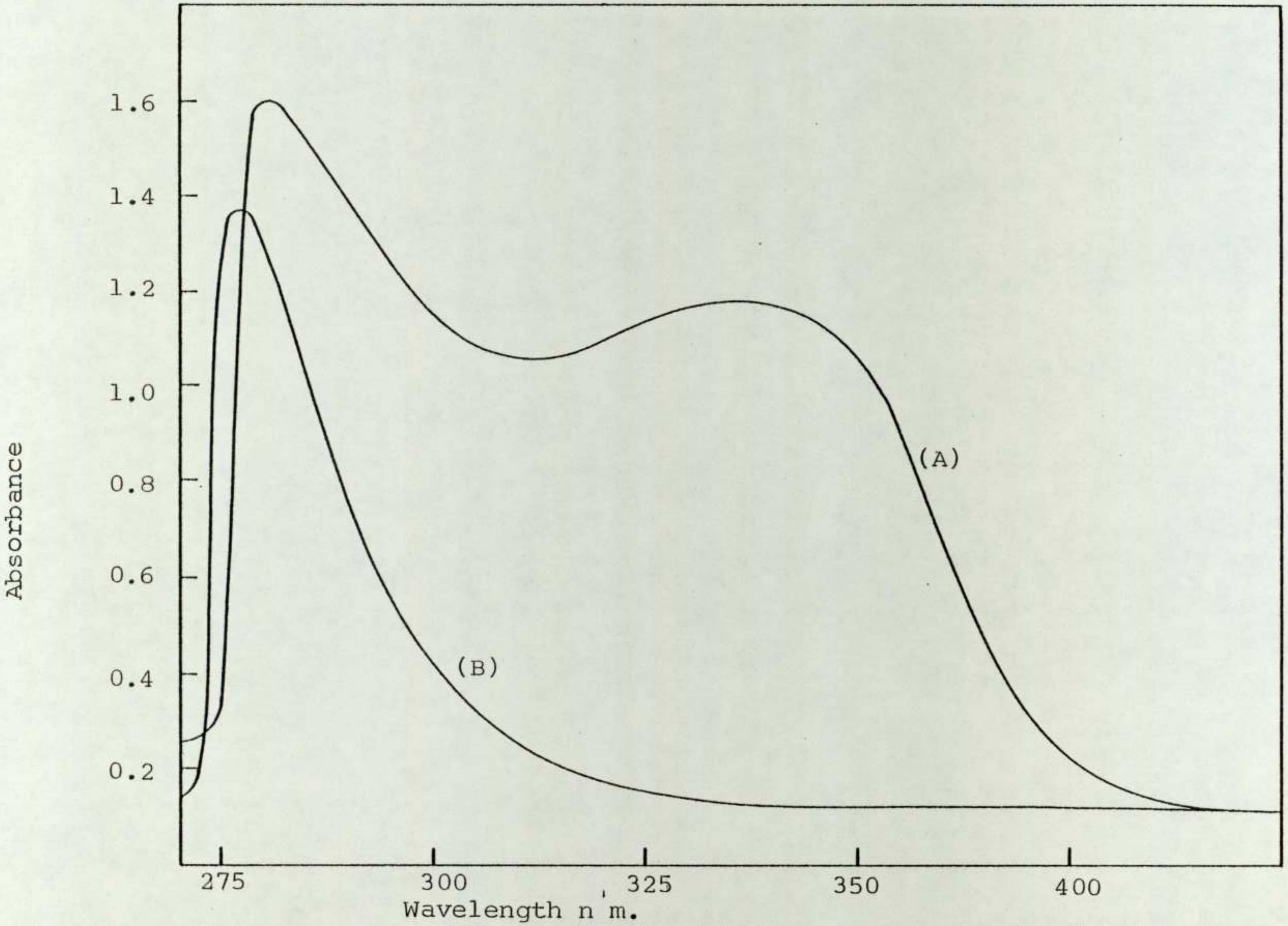
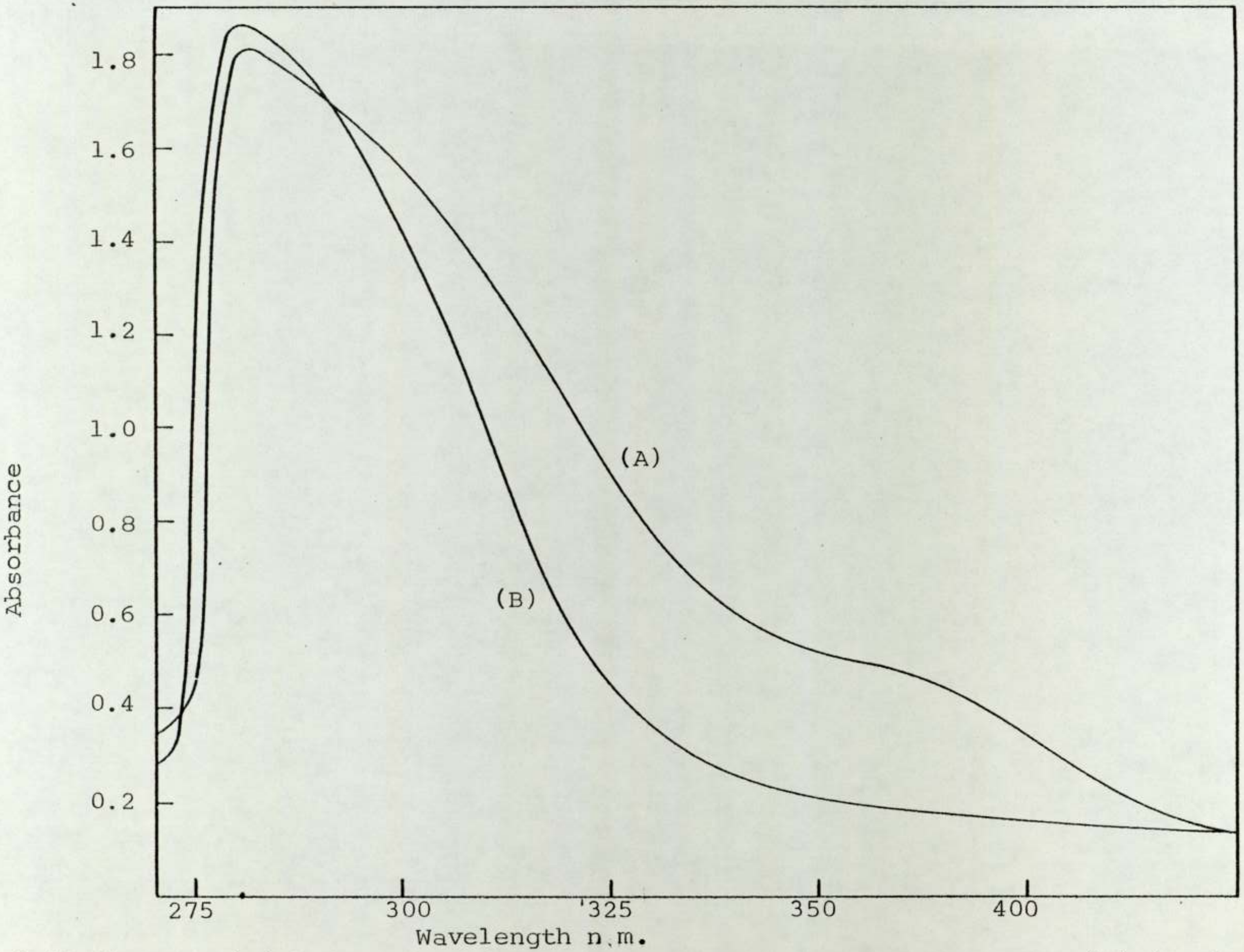


Fig (5:8) U.V visible spectra of p-EtOPhTeCl_3 (A) in benzene solution (B) in mixed solvent of benzene-methanol solution.



Fig(5:9) U.V. visible spectra of p-EtOPhTeBr$_3$ (A) in benzene solution (B) in mixed solvent of benzene methanol solution.

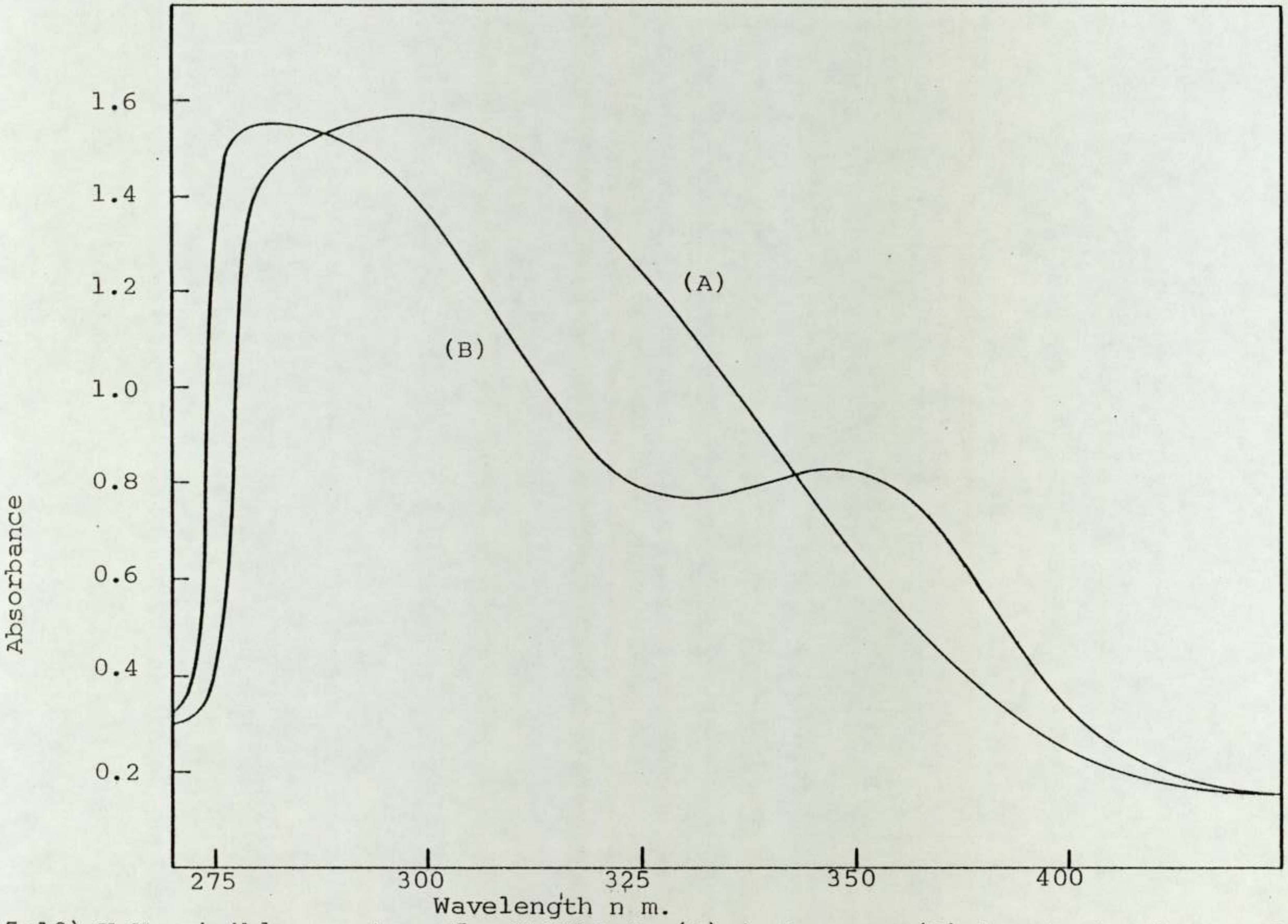


Fig (5:10) U.V. visible spectra of p-EtOPhTeI_3 (A) in benzene (B) in mixed solvent of benzene-methanol solution.

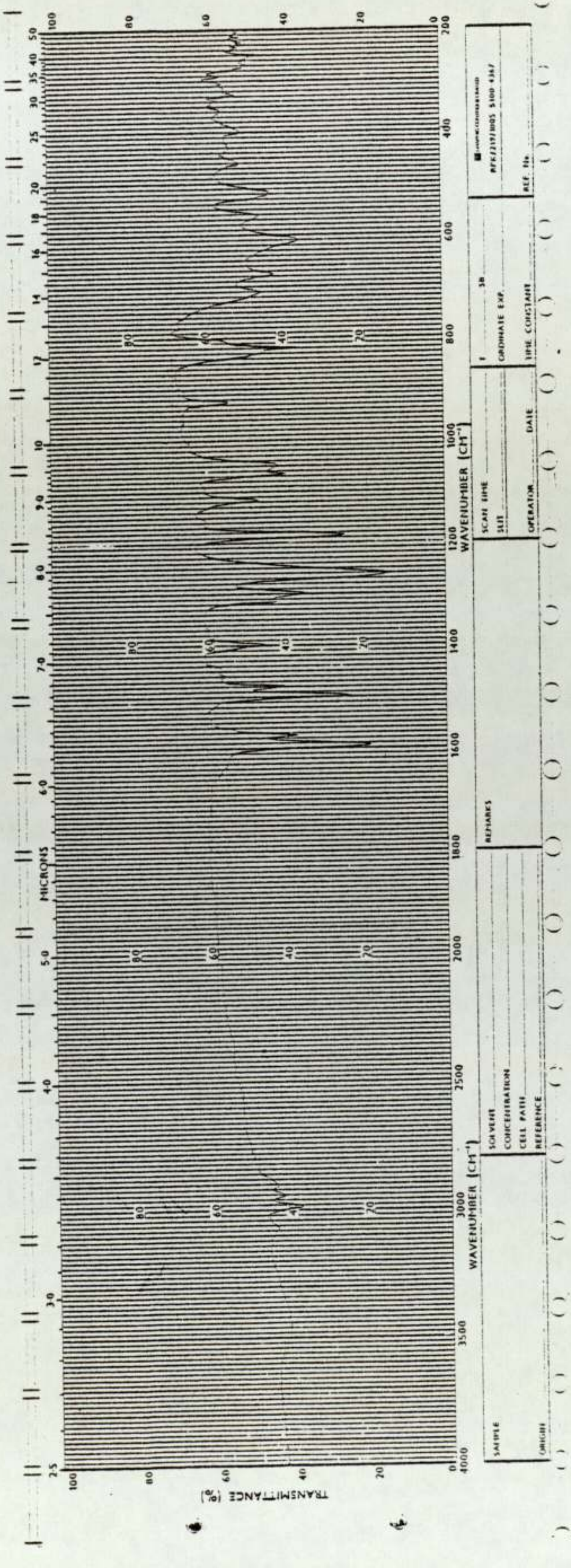


Fig (5:11) Infra-red spectrum of p-EtOPhTeCl(OH)(OCH_3)

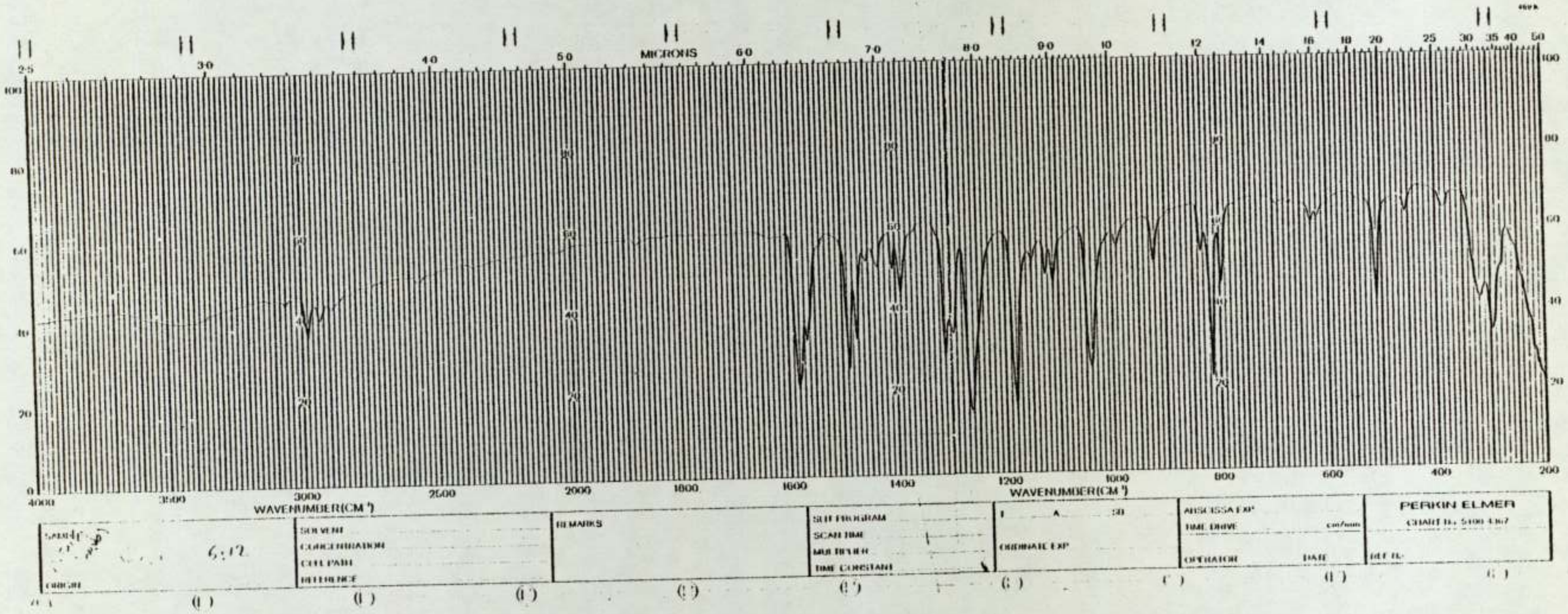


Fig (5:12) Infra-red spectrum of p-$EtOPhTeCl_3$

5:3 Discussion

The solvolysis of p-EtOPhTeX_3 under different reaction conditions (i.e. using mixed solvents in different compositions and under different temperatures) was studied. The reaction was carried out by measuring the decrease in recorded pH of the solution as the reaction goes towards completion. It was found that a pH meter with glass and calomel electrods responded adequately to the variation in the pH of the solution in a non-aqueous medium.

Robinson et al$^{(135)}$ found that the response of a glass electrode in alcohol-water mixed solvents is often substantially unimpaired at compositions below about 90% by weight of alcohol. However, in our measurements in benzene-methanol or dioxane-methanol, the mixed solvents ranging between 8 and 85% by volume methanol are very different from mixtures of 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 and calomel electrodes behave adequately and show good quantitive comparison of the acidities for the different experiments of solvolysis reaction. The behaviour is as though the meter readings still show a linear dependance on the true pH, but are governed by constants which vary with the solvent composition.

Acidity functions in different aqueous and non-aqueous organic solvents have been reported(136) and discussed. The main conclusion is that the acidity function(Q) varies linearly with acid concentration and can be represented by the equation:-

$$Q = M - n\log_{10}\left[H^+\right]$$

This conclusion is consistant with our acidity function measurements (i.e. pH meter readings). The final pH meter readings for the solvolysis reactions, listed in Table (5:1) and (5:5) vary linearly with the composition of the mixed solvents. The readings increase gradually as the molar concentration of methanol increases as shown in Figs (5:3) and (5:6). It was found that the range of the pH-meter readings is lower than the true value of $-\log_{10}\left[H^+\right]$ for the solution could be even if solvolysis of p-EtOPhTeCl$_3$ were complete (i.e. =3.6).

Although the difference between the acidity function (pH-meter readings) and the true pH of the medium under the same conditions varies with the solvent composition, it will not have any effect on the calculated rate constant discussed in this section. That is so because the rate equation (5:6) uses the difference between two readings; one at a measured time and that when the reaction is completed (the infinity reading). This eliminates the difference between the pH-meter readings and the real pH of the solution. Thus, the overall change in the pH-meter readings as the solvolysis reaction goes to completion still appears to be suitable function to follow for the kinetic measurements.

No definite conclusion can be drawn from the data available in explaining either the difference between the calculated pH and the final pH-meter readings of the solution, or the relationship between the solvent composition and the final pH-meter readings. The results may be influenced by several parameters, such as the liquid junction potentials of the electrodes, the affinity of the solvent(s) for the hydrogen ion or the equilibrium of the overall reaction producing the acid.

The results obtained from the observed rates of solvolysis, k_{obs}, of aryltellurium trihalides in benzene-methanol solution at different temperatures, show low values of the observed energy of activation. The observed $\Delta E^{\#}$ for trichloride is (7.6 ∓ 0.4) for tribromide is (8.3 ∓ 2.2) and for triiodide (10.7 ∓ 0.8) kJ,mol.$^{-1}$ In general the relative rates of solvolysis are trichloride > tribromide > triiodide. The above results are in agreement with related observations previously reported in the literature(23). The UV and visible spectra of p-EtOPhTeCl$_3$, before and after adding methanol to its solution in benzene, change more and more quickly than is the case for the tribromide and triiodide, see Figs (5:8), (5:9) and (5:10). That is probably bacause p-EtOPhTeCl_3 undergoes the solvolysis reaction faster than do the others. This fact may confirm the order of solvolysis mentioned above.

It has been suggested that the easy hydrolysis of aryltellurium trichloride relative to tribromide and triiodide is due to steric effects. The tellurium atom in the molecules of aryltellurium trihalides has vacant 4f orbitals(134) low enough in energy to allow bonding by accepting a lone pair electrons from oxygen of water molecules to form an unstable intermediate. The ionic radii of the halides increase in the order $Cl < Br < I$. Therefore, the trichlorides are more easily attacked at the central Te by a water molecule than are the tribromides, and in turn the triiodides. Also the greater electronegativity of chlorine leads to a higher positive effective charge on tellurium which again will favour attack by the nucleophile.

Petragnani(35) related the greater reactivity of the aryltellurium trichlorides as compared with the corresponding tribromides and triiodide to a decrease in the electrophilic character of the positive fragment ($ArTeX_2^+$), when X= bromine or iodine.

My results show that the solvolysis of p-EtOPhTeCl_3 is an acid catalysed reaction. Thus, the rate of solvolysis depends upon the dissociation of the resultant acid. The solvation of anions is favoured due to the formation of hydrogen bonds from the solvent to the anion in a given solvent(137). Hydrogen bonding is strongest for the smallest anions. Thus, the solvation of anions by protic solvents decreases in the order $Cl^- > Br^- > I^-$. This could mean that, through changes in the degree of dissociation, will have an influence on the catalysis of the reaction following the order $HCl > HBr > HI$.

The effect of the solvent composition on the observed rate of the solvolysis of p-EtOPhTeCl_3 was investigated. It was found that the rate of solvolysis in a mixed benzene-methanol solvent increases as the percentage of methanol decreases, as shown in Fig(5:1). The variation is not very great. A plot of k_{obs} versus the molar ratio of benzene/methanol in Fig (5:2) shows that the most pronounced increase in the rate of the solvolysis of p-EtOPhTeCl_3 as the molar ratio of benzene/methanol increases from zero. The rate of solvolysis reaches its highest value when the molar ratio is more than 1:1.

In contrast, the rate of solvolysis of p-EtOPhTeCl_3 in dioxane-methanol increases as the percentage of methanol by volume in the mixed solvent is increased as shown in Fig (5:4). A plot of k_{obs} versus the molar ratio of dioxane/methanol in Fig (5:5) shows a rapid initial decrease in the rate of the solvolysis of p-EtOPhTeCl_3

as the molar ratio of dioxane/methanol increases. The rate of solvolysis reaches its lowest limiting value when the ratio of dioxane/methanol is more than 0.5. The observed rate of solvolysis of p-EtOPhTeCl$_3$ in an aqueous dioxane mixture also increases as the percentage by volume of water increases.

I can find no single property that uniquely determines the observed rate of solvolysis of p-EtOPhTeCl$_3$ in different media. The changes may be related to the dependence of k_{obs} upon the equilibrium constant K_N and the final pH of the solution (equation 5:7). These constants are, in their turn, affected by several parameters in different media. Thus, the determination of K_N and final pH values of the solvolysis reactions, are both beyond the scope of this study.

The data available in the literature(138,139,140) show that the molecular interactions in binary liquid mixtures may effect the physical and chemical properties of each component or of the mixture, e.g. its density and boiling point. A plot of density for mixtures of benzene and methanol versus the mol percentage of methanol Fig (5:7) shows a negative deviation from linearity. While the equivalent plot for dioxane-methanol shows a positive deviation.

The negative deviation may be related to the fact that the interaction between methanol and benzene molecules is weaker than that between methanol molecules. The difference may be ascribed to the fact that hydrogen bonding in methanol-methanol is stronger than any interactions between methanol and benzene molecules could be. This weaker attraction between methanol-benzene molecules may provide more freedom for the methanol or protonated methanol molecules to attack the Te-Cl bonds as the percentage of benzene increases.

The plot of k_{obs} versus the molar ratio of benzene/methanol Fig (5:2) shows that the effect of increasing the molar concentration of the benzene component is limited above the molar ratio of 1:1 benzene/methanol. This limited effect may indicate that the interactive force between methanol molecules is disrupted by a benzene molecule, hence the effect is limited at 1:1 molar ratio of benzene/methanol.

The positive deviation from linearity in plot (5:7) for the mixed solvent of methanol-dioxane would then be due to the fact that the attraction between methanol and dioxane molecules is stronger than the average of dioxane-dioxane and of methanol-methanol interactions. The difference in the molecular interaction may arise because the two oxygen atoms of the dioxane have more electron availability than the single oxygen atom of the methanol molecules(141). Therefore, dioxane can interact with two methanol molecules (Fig 5:13). This could be mirrored in

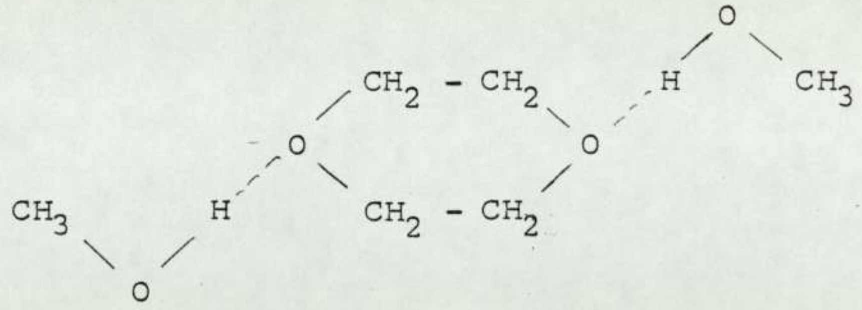


Fig (5:13)

the plot of k_{obs} versus the molar ratio of dioxane/methanol (Fig 5:5).

The plot shows that the effect of increasing the dioxane molar concentration is limited above 0.5 dioxane-methanol molar ratio. The molecular interaction of methanol-dioxane may preclude the nucleophilic attack of methanol on the tellurium atom in p-EtOPhTeCl$_3$ resulting in a decrease in the rate of solvolysis. By using the same ideas as above, the effect of increasing the water component in mixed dioxane-water solvent can be similarly interpreted.

The experimental results obtained after the evaporation of the solvent at reduced pressure from the solution of p-EtOPhTeX$_3$ in a mixture of benzene-methanol demonstrate the reversible nature of the solvolysis reaction. The position of the equilibrium, whose forward reaction we are studying here, mainly depends upon the concentration of HX. It has been pointed out that RMX$_3$ where M is Se or Te, can be regarded as a derivative of $RM(OH)_3$,(142) and that the trichloride could be prepared by the action of HX on the latter compound.

The increase in the carbon and hydrogen percentages and the decrease in the chlorine percentage found in the product of p-EtOPhTeCl_3 after the evaporation of its solution in a benzene-methanol mixture, may be due to the fact that appreciable amount of CH_3O^- have replaced Cl^- ions in the parent compound. A white precipitate of AgCl obtained when the vapours of the solvent are passed through a silver nitrate solution shows the partial removal of the resultant Cl^- ions as HCl during the evaporation of the solvent. Thus, the elemental analysis gives variable values for the chloride percentage in the product isolated after the experiment, but it is always less than the chloride percentage in the parent compound.

The reappearance of the yellow colour during the course of the solvent evaporation, combined with the elemental analytical results indicate the reversibility of the solvolysis reaction. It is obvious that the acid produced from the solvolysis reaction becomes more concentrated as the solvent removed. Hence, the reactant becomes more favoured as the pH decreases.

An attempt to force the forward reaction to completion was made by adding an excess of $NaOCH_3$ in pure methanol to a solution of p-EtOPhTeCl_3 in benzene-methanol. When the solvent was evaporated, a white precipitate was obtained. After recrystallisation, this product was found to be different from the yellow product which is isolated under the same conditions but without the addition of $NaOCH_3$. The elemental analysis of the product yielded the following values for carbon, hydrogen and chlorine respectively:- 32.3%, 4.2% and 10.4%. The analysis corresponds closely to the following formula:-

p-EtOPhTeCl(OH)(OMe)
(I)

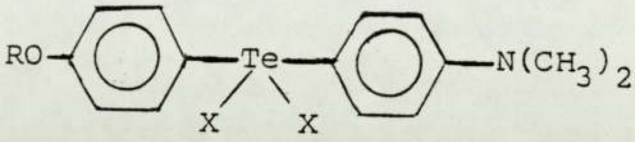
which requires 32.5% C, 3.9% H and 10.7% Cl.

Infra-red investigations of the product and the parent compound p-EtOPhTeCl_3 see Fig (5:11) and (5:12), show absorption bands in the spectrum of the product associated with the Te-O bond vibration.(23) This finding, combined with the elemental analytical results, helps to indicate that a chlorine atom in p-EtOPhTeCl_3 is replaced by CH_3O^-. The product, on reduction by $Na_2S_2O_5$ or Na_2SO_3, gives diaryl ditelluride.

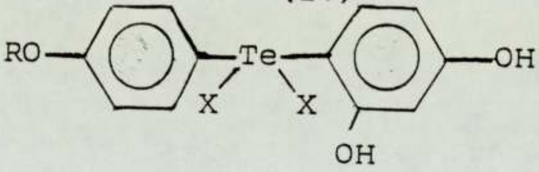
It has been reported by Petragnani(35) that only one of the halide atoms of the trihalide is replaced when the trihalides undergo condensation reactions with acetone, acetophenone, N-dimethyl aniline or resorcinol, to produce diorganyl tellurium dihalides. The products, aryl acetonyl tellurium dihalides (II) and aryl phenacyl tellurium dihalides (III), are hydrolysed in water:

$ArTeX_2(CH_2COCH_3)$ (II) $ArTeX_2(CH_2COC_6H_5)$ (III)

Whereas aryl-p-dimethylaminophenyl tellurium dihalide(IV) and aryl-2,4-dihydroxyphenyl tellurium dihalides (V) are unaffected.



(IV)



(V)

The hydrolyses of compounds (II) and (III) is consistent with the possibility that any isolated product (I) could be the result of the hydrolysis of the compound p-EtOPhTeCl$_2$(OMe) by moist air or by traces of water in the solvent used, although at the time I believe it to be dry.

Any explanation for the pathway of the preceding solvolysis reaction must take account of the geometrical structure of $ArTeCl_3$ in the solution. It has been shown (34) that the structure with minimum replusive effects for discrete molecules such as MX_4 having a lone pair of electrons is a trigonal bipyramid. Since the lone pair of electrons is attracted only by the central tellurium atom, this lone pair's electron density is concentrated closer to the central atom and occupies one of the equatorial positions. Moreover, the lone pair of electrons in an equatorial position is more favourable because it will repel only two bonded pairs of electrons at 90° angles to itself, as opposed to the axial position where three 90° angle repulsions would occur. The most favourable position for the bulky aryl group in $ArTeCl_3$, which minimizes the repulsion with the lone pair of electrons is also equatorial. Necessarily the third equatorial position is occupied by one of three halide atoms which leads to the structure shown in Fig (5:14).

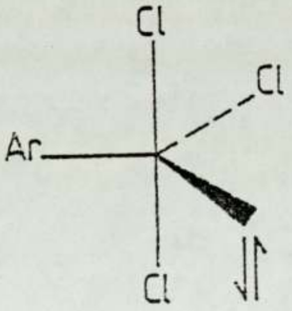
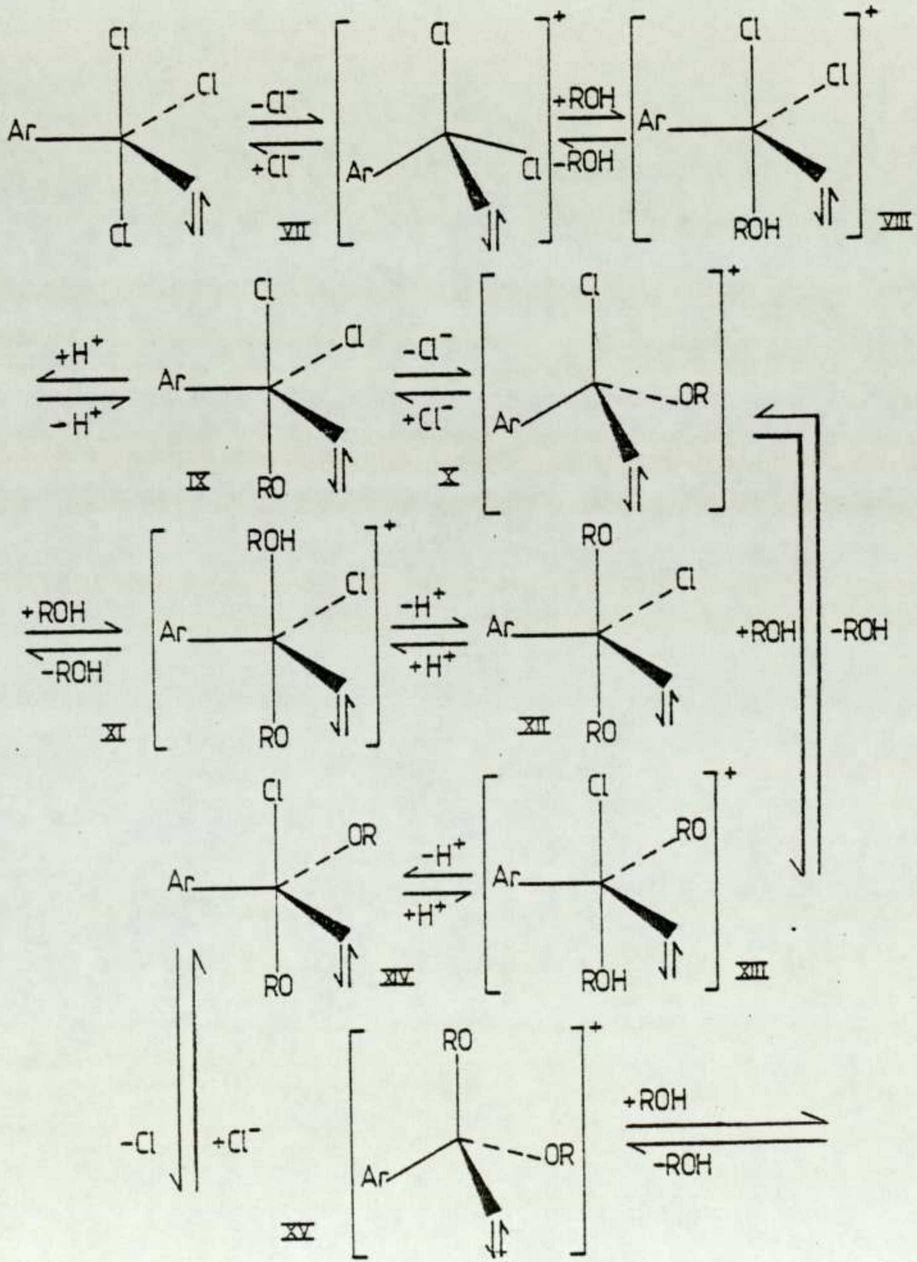
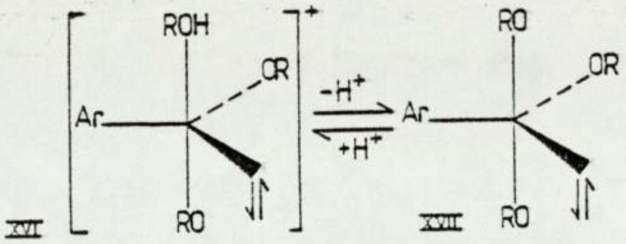


Fig (5:14)

The conclusion drawn from the data cited in the literature substantiate the trigonal bipyramidal shape of $ArTeCl_3$.(33,34)

Starting from the above structure, both dissociative and associative reaction mechanisms can be considered in attempting to explain the pathway of the solvolysis reaction of p-EtOPhTeCl$_3$. Consider firstly a completely dissociative pathway, and for convenience we will initially ignore acid catalysis. There is no evidence that one of the chloride ligands leaves the ArTeCl$_3$ molecule resulting in the formation of ArTeCl$_2^+$, but if we accept that the formation of ArTeCl$_2^+$ is feasible then a possible scheme for the dissociative pathway is:





The relatively weak apical Te-Cl bond in Fig (5:14) can be assumed to be that to be broken to form $ArTeCl_2^+$. This and the subsequent related intermediates are drawn as tetrahedral which can undergo nucleophilic attack by ROH (where R= H, CH_3). Such an attack will, by the principle of microscopic reversibility, result in apical occupation by the entering group ROH as shown in transition state VIII. This step should be followed by the elimination of the hydrogen ion from species VIII, resulting in compound IX. Notice that because the transition state is tetrahedral, there is never any problem in forming a product with both the spare pair of electrons and the aryl group in equatorial positions.

The second substitution step would presumably be similar to the first step, with the second entering group again becoming axial. Two different products are possible, XII and XIV. If the final substitution process requires axial loss of chloride then XII can not lose its last chloride ligand without first reverting to X and being converted to XIV. Notice that because of the presence of both the aryl group and the spare pair of electrons, pseudo rotation of the trigonal bipyramidal species will not be possible.

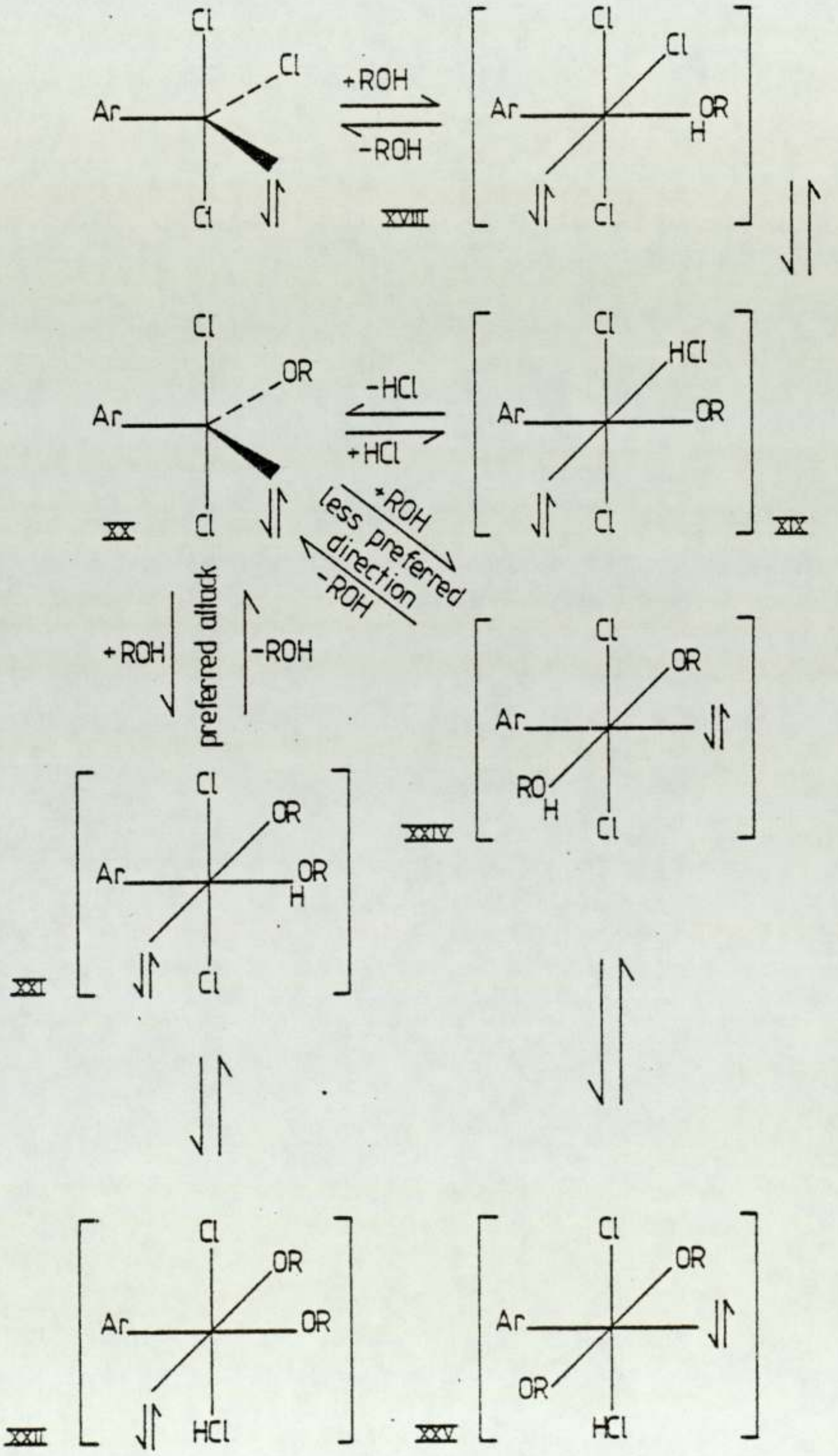
The only alternative for XII under dissociative conditions is to lose the chloride from an equatorial position. That does not seem to be likely. Therefore, the production of XII represents a mechanistic "dead-end" in solvolysis. This suggests that the substitution of the third chloride will be the slowest step if the reactions are dissociative.

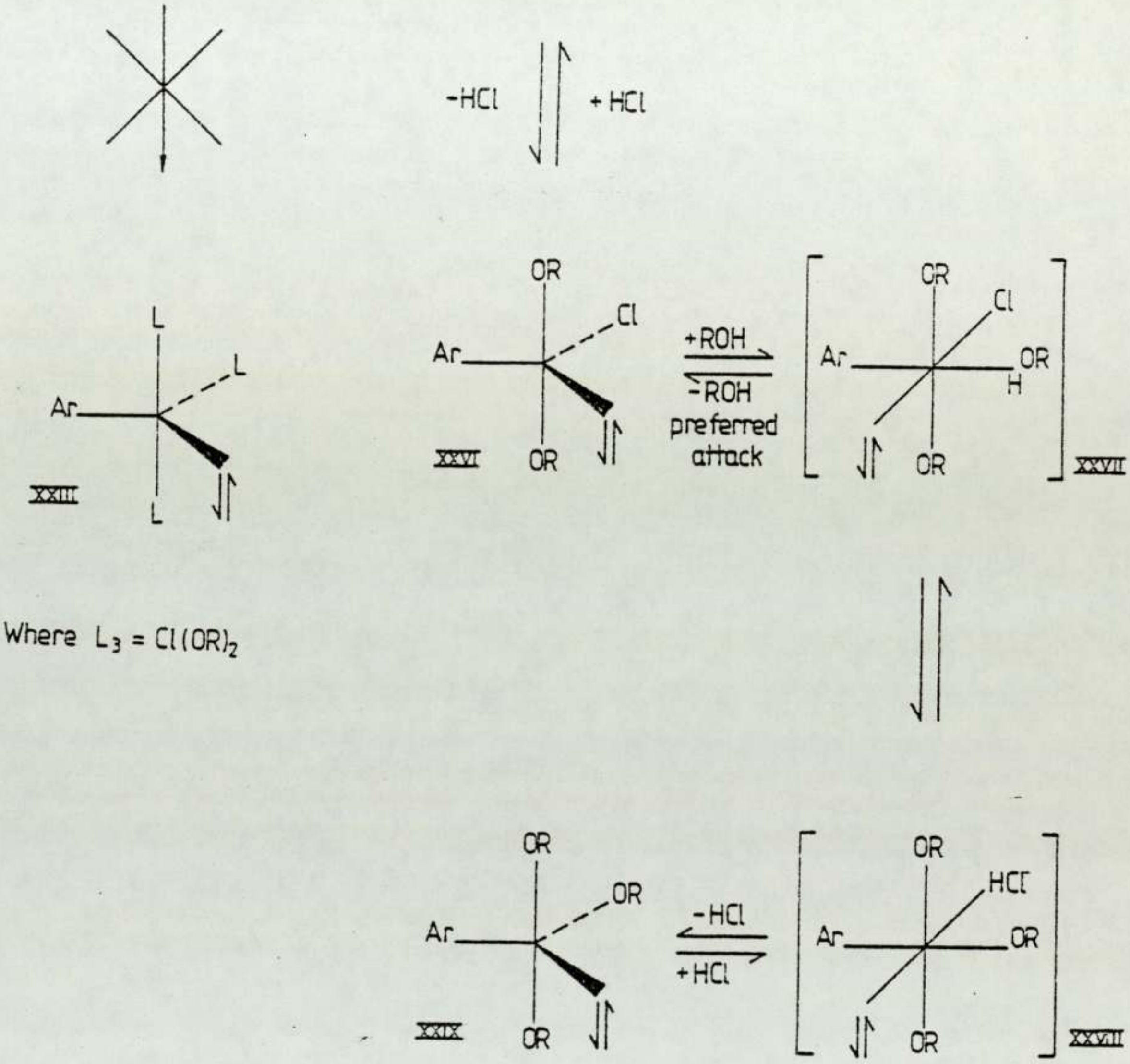
The acid catalysis of the solvolysis makes the dissociative mechanism even less likely because, as can be seen in the following equations:-

$$ArTeCl_3+H^+ \rightleftharpoons ArTeCl_3H^+ \rightleftharpoons ArTeCl_2H^{++} + Cl^-$$

A doubly charged transition state, $ArTeCl_2H^{++}$ is likely to be much less favourable than is $ArTeCl_2^+$. Therefore, my experimental findings seems to be in disagreement with the proposed dissociative mechanism for the solvolysis reaction of $ArTeCl_3$.

That means that the likely mechanism for the solvolysis reaction of $ArTeCl_3$ is one which proceeds via a series of associative substitution processes. The equatorial plane is less crowded than a plane involving the axial ligands. Therefore, it is safe to suggest that the nucleophilic attack by ROH on the central tellurium atom will be preferable in the equatorial plane. The bulky size of the aryl group will direct the attack of the entering group trans to its position. This position has less steric hindrance towards the entering group. The resulting transition state XVIII has an octahedral configuration, as shown in the following scheme suggested for the associative reaction mechanism:-





Where $L_3 = Cl(OR)_2$

It is reasonable to suggest that tellurium in oxidation state IV, with the electronic structure of $\left[K_r\right]4d^{10}\ 5S^2$ will favour this octahedral configuration. The proton which came into the transition state on the ROH can rapidly migrate around that molecule. Thus, XVIII and XIX can be regarded as being in equilibrium with each other. HCl will be a good leaving group under my experimental conditions and so XIX is easily able to lose an HCl molecule to give the trigonal bipyramidal product XX with its three co-planar ligands, Ar, OR and the spare pair of electrons in the equatorial positions. Notice that the entering group is co-planar with the original equatorial groups. Therefore, the newly formed equatorial arrangement must contain three ligands which were co-planar with the leaving group. So, to produce an acceptable trigonal bipyramidal product, two of the set of (aryl, leaving group, spare pair) must be trans to each other.

The compound XX may undergo another nucleophilic attack by ROH to commence the substitution of the second chloride ligand. This attack may occur either from the more favoured direction, that is trans to the aryl group, or along the less preferable direction, which is cis to the aryl group. The attack trans to aryl subsequently requires either the aryl group, or the spare pair of electrons to take up the unacceptable apical position if HCl is to be lost.

Thus, in order to lose a second chloride ligand and still keep both the aryl group and the spare pair of electrons in an equatorial environment, the second nucleophilic attack on the central tellurium atom must occur cis to the aryl group, as shown in transition state XXIV. When once that has been formed, it can react further just as did XVIII. It is reasonable to suggest that this step must be relatively slow, because it includes a less preferred pathway, that is a higher energy transition state.

The substitution of the third chlorine ligand on the compound XXVI may proceed in the same way as the first step in the above scheme. hence will be a fast process.

The above argument may be applied with the added feature of acid catalysis. It is reasonable to suggest that the hydrogen ion in the solution will attach to the lone pair of electrons on the tellurium atom resulting in the formation of a Te-H bond. This attack results in a reduction of the angular volume in the equatorial position occupied by that pair of electrons. This reduction in the angular volume may decrease the hindrance towards entering groups. Thus the reaction will be catalysed to a certain extent in the presence of hydrogen ions.

This new Te-H bond still requires an equatorial position just as the spare pair did. The occupation of an equatorial position by the Te-H bond follows because the Te-H bond is a short and strong sigma bond (compared to other bonds to Te). Hence, it will take up a position with two centre, two electron bonding (equatorial) rather than a three centre, four electron position (axial) with a build up of electron density.

When we consider an associative route then, we see that the bulky size of the entering group will make nucleophilic attack at the equatorial edge, cis to the aryl group, which is necessary for the second substitution difficult, hence, one chloride group may be readily substituted as shown in compound II through to V, with subsequent substitution being either slow or, with very bulky entering groups, not even possible. However, with an entering group of relatively small size, say H_2O, the attack in the cis position relative to the aryl group may be more feasible. Therefore, substitution by H_2O may occur for all the chloride groups of $ArTeCl_3$. The implication is that the degree of the substitution of $ArTeCl_3$ molecules depends upon the size of the entering group and the hydrogen ion concentration in the solution.

Hydrolysis of $ArTeCl_3$ will initially produce the compound $ArTe(OH)_3$. Although this has been reported in the literature(142,20), it is difficult to isolate. This is probably because the compound undergoes further reactions dependent on the pH of the medium. It has been reported that in acidic media the main product is ArTe(O)Cl, whereas in basic media the final product is either ArTe(O)OH or $(ArTeO)_2O$. Thus, the prediction is $ArTe(OH)_3$ may be isolated in almost neutral media, that is solutions in the pH range of 5 to 9. In conclusion, the solvolysis of $ArTeCl_3$ is acid catalysed. An associative pathway is the most likely one. The detailed consideration of such a pathway suggests as an abbreviated reaction sequence:-

$$\mathrm{ArTeCl_3 + HOR \xrightarrow{fast} ArTeCl_2(OR)+H^+ +Cl^-}$$

$$\mathrm{ArTeCl_2(OR)+H^+ \overset{K_N}{\rightleftharpoons} ArTeHCl_2(OR)^+}$$

$$\mathrm{ArTeHCl_2(OR)^+ +HOR \xrightarrow[slow]{k_5} ArTeCl(OR)_2+2H^+ +Cl^-}$$

$$\mathrm{ArTeCl(OR)_2+HOR \xrightarrow{fast} ArTe(OR)_3+H^+ +Cl^-}$$

The above reaction sequence shows the protonated tellurium species which is involved in determining the overall rate of the reaction. Earlier in this chapter, equations (5:1) to (5:3) of section 5:2, a similar scheme was advanced, based solely on the observed rate data. In that scheme protonation of $ArTeCl_3$ was assumed. While the earlier scheme cannot be ruled out on the available evidence, the later proposal seems more reasonable. Mathematically, both are equivalent.

Appendix 1

For the general case of a second order reaction :-

$$aA + bB \xrightarrow{k} C$$

the rate of reaction is given by:-

$$\frac{d[C]}{dt} = k[A][B] \qquad (1)$$

Assume one of the reagents, say A is in slight excess

i.e $[A]_o/[B]_o > a/b$, and let

$H = [A]_o / [B]_o$

If at time = 0 , $[C] = 0$, then the equation one can be integrated as

$$\frac{d[C]}{dt} = k\left\{[A]_o - a[C]\right\}\left\{[B]_o - b[C]\right\} \qquad (2)$$

$$kt = \int_o^c \frac{d[C]}{\left[[A]_o - a[C]\right]\left[[B]_o - b[C]\right]}$$

$$\text{Let } \frac{e}{[A]_o - a[C]} + \frac{s}{[B]_o - b[C]} = \frac{1}{\left[[A]_o - a[C]\right]\left[[B]_o - b[C]\right]}$$

$be + as = 0$

$[B]_o e + [A]_o s = 1$

$e = -\frac{a}{b} \cdot s$

$s = 1 / \left[[A]_o - \frac{a}{b}[B]_o\right]$

$$\therefore \quad kt = -\frac{a}{b} \cdot s \int_0^c \frac{d[C]}{[A]_o - a[C]} + s \int_0^c \frac{d[C]}{[B]_o - b[C]}$$

$$\text{or} \quad \frac{ktb}{s} = kt\left[b[A]_o - a[B]_o\right] = \int_0^c \frac{-ad[C]}{[A]_o - a[C]} + \int_0^c \frac{bd[C]}{[B]_o - b[C]}$$

$$kt\left[b[A]_o - a[B]_o\right] = \ln\left[\frac{[A]_o - a[C]}{[B]_o - b[C]}\right]_o^c$$

$$\therefore \quad k\left[b[A]_o - a[B]_o\right]t = \ln\left\{\frac{[B]_o\,([A]_o - a[C])}{[A]_o\,([B]_o - b[C])}\right\}$$

Since the reaction is followed spectrophotometrically with optical density = W_t, we need to convert this equation to the appropriate unit. now

$$W_t = E_A\left\{[A]_o - a[C]\right\} + E_B\left\{[B]_o - b[C]\right\} + E_C[C] + Z$$

Where Z = constant and E is the extinction coeffection

$W_o = E_A \cdot [A]_o + E_B[B]_o + Z$

But $[C]_f = [B]_o / b$

$$W_f = E_A\left\{[A]_o - \frac{a}{b}[B]_o\right\} + \frac{E_c\,[B]_o}{b} + Z$$

$$D_t = W_t - W_o = [C]\,(-\,aE_A - bE_B + E_C)$$

Where D_t represents the absorbance at time = t

$$D_f = \frac{[B]_o}{b} \left(- aE_A - bE_B + E_C \right)$$

Where D_f represents the final absorbance

Let $g = - a E_A - bE_B + E_C$

$[C] = D_t / g$

$[B]_o = b D_f / g$

$[A]_o = HbD_f / g = H[B]_o$

$$k\left\{b[A]_o - a[B]_o\right\}t = \ln \left\{ \frac{1}{H} \cdot \frac{(HbD_f / g) - (aD_t / g)}{(bD_f / g) - (bD_t / g)} \right\}$$

$$k\left\{b[A]_o - a[B]_o\right\} t = \ln\left\{ \frac{H D_f - (a D_t / b)}{H (D_f - D_t)} \right\}$$

Let $R = a / b H$ or $a[B]_o / b[A]_o$

$$k\left\{b[A]_o - a[B]_o\right\}t = \ln\left\{ \frac{D_f - D_t \cdot R}{D_f - D_t} \right\}$$

considering the specific examples of

$$3SO_3^{2-} + 2ArTeCl_3 \longrightarrow Ar_2Te_2 + \text{other products}$$

i) With SO_3^{2-} in excess

$[A]_o$ represents $[SO_3^{2-}]_o$ and $[B]_o$ represents $[p\text{-}EtOPhTeCl_3]_o$

$a = 3 \quad , \quad b = 2$

$$R = \frac{3[B]_o}{2[A]_o} = \frac{3[p\text{-EtOPhTeCl}_3]_o}{2[SO_3^{2-}]_o}$$

$$k_r\left(2[SO_3^{2-}]_o - 3[p\text{-EtOPhTeCl}_3]_o\right)t = \ln\left(\frac{D_f - D_t \cdot R}{D_f - D_t}\right) \qquad (3)$$

ii) With $p\text{-EtOPhCl}_3$ in excess

$[A]_o$ represents $[p\text{-EtOPhTeCl}_3]_o$ and $[B]_o$ represents $[SO_3^{2-}]_o$
$a = 2 \quad , \quad b = 3$

$$R' = \frac{2[SO_3^{2-}]_o}{3[p\text{-EtOPhTeCl}_3]_o} \qquad \text{or} \qquad R' = 1 / R$$

$$k_r\left(2[SO_3^{2-}]_o - 3[p\text{-EtOPhTeCl}_3]_o\right)t = -\ln\left(\frac{D_f - (D_t / R)}{D_f - D_t}\right) \qquad (4)$$

iii) With $2\ \text{ArTeCl}_3 = 3\ SO_3^{2-}$

$[A]_o / [B]_o = a / b$

$[A]_o = a[B]_o / b$

Substitute $[A]_o$ in equation 2

$$\frac{d[C]}{dt} = k\left(\frac{a[B]_o}{b} - a[C]\right)\left([B]_o - b[C]\right)$$

$$\frac{d[C]}{dt} = bak \left\{ \frac{[B]_o}{b} - [C] \right\} \left\{ \frac{[B]_o}{b} - [C] \right\}$$

$$\therefore \int_o^C - d[C] \Big/ \left\{ \frac{[B]_o}{b} - [C] \right\}^2 = - abkt$$

$$abkt = \left\{ 1 \Big/ \left(\frac{[B]_o}{b} - [C] \right) \right\}_o^C$$

$$\therefore \quad \frac{b}{[B]_o - b[C]} - \frac{b}{[B]_o} = abkt$$

$$\frac{1}{[B]_o - b[C]} - \frac{1}{[B]_o} = akt \qquad (5)$$

$$g = E_C - aE_A - bE_B$$

$D_t = g[C]$ or $[C] = D_t / g$

$D_f = [B]_o g / b$ or $[B]_o = bD_f / g = [A]_o \, g / a$

Substitute $[B]_o$ in equation 5

$$1 \Big/ \left[\left(b \, D_f / g \right) - b \, D_t / g \right] - \left[1 \Big/ \left(bD_f / g \right) \right] = akt$$

$$g / b \left\{ \left[1 / (D_f - D_t) \right] \right\} - (1 / D_f) = akt$$

$$\therefore \quad abkt / g = \left[1 / (D_f - D_t) \right] - (1 / D_f)$$

$$\text{Or } k_{obs} t = D_t / D_f \cdot (D_f - D_t) \qquad (6)$$

Equation 3,4,6, can be used with any reducing agent by altering the values of a and b .

Appendix II

```
5  REM  "((GGSS))THIS PROGRAM FIT TO FIND THE RATE OF REACTION BETWEEN ARTECL3 AND DIFFERENT REDUCING AGENTS "
10  HOME : PRINT : PRINT "INPUT THE CODE NUMBER OF THE REDUCING AGENTS": PRINT : PRINT "(S2O5-2COD. NUM. =1)": PRINT : PRINT
    "(SO3-2COD.NUM.=2)": PRINT : PRINT "(CR+2COD.NUM.=3)": PRINT : PRINT "(V+2COD.NUM.=4)"
15  INPUT WW
20  PRINT : PRINT "INPUT A0 , B0,= INITIAL CON . OF ARTEX3 AND REDUCING AGENT": INPUT A0,B0
30  PRINT : PRINT "INPUT R0 ,R1,= INITIAL AND FINAL PEN READING ": INPUT R0,R1
31  PR# 2: PRINT : PRINT : PR# 0
32  IF WW = 2 THEN  GOTO 36
33  IF WW = 3 THEN  GOTO 37
34  IF WW = 4 THEN  GOTO 38
35  PR# 2: PRINT "ARTECL3=";A0: PRINT "S2O5-2=";B0: PRINT "========": PR# 0: GOTO 40
36  PR# 2: PRINT "ARTECL3=";A0: PRINT "SO3-2=";B0: PRINT "======": PR# 0: GOTO 40
37  PR# 2: PRINT "ARTECL3=";A0: PRINT "CR+2=";B0: PRINT "========": PR# 0: GOTO 40
38  PR# 2: PRINT "ARTECL3=";A0: PRINT "V+2=";B0: PRINT "========": PR# 0
39  PR# 2: PRINT "R0=";R0: PRINT "R1=";R1: PRINT "========": PR# 0
40  PRINT : PRINT "INPUT D,=FINAL ABS, READING": INPUT D
50  DIM F(30),X(30),Y(30),RR(30)
60  PRINT : PRINT "INPUT N,=NO.OF POINTS": INPUT N
70  PRINT : PRINT "INPUT TT,T,=TIME FOR FIRST READING AND TIME INTERVAL": INPUT TT,T: GOTO 80
80  PRINT : PRINT "NOW INPUT THE INDIVIDUL READING, <<< RT >>> , IF YOU LIKE TO START <<< RT>>>AGAIN PRINT -1"
85 M = N - 1
90  FOR I = 0 TO M: INPUT RT
95  IF RT =  - 1 THEN  GOTO 85
100  LET F(I) = ((RT - R0) / (R1 - R0)) * D
110  IF WW = 1 THEN  GOTO 150
120  IF WW = 2 THEN  GOTO 181
130  IF WW = 3 THEN  GOTO 185
140  IF WW = 4 THEN  GOTO 185
150  LET R = (3 * A0) / (4 * B0)
160  IF A0 / B0 > 4 / 3 THEN  GOTO 190
170  IF A0 / B0 < 4 / 3 THEN  GOTO 200
180  IF A0 / B0 = 4 / 3 THEN  GOTO 210
181  LET R = (3 * A0) / (2 * B0)
182  IF A0 / B0 > 2 / 3 THEN  GOTO 190
183  IF A0 / B0 < 2 / 3 THEN  GOTO 200
184  IF A0 / B0 = 2 / 3 THEN  GOTO 210
185  LET R = (3 * A0) / B0
186  IF A0 / B0 > 1 / 3 THEN  GOTO 190
187  IF A0 / B0 < 1 / 3 THEN  GOTO 200
188  IF A0 / B0 = 1 / 3 THEN  GOTO 210
190  LET Y(I) =  -  LOG ((D - (F(I) / R)) / (D - F(I))): GOTO 220
200  LET Y(I) =  LOG ((D - (F(I) * R)) / (D - F(I))): GOTO 220
210  LET Y(I) = F(I) / (D * (D - F(I)))
220  LET X(I) = TT + (T * I)
270 K = K + X(I):J = J + Y(I):C = C + X(I) * Y(I):U = U + X(I) * X(I)
280  LET BB(I) = ((N * C) - (J * K)) / ((N * U) - (K * K))
282  IF WW = 1 THEN  GOTO 293
285  IF WW = 2 THEN  GOTO 295
290  IF WW = 3 THEN  GOTO 297
292  IF WW = 4 THEN  GOTO 297
293  LET KK(I) = BB(I) / ((4 * B0) - (3 * A0)): GOTO 360
295  LET KK(I) = BB(I) / (2 * B0) - (3 * A0): GOTO 360
```

```
297  LET KK(I) = BB(I) / (B0 - (3 * A0)): GOTO 360
300  LET KK(I) = BB(I) / (4 * B0 - 3 * A0)
360  NEXT I
370  FOR I = 0 TO M
380  LET B = 150 / (Y(0) - Y(M)):C = 5 - B * Y(M)
390  HGR : COLOR= 3: HPLOT 5,155 TO 275,5
400  FOR I = 0 TO M:H = 5 + 270 * I / M:V = B * Y(I) + C
410  HPLOT H + 2,V TO H - 2,V: HPLOT H,V - 2 TO H,V + 2: NEXT I
420  PRINT "WOULD YOU LIKE TO HAVE THE PRINT OUT  PRINT (( Y )) OR (( N ))": INPUT A$
430  IF A$ = "Y" THEN 460
440  IF A$ = "N" THEN 520
450  GOTO 420
455  RUN
460  PR# 2: PRINT : PRINT "Y(I)","X(I)"
470  PRINT "=====","====="
480  FOR I = 0 TO M
490  PRINT Y(I),X(I)
500  IF I = M THEN  PRINT "THE LINEAR-LEAST SQUARE MEHTOD GIVES A SLOPE =";KK(I)
510  NEXT I
515  GOTO 570
520  TEXT : PR# 0: PRINT "WOULD YOU LIKE ANOTHER TRY ? //PRINT (Y) OR (N)//"
530  INPUT Q$
540  IF Q$ = "Y" THEN 10
550  IF Q$ = "N" THEN 570
560  GOTO 520
570  PR# 0: TEXT : HOME :
580  PRINT "**** E N D ****"
```

Appendix III

```
5  REM  *** 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
34  DEF  FN Y(YI) = 1 / YI
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#2"
812  PRINT : PRINT NA$;"  (";DA$;")": PRINT
814  PRINT "  ";TITLE$;"  ": PRINT
816  IF S$ < > "Y" THEN 830
820  PRINT ST$: PRINT
825  PRINT "W = WEIGHTING FACTOR.  ": PRINT
830  IF IX = 1 THEN  GOSUB 2000: GOTO 975: REM   * PRINT FULL TABLE
840  GOSUB 2500: REM  * PRINT SHORT TABLE
975 SIGMA =  SQR (SR / (N - 2))
980 DC = SIGMA *  SQR (XX / D)
985 DM = SIGMA *  SQR (SU / D)
999 ::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
1000  REM - REGRESSION PARAMETERS
1020  PRINT "     SLOPE = ";M,"+/- ";DM;"  (";  INT (1000 * DM / M + .5) / 10;"%)": PRINT
1030  PRINT "INTERCEPT = ";C,"+/- ";DC;"  (";  INT (1000 * DC / C + .5) / 10;"%)": PRINT
1035  PRINT "THE VARIANCE OF THE FIT IS ";SIGMA
1040  PRINT "THE CORRELATION COEFFICIENT IS ";  INT (10000 * RO + .5) / 10000: PRINT
1200  PRINT  CHR$ (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$ = "Y" THEN  HOME : GOSUB 3030: HOME : GOTO 50
1320  GOTO 40
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"
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$: PRINT
3200  HOME : RETURN
3999 :::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::::
4000  REM  - TITLE PAGE
4010  PRINT "       xxxxxxxxxxxxxxxxxxxxx"
4020  PRINT "       * LINEAR REGRESSION *"
4030  PRINT "       xxxxxxxxxxxxxxxxxxxxx"
4040  PRINT : PRINT " BASED ON PROGRAM BY K.J.JOHNSON,"
4050  PRINT "<NUMERICAL METHODS IN CHEMISTRY> P. 246"
4060  PRINT : PRINT "THIS PROGRAM FITS DATA Y(X) TO"
4070  PRINT : PRINT "       Y = M*X + C"
4080  PRINT : PRINT "A MAXIMUM OF 40 DATA POINTS MAY BE USED"
4090  PRINT : PRINT "THE METHOD ALLOWS AN OPTIONAL WEIGHTING"
4095  PRINT "OF DATA ACCORDING TO:-"
4100  PRINT : PRINT "+1 FOR UNIT WEIGHTING (W=1)"
4110  PRINT " 0 FOR SCAL WEIGHTING (W=1/Y)"
4120  PRINT "-1 FOR INSTRUMENT PRINT "    (WHERE S IS THE STD. DEV.NPUT "PRESS <E;A$
4200  HOME : PRINT "THIS PROGRAM WILL CONVERT YOUR INPOU EXPECT TO BEPRINT

4210  PRINT "THE CURRENT FUNCTIONS ARE ": PRINT
RE20HELPECUES,ENTERED.": PRINT
4240  PRIIN NEW FUNCTIONS, ORANY OTHER KEY TO USE THE SAME FUNCTIONS.": GET27 THEN 4500
4260 ZX = 1: HOME : LIST 32,34
4270  PRINT : PRINT "DEFINUSED   ABOVE.  USE XI AND YI FOR THE INPUT     VAL4500  PRINT "HIT <ESC>IONS ARE  NOT IDENTITIES.  ": GET A$
```

Appendix IV

The reduction of $ArTeCl_3$ in aqueous dioxane (93% by volume) begins with the hydrolysis of $ArTeCl_3$ which can be represented as:-

$$ArTeCl_3 + mH_2O + [\overset{+}{H}] \xrightarrow{k_1} (Int) + (1+n)[H^+] + \text{other species}$$

Followed by the overall reaction :-

$$(Int)+(3/4)S_2O_5^{2-} +((9/4)-m)H_2O \xrightarrow[\text{fast}]{k_2} (1/2)Ar_2Te_2 +((9/2)-n)[H^+]$$

$+$ other species

Where (Int) is a tellurium containing intermediate, m and n are constants.

Let $[P_t] = 2[Ar_2Te_2]$, at time $= t$

$[H^+]_t = [H^+]_o + (9/2)[P_t]$

Where $[H^+]_o$ is the initial hydrogen ion concentration

$[ArTeCl_3]_t = [Te]_o - [P_t]$

Where $[Te]_o$ is the initial concentration of $ArTeCl_3$

$$\frac{d[P_t]}{dt} = k_r\left\{[Te]_o - [P_t]\right\}\left\{[H^+]_o + (9/2)[P_t]\right\}$$

$$\int_o^{P_t} \frac{d[P_t]}{\left[[Te]_o - [P_t]\right]\left[(2[H^+]_o/9) + [P_t]\right]} = \int_o^t \frac{9k_r}{2}\,dt$$

$$\text{Let} \quad \frac{x}{[Te]_o - [P_t]} + \frac{y}{(2[H^+]_o / 9) + [P_t]}$$

$$= \frac{1}{\Big[[Te]_0 - [P_t]\Big]\Big[(2[H^+]_o/9) + [P_t]\Big]}$$

Then $x - y = 0$ or $x=y$

$$\text{and} \quad x\left\{[Te]_o + (\ 2[H^+]_o \ / \ 9\ )\right\} = 1$$

$$\int_o^{P_t} \frac{d[P_t]}{[Te]_o - [P_t]} + \int_o^{P_t} \frac{d[P_t]}{(2\,[H^+]_o \ / \ 9) + [P_t]}$$

$$= \int_o^{t} k_r \ ((\ 9[Te]_o \ / \ 2\ ) + [H^+]_o\ ) \ dt$$

$$\therefore \ k_{obs} \ t = \ln \left\{ \frac{(2[H^+]_o \ / \ 9) + [P_t]}{[Te]_o - [P_t]} \right\} \left\{ \frac{9[Te]_o}{2[H^+]_o} \right\} \qquad (1)$$

$$\text{Where } k_{obs} = k_r(4.5[Te]_o + [H^+]_o\ ) \qquad (2)$$

The reduction is followed spectrophotometrically , hence:

$D_o = E_1[Te]_o + C$

Where C is constant

$D_t = E_1\Big[[Te]_o - [P_t]\Big] + (\tfrac{1}{2})E_2[P_t] + C$

E_1 and E_2 are the extinction coeffection for the reactant and prod.

$D_t - D_o = E_1[Te]_o - E_1[P_t] + (\tfrac{1}{2})E_2[P_t] + C - E_1[Te]_o - C$

$= ((\frac{1}{2})E_2 - E_1)[P_t]$

$D_f = E_2[Ar]_f + C = (\frac{1}{2})E_2[Te]_o + C$, Where $[Ar] = [Ar_2Te_2]$

$D_f - D_o = ((\frac{1}{2})E_2 - E_1)[Te]_o$

$$\frac{D_t - D_o}{D_f - D_o} = \frac{[P_t]}{[Te]_o}$$

Let $f = [P_t] / [Te]_o$

substitution f in equation 1

$$k_{obs}t = \ln\left\{\frac{(2[H^+]_o / 9[Te]_o + f}{(1 - f)2[H^+]_o / 9[Te]_o}\right\}$$

Let $A = 2[H^+]_o / 9[Te]_o$

Hence, $k_{obs}t = \ln\left[(A + f) / A(1 - f)\right]$

Or $k_{obs}t = \ln\left[(1 + (f/A)) / (1 - f)\right]$

Appendix V

```
5 REM  PROGRAM SAVED AS "LSLF"
10  TEXT : HOME : VTAB (8): PRINT "LEAST SQUARES PROGRAM FOR EQUATION        KT = LOG((1+F/A)/(1-F))"
20  PRINT : PRINT " F = (R-R0)/(RINF-R0), WHERE READINGS    ARE TAKEN AT CONSTANT TIME INTERVALS"
30  PRINT : PRINT " A RANGE FOR TRIAL VALUES OF A WILL BE   REQUIRED"
40  PRINT : PRINT " <PRESS ANY KEY TO START>": GET A$: HOME
50  DIM F(50),T(50),R(50)
55  VTAB (5): PRINT "WHAT TITLE DO YOU WANT FOR THIS DATA?": INPUT A$
56  PR# 2: PRINT A$: PR# 0
60  PRINT : PRINT " WHAT ARE TIME OF FIRST READING AND THE  TIME INTERVAL?": INPUT B,C
70  PRINT : PRINT " WHAT ARE R0 AND RINF?": INPUT D,E:E = E - D
80  PRINT : PRINT " INPUT R VALUES, TYPE -999 TO END":N =  - 1
90  INPUT R: IF R =  - 999 THEN 110
100 N = N + 1:R(N) = R:F(N) = (R - D) / E:T(N) = B + N * C: GOTO 90
110 SS = 1E6
120  PRINT : PRINT "WHAT UPPER AND LOWER VALUES FOR A ARE TO BE TRIED?": INPUT AU,AL
130  PRINT : PRINT "HOW MANY TRIALS ARE TO BE MADE IN THAT  RANGE?": INPUT M
140  FOR I = 0 TO M - 1:A = AL + (AU - AL) * I / (M - 1):Z = 0:Y = 0:S = 0
150  FOR J = 0 TO N
155 L =  LOG ((1 + F(J) / A) / (1 - F(J)))
160 Z = Z + T(J) * L:Y = Y + L * L: NEXT J
170 K = Y / Z: FOR J = 0 TO N:Z =  EXP (K * T(J))
180 Y = (Z - 1) / (Z + 1 / A) - F(J):S = S + Y * Y * E * E: NEXT J
190  IF SS > S THEN 330
200  NEXT I: PR# 0
210  PRINT : PRINT "DO YOU WANT TO TRY ANOTHER RANGE OF A   VALUES?": GET A$: IF A$ = "Y" THEN 120
220  IF A$ = "N" THEN 240
230  GOTO 210
240  PR# 2: PRINT "BEST FIT TO DATA HAS A= "AA", K= "KK"   AND SUM OF SQUARE DIFFERENCES= "SS
250  PRINT "DATA FIT IS AS FOLLOWS: T, R AND RCALC"
260  FOR J = 0 TO N:Z =  EXP (KK * T(J)):Y = E * (Z - 1) / (Z + 1 / A) + D
270  PRINT T(J),R(J),Y: NEXT J
280  FOR J = 0 TO 9: PRINT : NEXT J
290  PR# 0: HOME : PRINT "DO YOU WANT TO TRY ANOTHER SET OF DATA?": GET A$: IF A$ = "Y" THEN 55
300  IF A$ = "N" THEN 320
310  GOTO 290
320  END
330 SS = S:KK = K:AA = A: PRINT S,A,K: GOTO 200
```

Appendix VI

$$A + xCl^- \underset{}{\overset{K_R}{\rightleftharpoons}} A\,Cl_x$$

$$A + B \xrightarrow{k_2} AB$$

$$ACl_x + B \xrightarrow{k_3} A\,Cl\,B + (x-1)Cl$$

$$[A\,Cl_x] = K_R\,[A][Cl]^x \qquad (1)$$

Let $[P] = A\,B\ ,\ \ A\,Cl\,B$

$$\frac{d[P]}{dt} = k_2[A][B] + k_3[A\,Cl_x][B]$$

$$= k_2\,[A]\,[B] + K_Rk_3\,[A]\,[Cl]^x\,[B]$$

$$= (\,k_2 + K_Rk_3\,[Cl]^x\,)\ .\ [A][B]$$

From equation (1) $,\left[[A] + [A\,Cl_x]\right] / [A] = 1 + K_R[Cl]^x$

$$[A] = \frac{[A] + [A\,Cl_x]}{1 + K_R\,[Cl]^x}$$

$$\frac{d[P]}{dt} = \left\{ k_2 + K_Rk_3[Cl]^x \right\} \cdot \left\{ \left(\frac{[A] + [ACl_x]}{1 + K_R[Cl]^x} \right) . [B] \right\}$$

$$= \left(\frac{k_2 + K_Rk_3\,[Cl]^x}{1 + K_R\,[Cl]^x} \right) . \left([A] + [A\,Cl_x]\ .\ [B] \right)$$

At time = 0 , $[A] + [A\,Cl_x] = [a]$

At time = t , $[A] + [A\,Cl_x] = [a - p]$

$$\frac{d[P]}{dt} = \left(\frac{k_2 + K_R k_3 [Cl]^x}{1 + K_R [Cl]^x} \right) \left([a - p][B] \right)$$

For second order reaction:-

$$\underset{[a-P]}{A} + B \xrightarrow{k_r} P$$

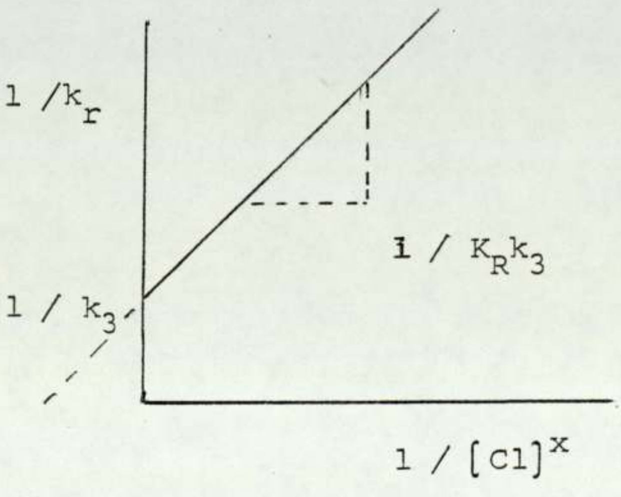
$$\frac{d[P]}{dt} = k_r [a - P][B]$$

Where $k_r = \dfrac{k_2 + K_R k_3 [Cl]^x}{1 + K_R [Cl]^x}$

If $k_2 = 0$

$$k_r = \frac{K_R k_3 [Cl]^x}{1 + K_R [Cl]^x}$$

$$1 / k_r = (1 / K_R k_3).(1 / [Cl]^x) + (1 / k_3)$$



Appendix VII

$$ArTe(OH)_{3-n}Cl_n + xCl^- \overset{K_o}{\rightleftharpoons} ArTe(OH)_{(3-n-x)}Cl_{(n+x)} + xOH^-$$

Where $[Cl] = \left[Y[T] + [KCl] \right]$ and $Y = 3-n$

Let A represent $ArTe(OH)_{(3-n)}Cl_n$ and B represent

$ArTe(OH)_{(3-n-x)}Cl_{(n+x)}$

$$K_o[A][Cl]^x = [B] \qquad (1)$$

$$[A] + [B] = [T] \qquad (2)$$

Where $[T]$ is the total concentration of tellurium species

$$K_o[A][Cl]^x = [T] - [A]$$

$$[A](1 + K_o[Cl]^x) = [T]$$

$$[A] = \frac{[T]}{1 + K_o[Cl]^x} \qquad (3)$$

From equation (1) $[A] = \dfrac{[B]}{K_o[Cl]^x}$

$$[B] = \frac{[T][Cl]^x K_o}{1 + K_o[Cl]^x}$$

$D_{(mix)}$ = total absorbance density i.e the absorbance when both forms of tellurium species are presented in the solution

$$D_{(mix)} = E_A[A] + E_B[B] + C$$

Where E is the extinction coefficient and c is a constant

From equation (2)

$$[B] = [T] - [A]$$

$$D_{(mix)} = E_A[A] - E_B[A] + E_B[T] + C$$

$$= [A](E_A - E_B) + E_B[T] + C$$

Substitution for A in equation (3)

$$D_{(mix)} = \frac{(E_A - E_B)[T]}{1 + K_o[Cl]^x} + E_B[T] + C$$

Whene $[Cl] = 0$ then $E_B = 0$

$\therefore$ the initial absorbance density $D_n = E_A[T] + C$

$$(D_{(mix)} - D_n) = \frac{(E_A - E_B)[T]}{1 + K_o[Cl]^x} + E_B[T] + C - E_A[T] - C$$

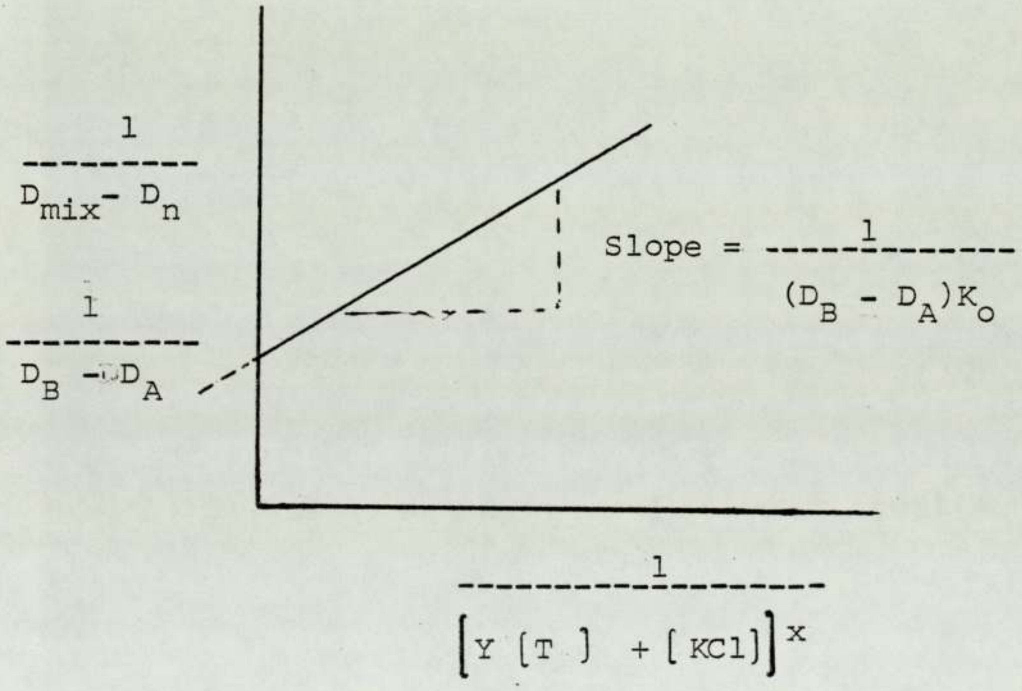
$$= \frac{(E_A - E_B)[T]}{1 + K_o[Cl]^x} + (E_B - E_A)[T]$$

$$= \frac{(E_A - E_B)[T] + (E_B - E_A)[T][1 + K_o[Cl]^x]}{1 + K_o[Cl]^x}$$

$$= \frac{(E_B - E_A)[T]K_o[Cl]^x}{1 + K_o[Cl]^x}$$

$$(D_{mix} - D_n) = \frac{(D_B - D_A)K_o\left[Y[T] + [KCl]\right]^x}{1 + K_o\left[Y[T] + [KCl]\right]^x}$$

$$\frac{1}{D_{mix} - D_n} = \frac{1}{(D_B - D_A)K_o} \cdot \frac{1}{\left[Y[T] + [KCl]\right]^x} + \frac{1}{D_B - D_A}$$


$\frac{1}{D_{mix} - D_n}$
$\frac{1}{D_B - D_A}$
Slope = $\frac{1}{(D_B - D_A)K_o}$
$\frac{1}{\left[Y[T] + [KCl]\right]^x}$

Appendix VIII

```
5  TEXT : HOME : PRINT "MODIFIED PROGRAM TO DEAL WITH AUTO-      CATALYTIC REACTION. HEN ASKED FOR PH    ENTER PEN READING ETC
     .": PRINT : PRINT
10  PRINT "WRITE THE NAME OF THE MIXED SOLVENTS USED": INPUT W$
11  PR# 2: PRINT W$: PR# 0
20  PRINT "B=H AT T=0 AND C=H AT INFINITY"
30  PRINT "K AND A ARE UNKNOWN CONSTANTS.BEST VALUES ARE FOUND BY A PROCESS OF TRIAL AND ERROR TO MINIMIZE THE SUM OF SQ. DIF
     FS. FOR PH"
40  PRINT : PRINT : PR# 0
50  PRINT "KT=LOG((A+H)(C-B)/((A+B)(C-H)))"
60  PRINT "B=H AT T=0 AND C=H AT INFINITY": PRINT : PRINT
70  PRINT "K AND A ARE UNKNOWN CONSTANTS. BEST      VALUES FOUND BY GUESSING AT K AND A TO  MINIMIZE THE SUM OF SQ. DIFFS. FOR
     PH"
80  PRINT : PRINT : PRINT "TRIES 5 VALUES FOR EACH IN SET RANGE": PRINT : PRINT
90  DIM T(30),H(30),L(30)
100  PRINT : PRINT "THE PROGRAM WILL DEAL WITH UPTO 31      POINTS. FOR MORE POINTS ALTER DIM LIMITSIN LINE 90":N =  - 1
110  PRINT : PRINT "WHAT IS TIME OF FIRST READING?": INPUT Z
120  PRINT "WHAT IS THE TIME BETWEEN READINGS?": INPUT X
130 V = 2.303:D = 0: PRINT : PRINT "WHAT ARE THE FINAL VALUES OF PH AND THE PEN READINGS?": INPUT C,E
135  PRINT "WHAT IS THE INITIAL VALUES OF PH AND PEN READINGS": INPUT CC,B
137  PR# 2: PRINT "FINAL PH AND PEN REDINGS ARE=",C,"AND",E
138  PR# 2: PRINT "INITIAL PH AND PEN READINGS ARE=";CC,"AND",B
139  PR# 0
140  LET D = (CC - C) / (E - B)
160  PRINT : PRINT "NOW TYPE IN THE SUCCESSIVE PEN READINGS,AT THE END TYPE IN -1"
170  INPUT F: IF F =  - 1 THEN 200
180 N = N + 1:P(N) = C + D * (E - F)
190 T(N) = X * N + Z:H(N) =  EXP ( - V * P(N)): GOTO 170
200 B =  EXP ( - V * CC):C =  EXP ( - V * C): GOTO 350
210  PR# 0: PRINT : PRINT "DO YOU WANT TO USE THE COMPUTER'S TRIAL VALUES OF "KL" <K> "KU" AND "AL" <A> "AU" ?     -
      ANSWER Y/N>>"
211  GET A$: IF A$ = "Y" THEN 220
212  IF A$ = "N" THEN 214
213  GOTO 210
214  PRINT : PRINT "TYPE IN YOUR LIMITS FOR K AND A"
215  INPUT KL,KU,AL,AU
220  FOR R = 0 TO 4: FOR J = 0 TO 5:K = KL + (KU - KL) * J / 5
230  FOR M = 0 TO 5:A = AL + (AU - AL) * M / 5:S = 0: GOTO 390
260  PR# 2: PRINT K,A,S
270  NEXT M: NEXT J: GOSUB 510
271  NEXT R: PRINT : PRINT : PR# 0: PRINT : PRINT
272  FOR I = 0 TO 4: FOR J = 0 TO 25
274 X =  PEEK ( - 16336): NEXT J: NEXT I
280  PRINT "ANOTHER TRIAL? ANSWER             <Y/N>": GET A$: IF A$ = "Y" THEN 301
290  IF A$ = "N" THEN 310
300  GOTO 280
```

```
301  PRINT "K= "KK" A= "AA" S= "SS: GOTO 210
310 O = 1:K = KK:A = AA: GOTO 390
320  PR# 2: PRINT "DATA FIT LISTING T THEN OBS AND CALC PH"
330  PRINT "USING K= "K"  AND A= "A
340  FOR I = 0 TO N: PRINT T(I),H(I),L(I): NEXT I
345  FOR I = 0 TO 9: PRINT : NEXT I: PR# 0: END
350 D = 0:E = D:F = D:G = D:S = D:SS = 1E6
360  FOR I = 0 TO N:L =  LOG (H(I) / (C - H(I))):D = D + L * T(I)
370 E = E + T(I) * T(I):F = F + T(I):G = G + L: NEXT I
380 K = (D * (N + 1) - F * G) / (E * (N + 1) - F * F):L = (D - K * E) / F:A = C *  EXP (L)
390  FOR I = 0 TO N:E =  EXP (K * T(I))
400 L(I) = ((A + B) * C * E - A * (C - B)) / ((A + B) * E - B + C)
410 S = S + (H(I) - L(I)) ↑ 2: NEXT I
420  IF O = 1 THEN 320
440  IF SS = 1E6 THEN 470
450  IF S > SS THEN 270
460 KD = K - KK:AD = A - AA:KK = K:AA = A:SS = S: GOTO 260
470 SS = S:KK = K:AA = A: PR# 2
475 KL = 0.8 * K:KU = 1.2 * K:AL = 0.8 * A:AU = 1.2 * A
480  PRINT "FIRST APPROXIMATION GIVES K = "K" , A="A" , S="SS: IF S = 0 THEN 220
490  PRINT : PRINT "VALUES OF K,A AND THE SUM OF SQUARED DIFFERENCES ARE ": PR# 0
500 S = 0: PR# 0: GOTO 480
510 KD = (KU - KL) / 2:AD = (AU - AL) / 2: IF (KU - KK) * (KL - KK) = 0 THEN 530
520 KD = 0.6 * KD: GOTO 540
530 KD = 1.5 * KD
540  IF (AU - AA) * (AL - AA) = 0 THEN 560
550 AD = 0.6 * AD: GOTO 570
560 AD = 1.5 * AD: GOTO 570
570 KL = KK - KD:KU = KK + KD:AL = AA - AD:AU = AA + AD
580  IF AL > 0 THEN  RETURN
590 AL = 0: RETURN
```

Appendix IX

The solvolysis of p-EtOPhTeCl$_3$ in general is represented in following sequence:-

$$A + [H^+] \xrightleftharpoons{K_N} B$$

$$A \xrightarrow{k_4} \text{Prod.} + n[H^+]$$

$$B \xrightarrow{k_5} \text{Prod.} + (n+1)[H^+]$$

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 $A \gg B$. For simplicity let Prod. = c

Let L= A+B+C

Assuming B is negligible at time = 0 , then

$A = L - C$

$B = K_N A[H^+]$

$[H^+] = n C$

And $A = L - ([H^+]/ n)$

Then $$d[H^+]/ dt = nk_4A + nk_5B$$

$$= n(k_4 + K_Nk_5[H^+])A$$

$$= (k_4 + K_Nk_5[H^+])(nL - [H^+])$$

$$\int_{H_o}^{H_t} \frac{d[H^+]}{(k_4 + K_Nk_5[H^+])(nL - [H^+])} = \int_o^t dt$$

$$\frac{1}{(k_4 + K_Nk_5[H^+])(nL - [H^+])} = \frac{Z}{k_4 + K_Nk_5[H^+]} + \frac{Y}{nL - [H^+]}$$

Then $K_Nk_5Y - Z = 0$, $Z = K_Nk_5 Y$

And $k_4 Y + nLZ = 1$, $Y(k_4 + n K_N k_5 L) = 1$

$$Y = \frac{1}{k_4 + nK_N k_5 L}$$

$$Z = \frac{K_N k_5}{k_4 + nK_N k_5 L}$$

$$\int_{[H^+]_o}^{[H^+]_t} \frac{K_N k_5 \, d[H^+]}{k_4 + K_N k_5 [H^+]} + \int_{[H^+]_o}^{[H^+]_t} \frac{d[H^+]}{nL - [H^+]} = (k_4 + nK_N k_5 L)t$$

$$(k_4 + nK_N k_5 L)\, t = \ln\Big[(k_4 + K_N k_5 [H^+] - \ln(nL - [H^+])\Big]_{[H^+]_o}^{[H^+]_t}$$

Let $X = K_N k_5 / k_4$ then

$$k_4(1+nLX)t = \ln\left\{\frac{(1 + X[H^+]_t)(nL - [H^+]_o)}{(1 + X[H^+]_o)(nL - [H^+]_t)}\right\}$$

If $nL = [H^+]_\infty$ this becomes

$$k_4(1 + [H^+]_\infty X)t = \ln\left\{\frac{((1/X) + [H^+]_t)([H^+]_\infty - [H^+]_o)}{((1/X) + [H^+]_o)([H^+]_\infty - [H^+]_t)}\right\}$$

If $k_4 = 0$ then

$$K_N k_5 [H^+]_\infty t = \ln\left\{[H^+]_t([H^+]_\infty - [H^+]_o) / [H^+]_o([H^+]_\infty - [H^+]_t)\right\}$$

$$k_{obs} = K_N k_5 [H^+]_\infty$$

$$k_{obs} t = \ln\left\{\frac{[H^+]_t([H^+]_\infty - [H^+]_o)}{[H^+]_o([H^+]_\infty - [H^+]_t)}\right\}$$

APPENDIX (X)

```
5  TEXT : HOME
10  REM  "<<<PROGRAM FIT TO FIND THE RATE OF SOLVOLYSIS OF ARTEX3>>>"
20  REM   "***CODE NAME OF THIS PROGRAM IS((TAHIR))"
30  PRINT : PRINT "WRITE TITLE FOR YOUR CALCULATION": INPUT A$: PR# 2: PRINT : PRINT : PRINT A$: PR# 0
40  PRINT : PRINT "WHAT ARE THE TIME OF FIRST READING AND TIME INTERVALS": INPUT Z,X
50  PRINT : PRINT "WHAT ARE THE FINAL VALUES OF PH AND THE PEN READING?": INPUT C1,R1
60  PRINT : PRINT "WHAT ARE THE INITIAL VALUES OF PH AND THE PEN READING?": INPUT C0,R0
70  PR# 2: PRINT "FINAL VALUES OF PH AND PEN READING ARE=";C1,"AND",R1
80  PRINT "INITIAL VALUES OF PH AND PEN READING ARE=";C0,"AND",R0: PR# 0
90 D = (C0 - C1) / (R1 - R0)
100  DIM T(30),L(30),H(30),P(30),BB(30)
110 V = 2.303
120  PRINT : PRINT "INPUT N=NO. OF POINTS": INPUT N
135  PRINT : PRINT "NOW INPUT THESUCCUSSIVE PEN READINGS"
140 M = N - 1
150  FOR I = 0 TO M: INPUT F
160 P(I) = C1 + D * (R1 - F)
170 T(I) = X * (I) + Z
175 H(I) =  EXP ( - V * P(I))
180 H0 =  EXP ( - V * C0):H1 =  EXP ( - V * C1)
196 L(I) =  LOG ((H(I) * (H1 - H0)) / (H0 * (H1 - H(I))))
197  NEXT I
220  FOR I = 0 TO M
225 K = K + T(I):J = J + L(I):A = A + T(I) * L(I):U = U + T(I) * T(I)
230  LET BB(I) = (N * A - J * K) / (N * U - K * K)
260  NEXT I
270  FOR I = 0 TO M
280  LET B = 150 / (L(0) - L(M)):C = 5 - B * L(M)
290  HGR : COLOR= 3: HPLOT 5,155 TO 275,5
300  FOR I = 0 TO M:H = 5 + 270 * I / M:V = B * L(I) + C
310  HPLOT H + 2,V TO H - 2,V: HPLOT H,V - 2 TO H,V + 2: NEXT I
315  PRINT "PRESS <Y> TO HAVE THE PRINT OUT OR ANY OTHER KEY FOR ANOTHER RUN ": INPUT Y$
317  IF Y$ = "Y" THEN  GOTO 340
320  RUN
340  PR# 2: PRINT : PRINT "VALUES OF L(I) AND T(I) ARE :- "
342  PRINT "L(I)","T(I)"
343  PRINT "====","===="
345  FOR I = 0 TO M
350  PRINT L(I),T(I)
352  IF I = M THEN  PRINT "THE LINEAR-LEAST SQUARE MEHTOD GIVES A SLOPE =";BB(I)
355  NEXT I
360  PR# 0: PRINT "***E N D***": TEXT
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