TO THE MEMORY OF MY FATHER

SOME MECHANISTIC STUDIES OF ORGANOTELLURIUM CHEMISTRY

BY

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SUMMARY

The work in this thesis is concerned with the mechanistic study of some organotellurium compounds, especially the diaryl-ditellurides. The effect of visible irradiation on the diaryl ditellurides in solution containing alcohol is described. The photoreaction was found to proceed under aerobic conditions via the breaking of the tellurium-tellurium bond, and the production of a free radical species is reported. The final product obtained from the photoreaction, an bis(aryltellurenyl)oxide, does not dissolve in organic solvents. The assignment of tellurium oxygen vibrational modes of these products is also given.

The reaction of iodine with diaryl ditellurides through the attack of the tellurium-tellurium bond is described. Evidence is cited for the existence of two species in solution as intermediate products, $Ar_2Te_2.I_2$ and $Ar_2Te_2.2I_2$, 1:1 and 1:2 complexes respectively, in equilibrium with the reactants. The values of the equilibrium constants for the 1:1 (K_1) and 1:2 (K_2) adducts show that the main product in the equilibria is the 1:1 adduct. Kinetic investigations give an independently determined value of K_2 which is in very good agreement with that obtained from the equilibrium studies.

Reactions of the diaryl ditellurides with transition metal complexes via an oxidative addition reaction have been investigated. Vaska's compound reacts with the diaryl ditellurides and kinetic studies using the UV-visible spectroscopic technique are described. The kinetics in each case obey the second order rate law,

$$\text{rate} = k_2 \left[IrCO(PPh_3)_2Cl\right] \left[Ar_2Te_2\right]$$

Infrared investigations show that the carbonyl band is shifted from its position in Vaska's compound ($1955cm^{-1}$) to ($2065cm^{-1}$) immediately after mixing the solutions of the reactants. The formation of a new band due to the carbonyl group of the product is observed. ^{1}HNMR, ^{13}CNMR, ^{31}PNMR and ^{125}Te NMR investigations of the product are also described.

Plausible reaction mechanisms of the above reactions of the diaryl ditellurides are suggested.

Key words

Tellurium
Irradiation
Diaryl Ditelluride
Kinetics

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The work described in this thesis was carried out between 1977 and 1980 at the University of Aston in Birmingham. It has been done independently, and has not been submitted for any other degree.

R. T. Mehdi.

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CHAPTER ONE

INTRODUCTION

The electronic structure of tellurium which is in group VIB of the periodic table is (Kr) $4d^{10}\ 5s^{2}\ 5p^{4}$. As a member of this group tellurium bears a resemblance to selenium and sulphur in many of its properties. On descending the group the elements become more metallic in nature. However, although tellurium shows some metallic properties, it is predominantly non metallic in character. The most common oxidation states are II and IV, other oxidation states are-II, VI.

The main purpose of the work explained in this thesis is to study the mechanisms of some new reactions of organotellurium compounds and some of other well known reactions as well. Although many of the known reactions have been in use for a long time, little or no work has been reported about the kinetics and mechanisms of them. The mechanisms of reactions of carbon compounds and square planar and 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.

The mechanisms of most of the common preparative routes to organotellurium compounds are not completely understood. Either because of difficulties involved in carrying out mechanistic studies or more usually a lack of suitable studies, very often reactions are incomplete, produce many by-products, or are not suitably homogeneous.

Tellurium and its compounds have numerous established uses.(1) One of these applications is in rubber compounding. Tellurium rubber is noted for its resistance to heat and abrasion. In many instances, the addition of tellurium increases the rate of vulcanization and improves the aging and mechanical properties of the elastomer. It is also used to improve the machinability of steel and copper and in ceramics and glass as a colouring agent. It has been used as a catalyst in the oxidation of propylene to acrylic acid in the same way as other catalysts such as cobalt, molybdenum or phosphorus oxide.(2).

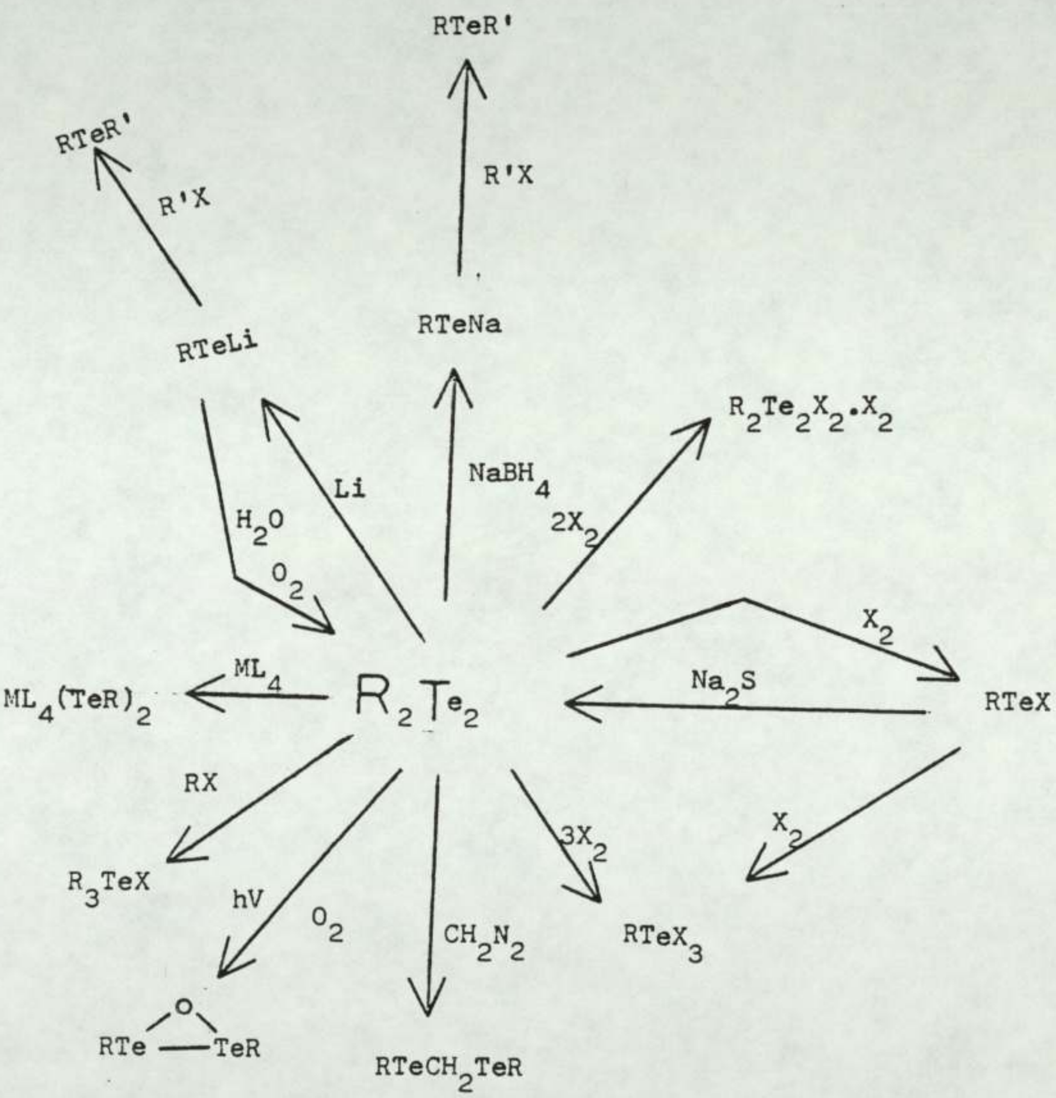
The work described in this thesis concentrates on the diaryl ditellurides, because of their easy preparation, reasonable stability and because of the strong characteristic colour of their solutions in organic solvents. The strong colour makes it easy to study the disappearance of the compound. The present work has mainly involved the investigations of some mechanistic studies using UV-visible spectroscopic techniques.

The work concerning organotellurium compounds which had been carried out up to 1971 has been reviewed by Irgolic.(3) Research during the period 1972 - 1979 has also been reviewed by Irgolic.(4-9) In 1971 Cooper published a book dealing with all aspects of tellurium chemistry, titled "Tellurium".(1)

Each chapter in this thesis contains a detailed introduction of aspects discussed in that chapter.

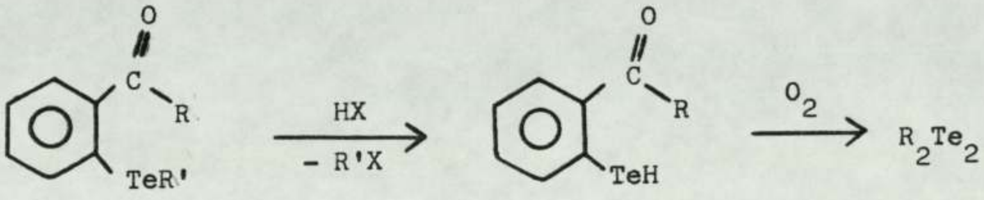
The most common preparative methods of the diarylditellurides are explained in detail in Chapter 2.

Background to Diorganoditellurides



Transformations of Diorganoditellurides

Piette has obtained several diarylditellurides with carbonyl or acetyl groups in the ortho-positions. These are prepared from aryl alkyl tellurides by cleavage of the alkyl group and aerial oxidation of the tellurol intermediate in acidic medium.(10)

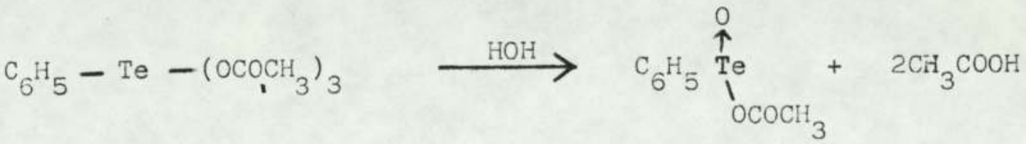


Methantellurol CH_3 TeH has been prepared from dimethyl ditellurides by dissolving the latter in liquid ammonia and was reduced with sodium metal. The solid obtained after evaporating ammonia was then treated with phosphoric acid. Upon melting, the acid reacts with the residue (CH_3 TeNa) to give methanetellurol.(11)

Attempts have been made to synthesize organotellurium acetates from the reaction of diphenylditellurides with lead tetra acetate. This reaction yields mainly the triacetate.(12-14)

$$(C_6H_5)_2Te_2 + 3Pb(OCOCH_3)_4 \xrightarrow{\text{benzene}} 2C_6H_5Te(OCOCH_3)_3 + 3Pb(OCOCH_3)_2$$

This hydrolyzes readily according to the following equation:



$$C_6H_5 - Te - (OCOCH_3)_3 \xrightarrow{HOH} C_6H_5\overset{\overset{O}{\uparrow}}{\underset{OCOCH_3}{Te}} + 2CH_3COOH$$

Phenyllithium telluride, generated from diphenyl ditelluride in tetrahydrofuran solution and lithium metal(15) was treated with alkyl halides to produce alkylphenyl tellurides, C_6H_5TeR. The rate of the ditelluride cleavage reaction is increased when the solution mixes well.

$$C_6H_5\,Te\,Te\,C_6H_5 \quad + \quad 2\,Li \xrightarrow{\qquad} 2\,C_6H_5\,Te\,Li$$

A number of arylalkyl tellurides, ArTeR, have been prepared by a variety of methods, including the reaction of aryl-alkali-metal tellurides, ArTeM(M = Li, Na), with aliphatic halides.

The aryl sodium tellurides, $4\text{-}RC_6H_4TeNa$ (R = H, CH_3, CH_3O) and $2,4-(CH_3O)_2\ C_6H_3TeNa$, were obtained by treating the solutions of diaryl ditellurides in absolute methanol with sodium tetrahydroborate.(56) When the reduction of the diaryl ditelluride was complete, the colour of the solution turned from dark red to light yellow, but these tellurides were not isolated.

It has been found that the orange to red diaryl ditellurides are rather stable compounds which can be handled in air without difficulties.(16) In the present work it is observed that diaryl ditellurides are affected by light under some conditions. When laboratory grade chloroform was used, first of all, as a solvent for ditellurides, it was observed by accident that the colour of diaryl ditelluride solutions disappears gradually over a few days when they are left exposed to light. With other solvents such as toluene, no such change is observed. The presence of the small amount of alcohol (~2%) in commercial chloroform is responsible for the fading of the colour. It was observed that when a toluene solution of a diaryl ditelluride with alcohol is irradiated with visible light under aerobic conditions, the orange/red colour of the ditelluride is bleached.

Therefore, in the preparation methods of the diaryl ditellurides, petroleum ether is recommended to be the best solvent used in the recrystallisation, rather than alcohols as mentioned in the literature. Furthermore, the preparation and the handling of the ditellurides should be carried out in the dark.

When certain ditellurides, such as the perfluoroethyl derivative, which is not affected by water, hexane, acetone or carbontetrachloride are exposed to sunlight for a long time, metallic tellurium is deposited leaving $(C_2F_5)_2Te$ which is unaffected by light.(17)

McWhinnie and Thavornyutikarn found that the 4 - methoxyphenyl derivative, must be stored in an ampoule in the dark. The 4 - phenoxyphenyl compound, slowly decomposes in petroleum ether solution and bis (2 - Naphthyl) ditelluride becomes yellow on storage.(18)

Petragnani and de Moura Campos have explained the formation of diaryl tellurides and ditellurides in the reaction of a Grignard reagent with tellurium tetrachloride on the basis of the following postulated mechanism. This mechanism is supported only by the observation of the final products, Ph_2Te_2, Ph_2Te, and $Te(MgBr)_2$, accompanied with the possibility of a radical dissociation of the ditelluride. This reaction is very complex and variable ratios of products can be obtained.(19)

$$PhMgBr + Te \longrightarrow PhTeMgBr$$

$$PhTeMgBr \longrightarrow PhTe^{\bullet} + MgBr^{\bullet}$$

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

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

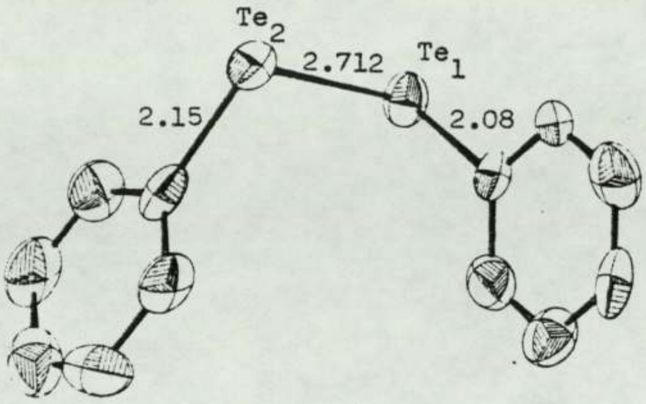
$$PhTe - TePh + PhMgBr \longrightarrow PhTeph + PhTeMgBr$$

Aromatic ditellurides are cleaved by aromatic Grignard reagents in ether solution to give the unsymmetric tellurides in quantitative yields:

$$Ar_2Te_2 + Ar'MgBr \longrightarrow ArTeAr' + ArTeMgBr$$

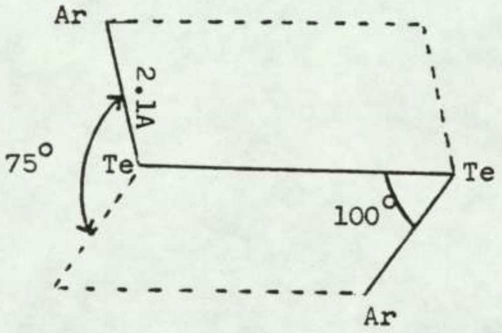
The aryl telluromagnesium bromide, which is formed in this reaction, precipitates, upon addition of petroleum ether. This unstable substance decomposes upon contact with the atmosphere to tellurium and hydrogen telluride.(20)

The structures of a number of diorganoditellurides have been determined from x-ray crystallographic studies. Kruse et al(21) have studied the crystal structure of bis-p-chlorophenyl ditelluride. It was found that the observed tellurium - tellurium and tellurium-carbon bonded separations are 2.702 ± 0.010 A, and 2.131 ± 0.14 A respectively. Similar values have been reported from subsequent investigations on diphenyl ditelluride.(22) It was found that the length of the tellurium - tellurium bond is 2.714 A, while the average of the observed tellurium - carbon bond distance is 2.115 A.



Configuration of diphenyl ditelluride molecule (22)

The C - Te - Te bond angle in diaryl ditellurides has been found to be between 90° and 100°. This indicates that the bonds have a high degree of p character. The C - Te - Te - C dihedral angles are of the order of 75°.



The dihedral angle of a diaryl ditelluride.

Because of the size of the tellurium atom, the tellurium - tellurium bond is both long and weak. Thus it is not surprising, with hindsight, to see that the ditellurides undergo photochemical reactions accompanied by Te - Te bond cleavage as explained in Chapter 3. It is not surprising either to see that when solutions of iodine and the ditellurides are mixed together, the Te - Te bond is cleaved after becoming attached to the iodine (Chapter 4).

Finally, it is not surprising for the ditellurides to undergo an oxidative addition reaction with some of the transition metal complexes, i.e. Vaska's compound, again via the cleavage of the Te - Te bond (Chapter 5).

Some workers have used the organo selenides and the organotellurides as photographic film additive instead of using silver salt. In reference (23) benzyl diselenide and diphenyl mercury of various weight percent mixtures loaded into polymeric matrices such as polyvinylchloride and poly (methylmethacrylate) serve as the basis for high resolution and medium contrast microimaging films. Ultraviolet irradiation of these colourless films results in the formation of dark mercury - selenide images in the light affected areas.

Marsh et al have published a few patents concerning the photosensitive films comprising the organodiselenide compounds, RSe_2R^1 (R,R^1 = alkyl or aralkyl).(24-26)

A microimaging process has been described which involves imagewise UV exposure of a compound consisting of a polymeric binder containing a photochemically reactive diselenide, a tertiary phosphine or phosphite, and an organic peroxide. Heating is then carried out at $>100^{\circ}C$ for a time sufficient to enhance the image contrast.(25)

Microimaging compounds giving stable images of high contrast and resolution, which may be developed by gentle heating, are composed of a polymeric binder containing the same compounds mentioned in reference (25) above.(26)

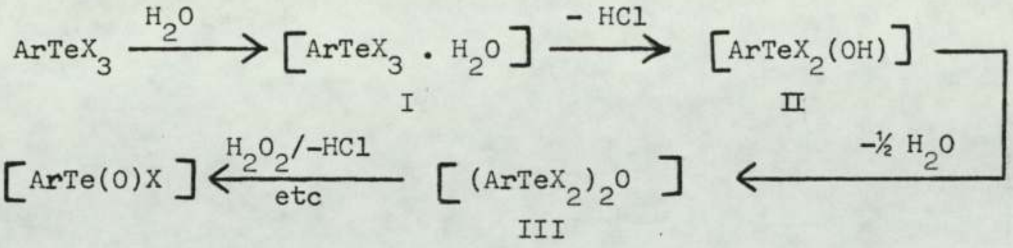
Recently several American and Japanese patents have been published concerning the use of organotellurium compounds in photographic emulsions. In the main the diaryl ditellurides have been used in most of these patents as catalysts. Lelental and Gysling(27) have used the following diaryl ditellurides as catalysts in the heat - developable photographic materials and process:-

Ph_2Te_2, $(p-CH_3C_6H_4)_2$ Te_2, $(p-CH_3OC_6H_4)_2$ Te_2, $(p-BrC_6H_4)_2$ Te_2, and $(1 - naphthyl)_2Te_2$.

Matsui et al(28) published another patent concerning photosensitive imaging materials based on the photoinduced reduction of tellurium compounds. A photosensitizer was used which decomposes the tellurium compound under irradiation with light of the appropriate wavelength.

More details will be given about some organotellurium photosensitive compounds in the introduction to Chapter 3.

Thavornyutikarn and McWhinnie(29) investigated the hydrolysis of phenyl and 4 - ethoxyphenyltellurium trihalides in neutral aqueous media. It was considered to proceed in a stepwise manner in which 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:-



$$\begin{tikzcd}
ArTeX_3 \arrow[r, "H_2O"] & \left[ArTeX_3 \cdot H_2O\right] \arrow[r, "- HCl"] & \left[ArTeX_2(OH)\right] \arrow[d, "-\frac{1}{2} H_2O"] \\
\left[ArTe(O)X\right] & \left[(ArTeX_2)_2O\right] \arrow[l, "H_2O_2/-HCl"', "etc"] & \arrow[l]
\end{tikzcd}$$

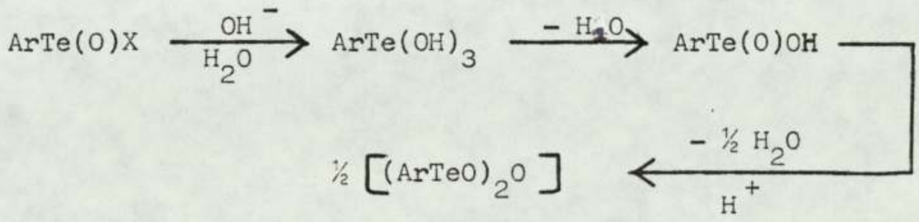
I

II

III

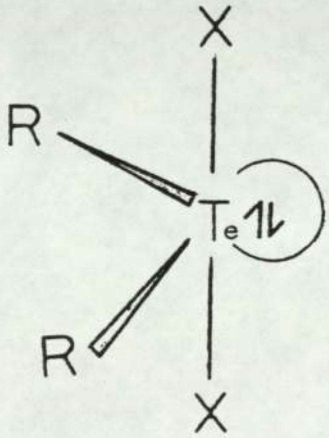
Attempts to isolate compounds corresponding to III failed. Only ArTe(O)X, or a mixture of $ArTeX_3$ and ArTe(O)X, could be obtained at various reaction times and conditions. Thus, if stages corresponding to II and III are involved, the intermediates must be short lived.

The hydrolyses of $ArTeX_3$ and ArTe(O)X in alkaline media also lead to the formation of similar compounds, hence the initial stage of these reactions probably follows a scheme similar to the above equation. The product isolated from the alkaline medium shortly after mixing has the composition $(p - EtO\ C_6H_4)\ TeO(OH)$ which, on acid treatment, is converted to $[(p - EtO\ C_6H_4)\ TeO]_2O$ therefore a scheme such as the following equation is appropriate:-



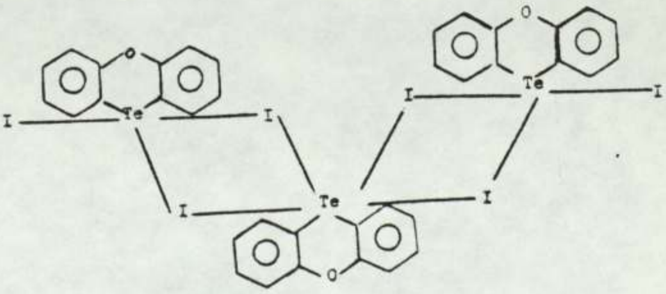
$$\begin{tikzcd}
ArTe(O)X \arrow[r, "OH^-", "H_2O"'] & ArTe(OH)_3 \arrow[r, "- H_2O"] & ArTe(O)OH \arrow[d] \\
& \frac{1}{2}\left[(ArTeO)_2O\right] & \arrow[l, "- \frac{1}{2} H_2O", "H^+"']
\end{tikzcd}$$

McWhinnie et al$^{(30)}$ have calculated that in a series of the diorganotellurium dihalides R_2TeX_2 (R = p - tolyl, o - tolyl, p - $MeOC_6H_4$, C_6F_5 ; x = Cl, Br, I), the molecules have Ψ- trigonal bipyramidal structures with axial halogen atoms, (represented by group x in the structure given below), regardless of the nature of the substituents in the aryl ring. The equatorial positions are occupied by the two remaining organic groups and the non-bonding electron pair, which are of predominantly s character.



It has been suggested that in all the examples which have been studied, the axial bonds have been longer and weaker than the equatorial bonds.

McCullough$^{(31)}$ has determined the structure of phenoxatellurium 10, 10 - diiodide, $C_{12}H_8OTeI_2$. It was found that tellurium forms bonds with carbon atoms at 2.09 and 2.11 A. It also forms weak bonds with iodine atoms in each of two neighbouring molecules with Te----I distances of 3.739 and 3.788 A.



CHAPTER TWO

2. Experimentation

2.1 Chemicals

All chemicals used were obtained from the usual commercial sources and 'AnalaR' grades were used when necessary. The important starting material, tellurium tetrachloride ($TeCl_4$)was supplied by British Drug House (BDH) in a sealed bottle. The precious metal salts (Pt, Ir) were purchased from Johnson Matthey Chemicals Ltd.

2.2 Solvents

All solvents used were obtained from commercial sources. If pure solvents were needed, they were purified according to the standard literature methods.(32) Generally all the solvents were dried and distilled prior to use.

When deoxygenated solvent was required the solvent was frozen in liquid nitrogen and the flask connected to a vacuum line to remove air. This procedure was repeated three times at least for each solvent.

2.3 Physical Measurements

2.3.1 Ultra Violet and Visible Absorption Spectroscopy

Ultra violet and visible absorption spectra and kinetic studies were taken on a Pye Unicam SP8 - 100 spectrophotometer (or) and Pye Unicam SP6 - 400 spectrophotometer used in conjunction with a Pye Unicam AR 55 linear recording unit. The solution spectra were measured in the range 1000 - 280 nm. The solution and the solvent for comparison were both contained in either 4cm, 1cm, or 0.5cm, glass or quartz cells.

The cell compartments of these spectrophotometers are 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 taken on a Perkin Elmer 457 or a Perkin Elmer 599B spectrophotometer , on the range of 4000 - 250 cm^{-1} and 4000 - 200 cm^{-1} respectively. The solid state spectra were recorded either as a nujol mull, or as a potassium bromide disc, or Caesium iodide plates. Solution spectra were recorded, using a matched pair of semi-perm cell type 1010, path length 1mm with sodium chloride windows.

2.3.3 Electron Spin Resonance (ESR) Spectroscopy

The ESR spectra of complexes were determined at room temperature in solution, using JEOL JES-PE-1 spectrometer in the department.

When the sample had to be irradiated while placed within the cavity of the ESR machine, two convex lenses (10cm focal length) were used to focus the light from a photographic bulb (275 watt) directly on to the sample capillary.

2.3.4 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton magnetic resonance spectra were run on a Perkin Elmer R12B spectrometer, operating at 60 MHz and 34°C, or Varian HA 100D spectrometer at 100 MHz and 32°C. Appropriate solvents were chosen for each sample and tetramethyl siliane (TMS) was used as an internal reference. A JEOL FX 90Q fourier transform NMR instrument has also been used recently, operating at 90 MHz and 35°C, to determine the NMR spectra of ^{1}H (89.56 MHz), ^{13}C (22.50 MHz) and ^{31}P (36.20 MHz).

^{125}Te NMR spectra were recorded on the Brucker FT multinuclear NMR spectrometer of the Universite de Rouen in France.

2.3.5 Thin Layer Chromatography (TLC)

The TLC on silica with a standard eluotropic series of solvents was employed, to determine the number of species present in certain solutions. Chromatograms were developed with iodine.

2.3.6 Melting Points

The melting points of all solid compounds were determined with a Gallenkamp melting point apparatus and are uncorrected.

2.4 Computation

All computer programmes were written in either algol or basic, and run on an ICL 1905A computer at the Computer Centre, University of Aston, Gosta Green, Birmingham, B4 7ET.

2.5 Analysis

Micro-analysis for carbon, hydrogen, phosphorous and halogen were done by the micro-analytical laboratory of the Chemistry Department. Tellurium was determined as below.

2.6 Volumetric Determination of Tellurium in Organic Compounds(33,34)

The sample containing 0.075 to 0.25 gm of tellurium was weighed into a 400 ml beaker. Concentrated nitric acid (10ml) was added, and the mixture was warmed until a pale coloured solution was obtained. It must not be permitted to go to dryness. After cooling, 1:1 nitric acid (10ml) and 70% perchloric acid (10ml) were added, and the mixture was then continuously heated until strong fumes of perchloric acid and a colourless solution were obtained. When the volume became less than (10ml) the solution was cooled and diluted to (200ml), and sufficient 0.1 N potassium dichromate was added to provide an excess of at least (5ml).

The solution was stirred and was allowed to stand at room temperature for at least 30 minutes. Excess 0.1N ferrous ammonium sulphate was then added, and the mixture was back-titrated with the 0.1 N potassium dichromate solution, using N-phenyl anthranilic acid as indicator, which added just before the back-titration.

2.7 Kinetic Studies by the Use of a Flow System

2.7.1 Apparatus for Flow Studies

This apparatus was designed to undertake a kinetic study of the photochemical reaction of diarylditelluride at fixed temperatures. The apparatus is diagramatically shown in Fig. 1, and consists basically of a 100ml round bottomed flask, enclosed in a glass jacket with provision for a continuous flow of water from a thermostated water bath to keep the contents of the flask at a constant temperature.

With the help of a peristaltic pump, the toluene solution of the ditelluride is continuously passed through a 1cm quartz cell for spectrophotometric measurement.

It was found that PVC is the best material for the flexible tubing as it is less affected by the organic solvents.

The tube leading to the spectrophotometer has a bypass arm; Y shape glass tube; which can take any excess solution back to the flask. The round bottomed flask is serviced by rubber bung; size 10mm; which contains the tubes of the peristaltic flow circuit.

The irradiation of the contents of the reaction flask is done by using a 60 watt domestic light bulb fixed at a distance of 6cm lower than the flask.

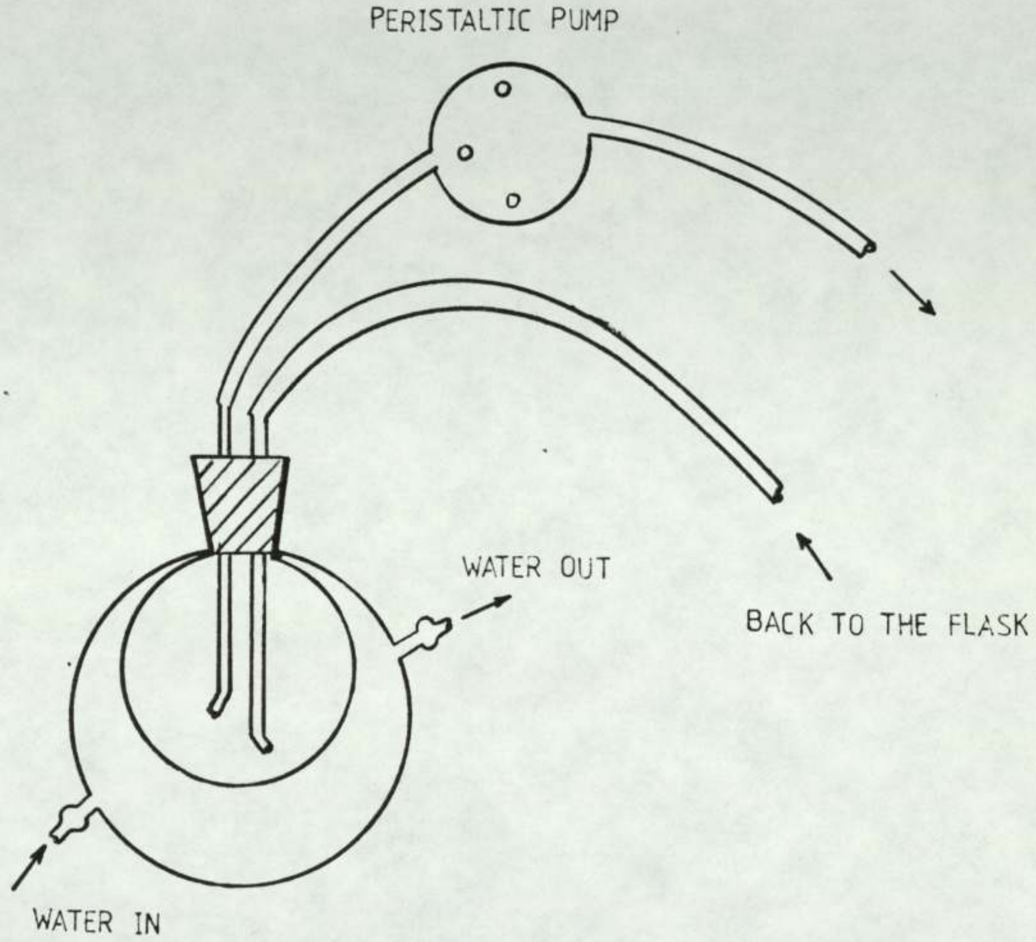


Figure 1

Apparatus used in the study of the photochemical reaction of diaryl ditelluride at fixed temperature.

2.7.2 Procedure

The thermostating assembly of the water bath is adjusted to the required temperature and switched on. The peristaltic flow circuit is flushed through, first with pure toluene, so that the tubes become saturated with the solvent. At the same time the spectrophotometer is zeroed.

In a similar fashion, the toluene solution of the compounds under study is pumped continuously through the flow cell and back to the flask in a closed circuit, at the rate of about 40ml/min., for about 10 minutes to bring the reaction mixture, to the constant temperature of the water bath. Then the 60 watt light bulb is switched on and the recording of the absorbance measurements started simultaneously.

After the completion of each experiment, the flask is emptied and the whole assembly is washed with acetone and dried. The flexible tubings are replaced periodically.

The experimental technique is essentially the same for all the kinetic studies carried out by flow system. Therefore, a generalized procedure is described above. Wherever specific differences arise they are mentioned in the relevant section.

2.7.3 Equipment

Spectrophotometer, Pye Unicam SP6 - 400 used with a Pye Unicam AR 55 linear recording unit, and Pye Unicam SP8 - 100 spectrophotometer.

Peristaltic pump

Thermostat bath

Circulating pump

60 watt domestic light bulb.

2.8 Kinetic Studies by the Use of a Dual Syringe System

2.8.1 Apparatus for a Stopped-flow Studies

In contrast to the previously explained system, this apparatus was designed to carry out the kinetic studies of fast reactions which could not be studied by the methods usually available. This apparatus is diagramatically explained in Fig. 2. It consists of two interconnected glass syringes enclosed in a glass jacket through which water at a constant temperature can flow.

Each of the two dual syringes is equipped with a tap, the purpose of which is to allow the liquids to be drawn in to the syringes, from the separate reservoirs. When the taps are turned into a different position, and the plungers of both the syringes simultaneously pressed, the solutions can be delivered to the mixing chamber, leading to the spectrophotometer cell.

2.8.2 Procedure

Before the start of the experiment the dip cooler is switched on to bring the temperature of the cooling water (containing the recommended amount of methanol$^{(35)}$ down to about 6°C. Then the

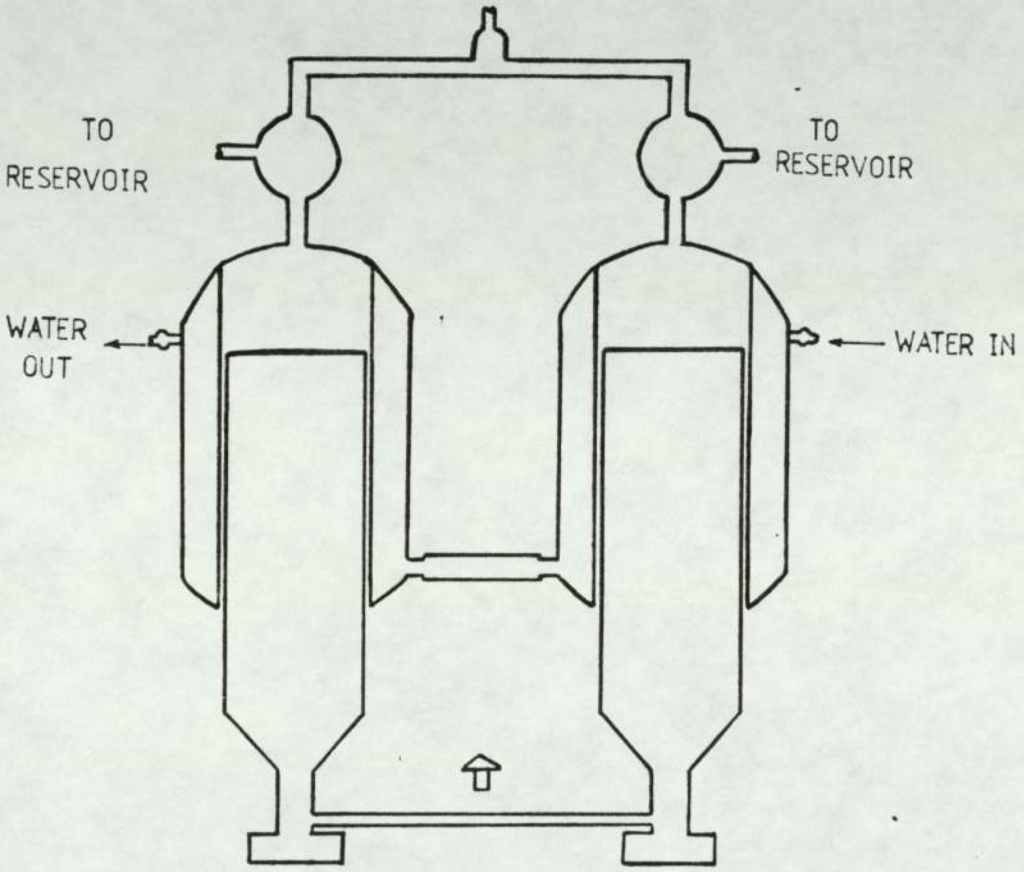


Figure 2

A dual syringe system used for stopped-flow studies of fast reactions.

circulating pump is switched on and the two reacting solutions drawn into the respective syringes.

Although the two solutions have been cooled down to the desired temperature, but beforehand they are left in the syringe assembly for a few minutes to reach a constant temperature.

After the spectrophotometer has been zeroed, and the recorder switched on, the plunger on the syringes is pushed gently. This transfers the two solutions to the mixing chamber where they can react together, the resultant solution being delivered to the spectrophotometer cell.

A problem is encountered in this experiment that because of the low temperature, about 6°C, of the solutions, there was a great amount of condensation on the outer surface of the quartz spectrophotometer cell. This is overcome by placing dry silica gel within the cell housing, in addition to flushing it with nitrogen to minimize further the moisture content of the air around the cell.

2.8.3 Equipment

Spectrophotometer Pye Unicam SP8 - 100
RU 5 Dip Cooler machine
Circulating pump.

2.9 Preparations

2.9.1 Diaryl Ditellurides

All of the diaryl ditellurides are prepared according to the methods mentioned in the literature, with slight modifications, i.e. all of the preparations and manipulations of the diaryl ditelluride solutions are carried out in the dark. Also petroleum ether is used as a recrystallisation solvent instead of alcohol as recommended in some methods.

2.9.1.1 Preparation of Bis-p-phenetyl Ditelluride(36)

2.9.1.1.1 p-phenetyltellurium Trichloride

Phenetol (17.0g), tellurium tetrachloride (12.0g) and dry chloroform or carbon tetrachloride (75ml) are mixed together, and heated under reflux with exclusion of moist air, during 2 hours. Hydrogen chloride is evolved and the solid dissolved. During heating a copious precipitate of glistening yellow flakes, consisting of practically pure p-phenetyltellurium trichloride, which was removed after one day, washed with a little cold chloroform, and dried. Yellow crystals (14.6g) were obtained and melted at 184 - 186°C (lit.(36) 182 - 183°C), without further recrystallization.

(Found : C, 27.0%, H, 2.5%; $C_8H_9Cl_3OTe$ requires: C,27.1%, H, 2.55%).

2.9.1.1.2 Bis-p-phenetyl Ditelluride

p-phenetyltellurium trichloride (6g) was reduced, at 0°C with (11.3g) of potassium metabisulphite in water (50ml). The solution was slowly added, with continuous stirring. The orange precipitate appeared, after the solution was used up, stirring was continued for another hour. The product was filtered and dried over P_4O_{10} in a vacuum desiccator. The ditelluride was then recrystallized from petroleum ether (bp 80 - 100°C) in fluffy masses of brilliant, orange-red needles or golden-orange plates, melting at (102 - 104°C) to a deep red liquid (lit.(36) 107 - 108°C). (Found : C, 38.5; H, 3.6; Te, 51.3; requires: C, 38.6; H, 3.6; Te, 51.3%).

2.9.1.2. Diphenyl Ditelluride(37)

Phenylmagnesium bromide (45.3g) which was prepared from 52g of phenylbromide and 8g of magnesium; in 250ml of tetrahydrofuran; was placed in a 500ml Erlenmeyer flask, which was kept open to the atmosphere. Tellurium powder (33g) was stirred into the Grignard solution. The reaction started in a few minutes. As soon as some ditelluride had formed, by the appearance of a red colour, the solution was cooled to 0°C. Oxygen was flowed into the flask from time to time for an hour. The mixture was then warmed to room temperature and stirred for an addition 1.5h. The mixture was then poured into a large beaker and allowed to stand overnight in contact with the atmosphere.

The solid red product was treated with an aqueous ammonium chloride solution. From this heterogeneous mixture the diphenyl ditelluride was extracted with diethyl ether. Orange-red crystals of diphenyl ditelluride were obtained upon evaporation of the ether. The ditelluride was then re-crystallized from petroleum ether (bp 30 - 40°C). The orange needle crystals are melted at 65 - 66°C (lit.(37) 66 - 67°C).

(Found : C, 35.3; H, 2.5; Te, 62.3; requires: C, 35.3; H, 2.5: Te, 62.3%).

2.9.1.3 Bis-p -chlorophenyl Ditelluride(38)

2.9.1.3.1 p-chlorophenyltellurium Trichloride

A mixture of (2.7g) of tellurium tetrachloride and (3.5g) of p-chlorophenyl mercuric chloride in (30ml) of dry dioxane, was boiled for 4 hours in a round bottomed flask fitted with a reflux condenser protected by a calcium chloride tube. The colourless plates of the complex compound of mercuric chloride with dioxane were filtered off, and dioxane was vacuum-distilled from the filtrate. The residue was crystallized from a large volume of benzene to remove traces of mercuric chloride. The substance was recrystallized from a mixture of benzene and petroleum ether. (Found : C, 20.2; H, 1.2; $C_6H_4TeCl_4$ requires: C, 20.9; H, 1.2%).

2.9.1.3.2 Bis-p-chlorophenyl Ditelluride

A ground mixture of (.01 Mole) of the p-chlorophenyltellurium trichloride and (.08 mole) of $Na_2S.9H_2O$ was heated with stirring in a boiling water bath for 20 - 30 minutes. The resulting mixture was diluted with ice water, and precipitate of the diarylditelluride was filtered off, washed with water, dried in a vacuum desiccator, and recrystallized from petroleum ether or benzene. The percentage of Te found was 53.5; $C_{12}H_8Cl_2Te_2$ requires Te 53.4%.

2.9.1.4 Bis-p-tolylditelluride(39)

2.9.1.4.1 p-tolyltelluritrichloride

The procedure was carried out similar to the synthesis of p-chlorophenyltelluritrichloride. p-tolylmercuric chloride (3.3g) and tellurium tetrachloride (2.7g) were refluxed for one hour in dry dioxane (20ml). The colourless crystals were obtained from benzene-petroleum ether, melted at 180° - 182°C. On analysis the percentage of C, H, and Te found were 25.8; 2.9 and 39.4 respectively. $C_7H_7TeCl_3$ requires C 25.8, H 2.9, Te 39.3%.

2.9.1.4.2 Bis-p-tolylditelluride

p-tolyl telluritrichloride (1.3g) was dissolved in 2N sodium hydroxide (5ml) and neutralized with dilute acetic acid, causing the separation of a white amorphous solid. Potassium metabisulphite (2g) was then added and after standing for 30 minutes at room temperature the solution was extracted with ether. After drying and evaporating, the crude ditelluride was recrystallized from ether, it formed bright orange felted fibres, m.pt. (50 - 52°C) lit(39) (52-54°C). On analysis the percentages of C, H and Te found were 38.3; 3.2 and 58.5 respectively. $C_{14}H_{14}Te_2$ requires C 38.4, H 3.2, Te 58.4%.

2.9.2 Sublimation of Iodine(40)

This process is employed to separate volatile substances from non-volatile impurities. The iodine was placed in a porcelain dish, and was gently heated, the vapour then condensed upon a flask containing cold water.

Iodine (10g) was ground together with (4g) potassium iodide; any chloride or bromide present will thus be retained as the non-volatile potassium salts; the mixture was transferred to a beaker, a flask almost filled with cold water was placed on the beaker. It was heated gently until sufficient iodine was sublimed on to the bottom of the flask, after allowing to cool, the flask was removed with iodine adhering to it. Cold water was passed rapidly through the flask; then the whole of the crust was removed by a clean glass rod and was collected on a clock glass.

The sublimation was then repeated without the addition of potassium iodide. The sublimate was removed as before and dried in a desiccator containing calcium chloride.

2.9.3 p-phenetyltelluriumtri-iodide(41)

Bis-p-ethoxyphenyl ditelluride (1.0g) reacted with iodine (1.6g) in carbon tetrachloride. The product obtained was recrystallized from benzene afforded black needle crystals, which melted at

133 - 134°C (lit.(41) 133 - 134°C).

(Found : C, 15.5; H, 1.4; $C_8H_9I_3O$ Te requires: C, 15.3; H, 1.45%).

2.9.4 Tetrakis (triphenylphosphine) platinum (0)(42)

Triphenylphosphine (15.4g) was dissolved in (200ml) of absolute ethanol at 65°C. When the solution was clear a solution of (1.4g) of potassium hydroxide in a mixture of 32ml of ethanol and 8ml of water was added. Then (5.24g) of potassium tetrachloroplatinate (II) dissolved in 50ml of water was slowly added to the alkaline triphenylphosphine solution while stirring at 65°C. The addition should be completed in about 20 minutes. A pale yellow compound begins to separate within a few minutes. After cooling the compound was washed with 150ml of warm ethanol then with 60ml of cold water, and again with 50ml of cold ethanol. The resulting yellow powder was dried in vacuo for 2 hours. The compound must be stored under pure nitrogen.

2.9.5 Trans-chlorocarbonylbis (triphenylphosphine) iridium(43)

In a 250ml round bottomed flask (3.25g) of iridium (III) Chloride 3-hydrate was mixed with (13.1g) of triphenylphosphine, and 150ml of dimethylformamide, the mixture was heated at vigorous reflux for 12 hours. The resulting red-brown solution was filtered while hot, 300ml of warm methanol was rapidly added with stirring.

The mixture was then cooled in an ice bath, and the yellow crystals were collected on a filter and washed with 50ml of cold methanol.

2.9.6 Pentacyanocobaltate (II)(44)

The solution of ($Co(CN)_5^{3-}$) was simply prepared by addition of excess potassium cyanide to a solution of cobaltous chloride; about 6 : 1 ratio in concentrations respectively; in an inert atmosphere. The light brown cobaltous cyanide which initially precipitated re-dissolved forming an olive-green solution of the penta co-ordinate complex anion. It was found that the reaction took place both in the aqueous and methanolic media as mentioned in the literature.(45)

2.9.7 Phenetyllithium Telluride(46)

Bis-p-phenetyl ditelluride (0.01 mol) was dissolved in dry tetrahydrofuran (100ml) and placed into a 250ml three necked flask equipped with a high speed wire stirrer and a nitrogen inlet tube. The solution was kept under an inert atmosphere of nitrogen. Freshly cut small pieces of lithium metal (0.02 mol) were added through the third neck.

The mixture was stirred for eight hours at room temperature, then the initially dark red solution became yellowish-brown. After the removal of the unreacted lithium metal, the spin trap was added to stabilise the free radical of p-phenetyltelluride. The mixture was added to a capillary tube and an ESR spectrum of this sample was obtained.

2.9.8 Phenetyl Lithium

Butyl lithium (0.1 mole) was added to p-phenetyl bromide (0.1 Mole) under an inert atmosphere. A dry box was used to maintain the protection from moisture. The spin trap was added to stabilise the free radical of p-phenetyl. The reactants were mixed well, and added to a capillary tube. The ESR spectrum of this sample was obtained.

2.9.9 Filter Solution for Isolation of the Wavelengths Region Between 4045 - 4078A

Components	1	2	3
	$CuSO_4.5H_2O$ 0.44g/10ml. 2.7M NH_4OH	$I_2$0.75g in 100ml CCl_4	Quinine hydrochloride, 2g/100ml. H_2O
Path Length	10cm	1cm	1cm

Fig. 3 illustrates the transmission of the filter combination for isolation of the wavelengths region between 4045 - 4078A due to the literature.(47)

The absorbance spectra shown in Fig. 4 for the filter components, shows the window which had been left for the wavelengths around 4000A. This filter was used to determine the quantum yield of the radiation as explained in the next section.

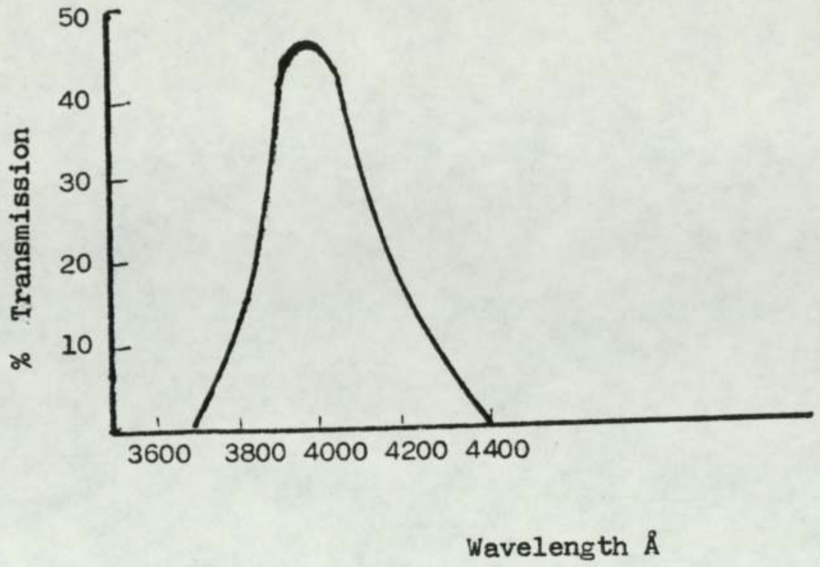


Figure 3 : Transmission of the filter combination for isolation of 4045 - 4078A wavelengths.

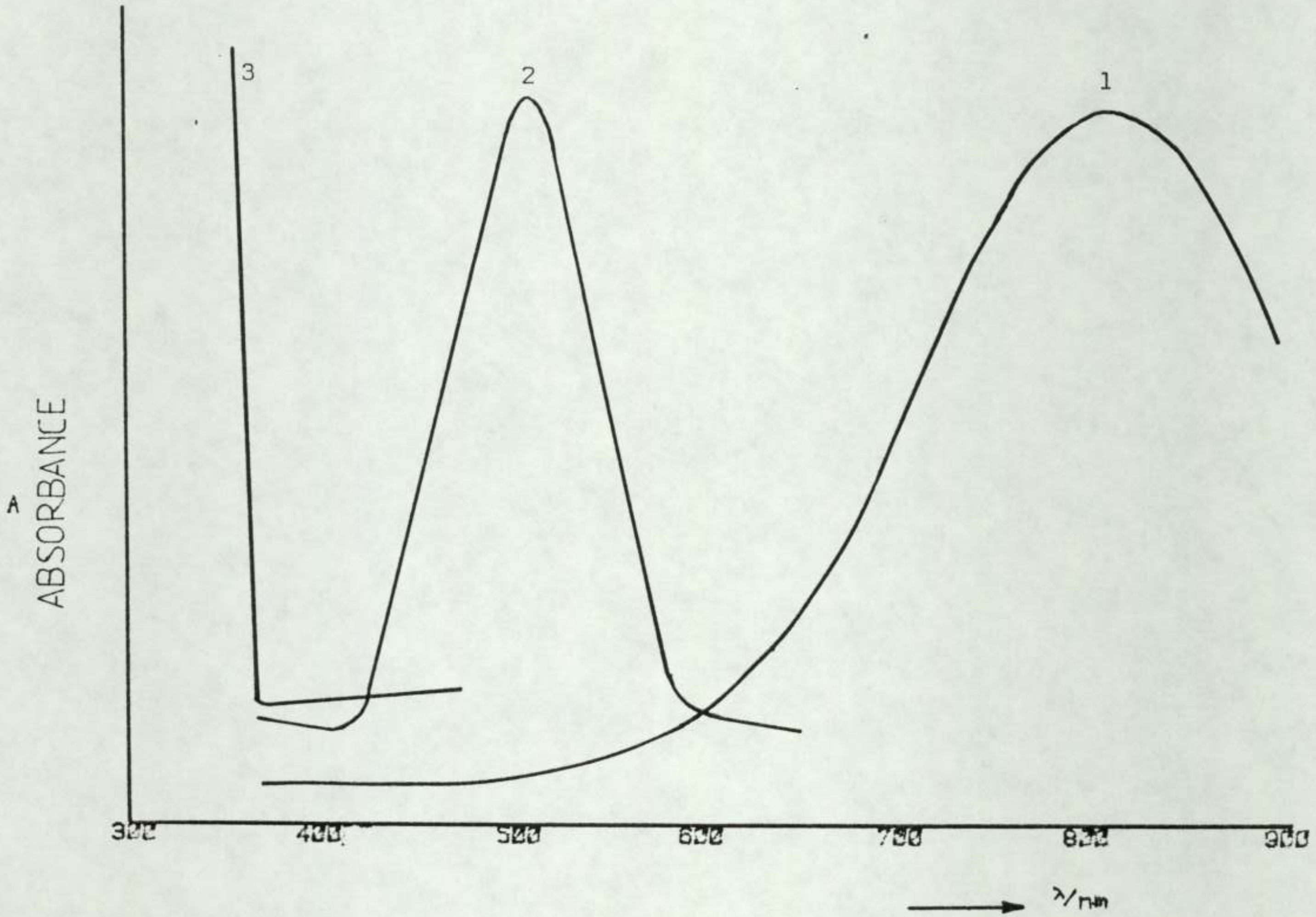


Figure 4 The absorbance spectra of the filter solution components:-

1 - cupric sulphate; 2 - iodine; and 3 - quinine hydrochloride.

2.9.10 Liquid Phase Chemical Actinometry(48)

2.9.10.1 Reagents

Solution of 0.1% (by weight) 1,10 - phenanthroline in water. Buffer solution prepared from 600ml of 1N NaO_2CCH_3 and 360ml 1N H_2SO_4 diluted to 1 litre. Solution of 0.15 M potassium ferrioxalate.

2.9.10.2 Preparation of Potassium Ferrioxalate

Pure solid reactant was prepared by mixing 3 volumes of 1.5M $K_2C_2O_4$ solution and one volume of 1.5 M $FeCl_3$ solution with vigorous stirring. The precipitated $K_3Fe(C_2O_4)_3.3H_2O$ **was** re-crystallized three times from warm water and then dried in a current of warm air.

In the present work with the ditelluride, calculations show that essentially all the light incident on the reactants is absorbed. To determine the intensity of the incident radiation 0.15 M solution of potassium ferrioxalate was used as recommended in the literature.(48)

To prepare 0.15 M solution of $K_3Fe(C_2O_4)_3$, (7.37g) of the solid were dissolved in 80ml of H_2O, 10ml 1.0N H_2SO_4 were added, and the solution was diluted to 100ml and mixed. For all quantitative work the preparation and the manipulation of the ferrioxalate solutions must be carried out in a dark room.

2.9.10.3 Determination of the Quantum Yield(48)

To determine the quantum yield, the following procedure had been followed:

1. To the round bottomed flask mentioned in Section 2.7.1, 85ml of potassium ferrioxalate 0.15M solution was added, as an actinometer. It was irradiated for 80 minutes, after that 10ml of the photolyte solution was taken into a small volumetric flask of 25ml. About 2ml of the phenanthroline solution and 5ml of buffer solution (both mentioned in Section 2.9.10.1) were added. The solution then diluted to the mark of the flask with water, mixed well and allowed to stand for one hour.

Another solution was prepared as an identical but un-irradiated, for use as the blank in the reference beam, and it was allowed to stand as before. Then the transmission of the solution was measured in the spectrophotometer at 510 nm in a 1cm quartz cell, using the blank solution in the reference beam.

2. The toluene solution of 10^{-3}M bis-p-phenetylditelluride with 20% ethanol was added to the flask mentioned above, instead of the ferrioxalate solution and was irradiated through the filter solution as described above. The absorbance was monitored in the spectrophotometer at 395 nm each 30 minutes.

2.9.11 Attempts to React Tetrakis (triphenylphosphine) Platinum with Diarylditellurides

Bis-p-phenetylditelluride 2.48g was dissolved in 150ml of dry toluene in a round bottomed flask 250ml which was surrounded by aluminium foil. Platinum tetrakis-triphenylphosphine 6.2g was added with continuous stirring under dry nitrogen.

The mixture was kept stirring for 24 hours, but no reaction seems to take place.

2.9.12 Reaction Between Potassium Pentacyanocobalt and Diarylditelluride

This reaction was followed by adding two different amounts of the diarylditelluride, as described below:

1. Bis-p-phenetylditelluride 2.48g was dissolved in 200ml of warm methanol, and then added to a 0.005mol solution of freshly prepared potassium pentacyano cobalt as described in Section 2.9.6, in a 500ml round bottomed flask surrounded by aluminium foil.

The mixture was then stirred for a few minutes under an inert atmosphere, then the solvent removed with the help of a rotatory evaporator and the product obtained.

2. The above procedure was also repeated using trace amounts of bis-p-phenetyl ditelluride instead of the larger quantities mentioned above. The product obtained in both cases could not be characterised fully.

2.10 Preparation of Some New Compounds

2.10.1 Bis(p-ethoxyphenyltellurenyl) Oxide

The toluene solution of bis-p-phenetylditelluride (.005M) in presence of a small amount of ethanol, was irradiated with visible light from a 60 watt domestic bulb. After irradiating the reaction mixture for one hour, the orange-red colour of the solution had disappeared. After evaporation of the solvent an oily product was obtained, which was dried under vacuum.

The dried solid bis(p-phenetyltellurenyl)oxide was found to melt at 150°C, and the elemental analysis yielded the following values for carbon, hydrogen and tellurium respectively, 37.7; 3.6 and 50 percent. $C_{16}H_{18}O_3Te_2$ requires : C 37.5; H 3.5; Te 49.5%.

In the same way diphenylditelluride was irradiated and the product obtained was bis (phenyltellurenyl) oxide.

2.10.2 Iridium Bis-triphenyl Phosphine Carbonyl Bis-p-ethoxyphenyltelluride Chloride

To a solution of bis-p-ethoxy phenylditelluride (4.96g in 150ml of dry toluene) in a round bottomed flask (7.79g) of iridium bis-triphenylphosphine carbonyl chloride was added with continuous stirring. The round bottomed flask had been surrounded by 'aluminium foil' to protect the reaction mixture from the effect of light.

The mixture was kept stirring for two hours with gentle heating under an inert atmosphere. After this period of time the homogenous solution produced was transferred to a rotatory evaporator to remove the solvent. After evaporation of most of the solvent, a light brown solid substance was left behind, which was dried over P_4O_{10} in a vacuum desiccator overnight. The dried material had a melting point of 70°C and the elemental analysis yielded the following values: C 49.1; H 3.9; Cl 4.4; P 6.5; Te 20.2%; $C_{53}H_{48}O_3Te_2P_2I_rCl$ requires, C 49.8; H 3.8; Cl 2.8; P 4.9; Te 20%.

Using the same procedure with different diarylditelluride, i.e. diphenyl ditelluride, bis-p-tolyl ditelluride and bis-p-chlorophenyl ditelluride, the following products were obtained, respectively:

Iridium bis-triphenylphosphine carbonyl bis-phenyltelluride chloride;
Iridium bis-triphenyl phosphine carbonyl bis-tolyl telluride chloride, and
Iridium bis-triphenylphosphine carbonyl bis-p-chlorophenyl telluride chloride.

CHAPTER THREE

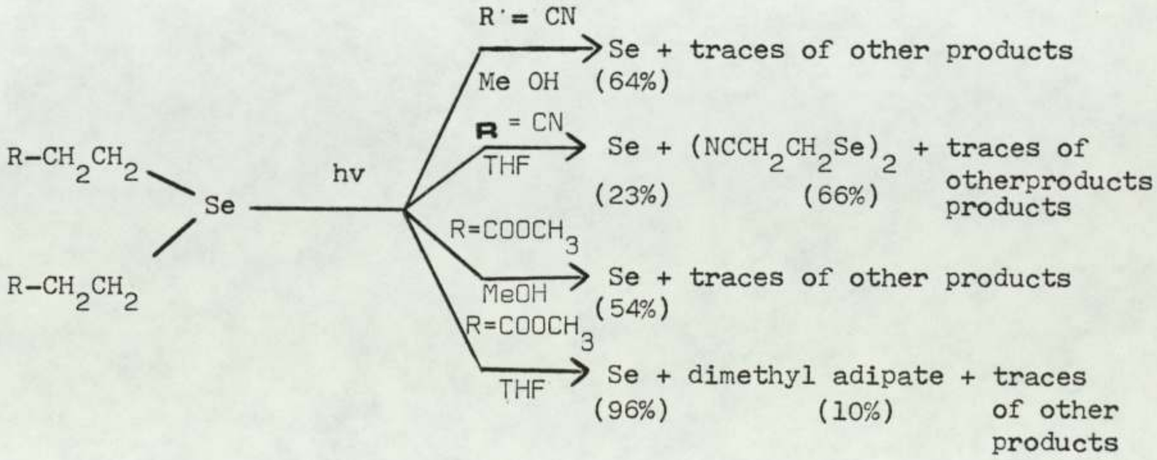
IRRADIATION OF DIARYL DITELLURIDES IN SOLUTION

INTRODUCTION

A review of the literature shows that not much work has been reported dealing with photoreactions of organic tellurium and selenium chemistry as indicated below.

The photolysis of bis (2-cyanoethyl) selenide was reported to give a complex mixture of products. The reaction is strongly solvent-dependent. In methanol solution, the major product (64%) is elemental selenium, with traces of other products, but in tetrahydrofuran solution less elemental selenium is obtained and most of the product (66%) was the diselenide.(49)

The same procedure was repeated with bis [2-(methoxycarbonyl) ethyl] selenide. By using methanol and tetrahydrofuran as solvent, the major product is elemental selenium 54% and 96% respectively, with some traces of other products.(49)



The preparation of tellurium perfluoroalkyls by photolysis of dimethyl telluride in the presence of perfluoro alkyl iodides under very mild conditions, has been reported.(50) By condensing dimethyl telluride and perfluoroalkyl iodide in a vycor tube and subjecting the system to UV light, the perfluoroalkyl substituted telluride is obtained, with good conversion of the iodide.

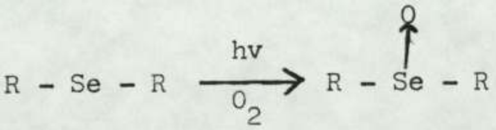
$$\underset{a,b}{RfI} + CH_3 - Te - CH_3 \xrightarrow[20h]{hv} \underset{a,b}{Rf\text{-}TeCH_3} + \underset{a,b}{Rf\text{-}Te\text{-}Rf}$$

a $Rf = CF_3$

b $Rf = C_2F_5$

The oxidation of selenides to selenoxides with photochemically generated singlet oxygen was described recently.(51)

Dialkyl and arylalkyl selenides are oxidized to form selenoxides under irradiation in methanol solution in the presence of rose bengal and oxygen.



$$R - Se - R \xrightarrow[O_2]{hv} R - \overset{\overset{O}{\uparrow}}{Se} - R$$

The yields of selenoxides are very high, no selenone formation is observed in any of the reactions. In some cases the known thermal elimination of selenenic acids, RSeOH occurred, leading to formation of olefins. This is especially pronounced with β-hydroxy selenides which undergoes partial conversion into alkyl alcohols. The yields of alkyl alcohols increase with rising temperature and duration of irradiation. This alkyl alcohol is not oxidised on irradiation.(51)

Some studies have also been made on photochemical reactions of diselenides. Irradiation of dibenzyl diselenide with 350 nm light in the presence of oxygen affords benzaldehyde and elemental selenium(52), whereas irradiation in the absence of oxygen leads to dibenzyl selenide and selenium.(52-54)

$$PhCH_2 - Se - Se - CH_2\,Ph \xrightarrow[O_2]{hv,\,350nm} 2PhCHO + 2Se$$

$$PhCH_2 - Se - Se - CH_2\,Ph \xrightarrow[O_2\ \text{excluded}]{hv,\,350nm} PhCH_2 - Se - CH_2Ph + Se$$

It seems that both Se - Se and C - Se scissions are possible in the photolysis of dibenzyl diselenide, the benzylselenyl radicals if initially formed might combine or attack the weak Se - Se linkage leading to radical displacement and reformation of dibenzyl diselenide. Neither of these reactions leads to the observed photoproducts. Therefore, the most probable step leading to the formation of the observed photolysis product is the C - Se scission.(53)

The first photochemical deselenation of a diethyl diselenide by a diphenyl methyl phosphine was described by Cross and Millington.(57) This reaction proceeds smoothly under UV irradiation and in the absence of air by an $EtSe^{\bullet}$ radical chain mechanism to form diethyl selenide and Ph_2MePSe in high yield.

More detailed results were recently published on this photoreaction(58) although cleavage of Se - C bonds may be involved in the UV irradiation of the diselenide, cleavage of Se - Se bonds seems more important in these reactions.

Irradiation of dibenzyl diselenide in the presence of an excess of triphenyl phosphine in degassed acetonitrile at 350nm yields 66.1% of dibenzyl selenide, 32.3% of bibenzyl and 65.1% of triphenyl phosphine selenide.(54)

Under these conditions, the formation of elemental selenium is completely suppressed. In the presence of molecular oxygen, triphenyl phosphine selenide reacts further to produce triphenyl phosphine oxide and elemental selenium.(54)

$$\underset{1}{PhCH_2 - Se - Se - CH_2Ph} + (Ph)_3P \xrightarrow[\text{excluding air}]{hv}$$

$$\underset{2}{PhCH_2SeCH_2Ph} + (CH_2Ph)_2 + \underset{3}{(Ph)_3\ PSe}$$

The major primary photoprocess in the conversion of 1 to 2 + 3 in the above equation is the facile Se - Se bond cleavage. It appears that benzyl selenyl radicals are trapped by triphenyl phosphine to form triphenyl phosphine selenide and benzyl radicals, which subsequently react to form bibenzyl and dibenzyl selenide.(54)

$$PhCH_2\text{-}Se\text{-}Se\text{-}CH_2\text{-}Ph \xrightarrow{hv} 2\ PhCH_2\text{-}Se^{\bullet}$$

$$PhCH_2\text{-}Se^{\bullet} + (Ph)_3P \longrightarrow Ph\dot{C}H_2 + Ph_3\text{-}PSe$$

$$Ph\dot{C}H_2 + PhCH_2\text{-}SeSeCH_2Ph \longrightarrow PhCH_2SeCH_2Ph + PhCH_2Se^{\bullet}$$

$$2\ Ph\dot{C}H_2 \longrightarrow PhCH_2CH_2Ph$$

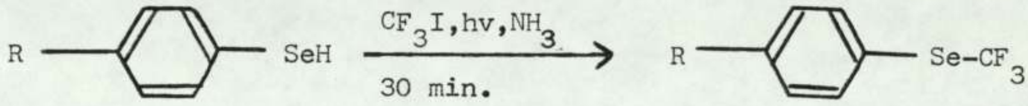
The work described here started as a result of the use of laboratory grade chloroform as a solvent for ditellurides. Accidentally it was observed that the colour of the diaryl ditelluride solution disappears gradually with time, but no such change is observed with other solvents such as toluene. Perhaps it is the small amount of alcohol present in commercial chloroform which is responsible for the lowering of the colour.

Over the period of the last two/three years, since the present study into the kinetics of photoreactions of the diaryl ditelluride compounds was initiated, many related reports have appeared in the literature.

The photochemical oxidation of dibenzyl telluride in carbon tetrachloride solution, after 24 hours of irradiation produces black elemental tellurium and benzaldehyde (42 - 66%) depending on the concentration of the dibenzyl telluride (low concentration gives less benzaldehyde), with some traces of other products.(59)

The photoreactions of selenides and tellurides which do not deposit elemental chalcogenes upon irradiation, has also been described in the literature. Therefore, although the elimination of elemental selenium(60) and tellurium(59) is an important reaction pathway, it is not a general rule.

Trifluoromethyl iodide reacts with selenophenols under UV irradiation of their liquid ammonia solution to give the perfluoroalkylated selenides.(61)



$R = H, CH_3, CF_3, Br$

Diaryl diselenides also enter into the perfluoroalkylation reaction in liquid ammonia solution after previous reduction to the corresponding selenophenols with metallic sodium.

$$C_6H_5\,Se\,Se\,C_6H_5 \xrightarrow{Na} C_6H_5\,Se\,Na \xrightarrow{RfI,hv} C_6H_5\,Se\,Rf$$

$Rf = CF_3, C_3F_7$

Related reactions between the phenylselenide(62) or phenyltelluride(63) anion and haloarenes have been observed. They were reported to undergo photo-SR_N1 mechanism of aromatic substitution reactions upon irradiation in liquid ammonia.

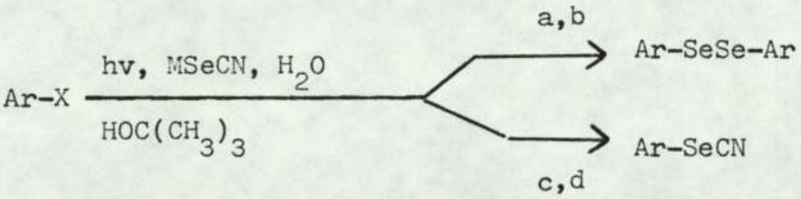
$ArX + PhTe^{-} \longrightarrow (ArX)^{\overline{\bullet}} + PhTe^{\bullet}$

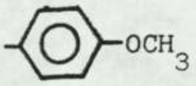
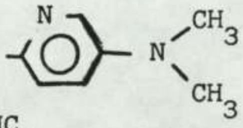
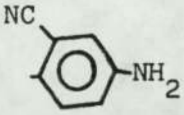
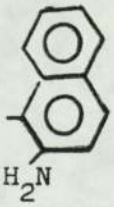
$(ArX)^{\overline{\bullet}} \longrightarrow Ar^{\bullet} + X^{-}$

$Ar^{\bullet} + PhTe^{-} \longrightarrow (ArTePh)^{\overline{\bullet}}$

$(ArTePh)^{\overline{\bullet}} + ArX \longrightarrow ArTePh + (ArX)^{\overline{\bullet}}$

It has been found that irradiation of water-alcohol solutions of the halogen derivatives of benzene, naphthalene and heterocyclic series containing a donating group (OCH_3, NR_2), or donating and accepting (NH_2,CN) groups, in the presence of selenocyanate ion stimulates the formation of diaryl diselenides or aryl-selenocyanates, as shown below.(55)

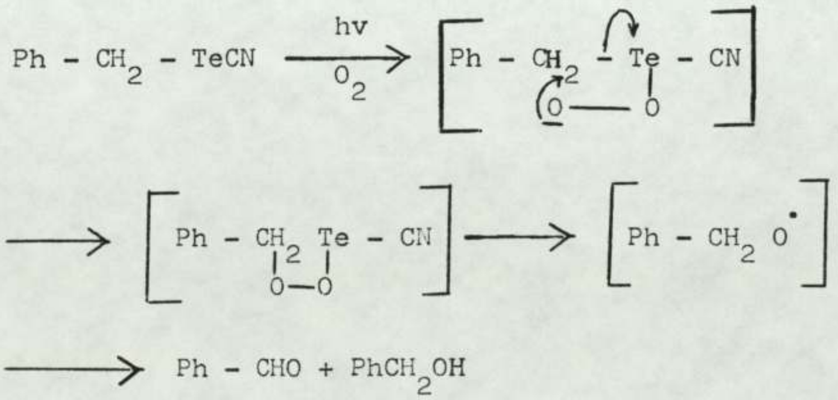


	M	X	Ar
a	Na	Cl	
b	K	Br	
c	K	Cl	
d	K	Cl	

The reaction is of interest as a preparative method for the introduction of selenium into the aromatic ring.

The response of benzyl tellurocyanate on exposure to light and air was reported recently to be its darkening. It is stable to light alone, in the absence of oxygen. A solution of the benzyl tellurocyanate in $CDCl_3$ can be irradiated under nitrogen for 40 hours without decomposition.(64) Under the same conditions, but with an oxygen atmosphere, a black precipitate of elemental tellurium is obtained, while the final solution **contains** only a mixture of benzaldehyde (60%) and benzyl alcohol (40%).(64)

The mechanism of this first and only photo-oxidation of a tellurocyanate reported in the literature, so far, could involve an attack by singlet oxygen to give the 1,3 - dipolar peroxide as shown below. Rearrangement of this compound may give an unstable benzyl peroxytellurocyanate, from which benzaldehyde and benzyl alcohol are derivable by way of benzyloxy radicals.(64)



Very few studies have been made on photochemical reactions of diorgano ditellurides. The first report on the photochemistry of ditellurides was published by Spencer and Cava(59) in 1977. Dibenzyl ditelluride was reported to be very sensitive to UV light and produces in the presence of oxygen the same photoproducts obtained from dibenzyl diselenide(59) under identical reaction conditions, except tellurium instead of selenium.

$$PhCH_2TeTeCH_2Ph \xrightarrow[O_2]{hv} PhCHO + PhCH_2OH + PhCH_3 + PhCH_2CH_2\,Ph + Te$$

In the absence of oxygen parallelism is also observed in the photochemical behaviour of the ditelluride(59) and the diselenide.(64)

Ultraviolet irradiation of solutions of R_2Te_2 (R = Et or $PhCH_2$) produces R_2Te and Te quantitatively.(59,65) In the presence of tertiary phosphines, $R'_3\,P$ $\left[R'_3 = Ph_2Me \text{ or } Ph_2\ (CH_2PPh_2)\right]$, the reactions were accelerated via the formation of R'_3PTe, which decomposes to liberate Te and reform R'_3P. All the reactions were interpreted in terms of an initiation step involving photochemical cleavage of Te-C bonds. Comparisons with analogous reaction of R_2Se_2 suggest that an X - C bond is more easily cleaved by UV radiation as the group was descended where X represents the group VI element.

The pulse radiolysis of some diaryl selenide, diaryl diselenide, diaryl telluride and diaryl ditelluride in neutral and acidic methanolic solution permitted the observation of transients assigned to the radicals $\mathrm{ArSe}^{\bullet}$, $\mathrm{ArSeSe}^{\bullet}$, and $\mathrm{ArTe}^{\bullet}$.(66)

For the diselenide two reaction modes are proposed, one producing $\mathrm{ArSe}^{\bullet}$ radical and the other $\mathrm{ArSeSe}^{\bullet}$ radical. In the cases of mono and ditelluride solutions no information was obtained indicating the observation of $\mathrm{ArTe}^{\bullet}$ radical. The presence of this radical was merely assumed.(66)

The preceding paragraphs summarise the published literature in this area. We now turn to the original work covered by this thesis.

Under aerobic conditions, irradiation with visible light of a toluene solution of a diaryl ditelluride also containing alcohol results in the bleaching of the orange/red colour of the ditelluride. There is an initial induction period, which is then followed by a rate profile which is fitted by the equation

$$\sqrt{\left[\mathrm{Ar_2Te_2}\right]} = k_{obs}\left[\mathrm{EtOH}\right] + \mathrm{Constant}$$

The half order equation probably indicates the homolytic cleavage of the Te – Te bond. The activation energy is small indicating radical processes.

The effect of alcohol on this reaction was found to be first order with its concentration.

It was also found that alcohols with an α- hydrogen, i.e. methanol, ethanol, propanol ------- etc., effect the reaction. Those alcohols without an α- hydrogen which were examined did not effect the reaction.

ESR studies by irradiating the ditelluride while in the cavity of the ESR Machine, give a spectrum with a broad signal. This could indicate the involvement of a free radical process.

The broad infrared band between (750-550cm^{-1}) indicates the involvement of Te - 0 bond in the product of the irradiation.

RESULTS

Toluene solutions of bis-p-phenetyl ditelluride with added ethanol were irradiated by a 60 watt domestic light bulb, while being pumped continuously through a spectrophotometer cell and back to the flask in a closed circuit as explained in Section 2.7.

Firstly it was established that all results obtained are reproducible. It was found that the plots of absorbance with respect to time had two distinct parts. An induction period could be clearly identified.

The effect of the presence of oxygen on the reaction was investigated by carrying out the experiment under three different atmospheric conditions as indicated in Fig. (1). Under a normal atmosphere (air), under an oxygen atmosphere, and lastly under an inert (nitrogen) atmosphere.

It was observed that the induction period lasted for ~ 15 minutes under normal atmospheric conditions, but that it lasted longer in the case of the inert atmosphere. In the case of excess oxygen there was no detectable induction period in the curve.

The rate of the reaction for the rest of the curve fitted the equation

$$\sqrt{Dt - D_{\infty}} = -k_{obs}t + X$$

The rate constants for the above three conditions were found to vary in the following order, excess oxygen $>$ normal condition $\gg$ inert atmosphere. The numerical values of these rate constants are shown in Table (1).

In the case of the inert atmosphere, although the solvents have been deoxygenated and a dry box used to maintain the absence of oxygen, the atmosphere is still not absolutely inert. It is certain that some oxygen will have got in during setting up of the apparatus, and perhaps also during the course of the experiment, because of the porosity of the tubes used in the kinetic apparatus, Section 2.7.

For the same, above mentioned, reasons, the experimental technique described was found not to be very accurately reproducible when using atmospheres other than normal air.

The above experiment under air was repeated at different temperatures(20 - 55°C) at 5°C intervals. The absorbance time data was fed to the computer to obtain the rate of reaction under these different temperatures, using the least squares computer program (Appendix 1). The plot of rate of reaction against temperature shows that there is no significant variation of rate with temperature, see Figure (2), at least when the temperature lies within (20 - 50°C), as shown in Table 2.

As with the temperature, the effect of the concentration of alcohol on the rate of reaction was also studied. The concentration of alcohol was varied from (7.5 - 30%), and the value of rate of reaction was obtained as above (Table 3). The plot of rate of reaction against concentration of alcohol gives a straight line passing through the origin, as shown in Figure 3.

To investigate the role of the alcohol, various alcohols, some containing α- hydrogen and some not, were used in place of ethanol. Three alcohols of the former type; methanol, ethanol and propanol; and two of the latter type (tertiary butanol and phenol) were used. The effect of methanol is similar to that of ethanol and propanol, as shown in Table 4, whereas in the presence of tertiary butanol and phenol the reaction does not take place.

Experiments were also carried out in the presence and absence of small amounts of water. The same rate of reaction is obtained in both cases.

After the experiments with bis-p-phenetyl ditelluride, work was undertaken using diphenyl ditelluride. The behaviour of the latter is very similar to that of the former, the only difference being that with diphenyl ditelluride the reaction is much faster than with bis-p-phenetyl ditelluride.

To determine the quantum yield of the photochemical reaction, potassium ferrioxalate was used for solution - phase chemical actinometry. This compound is very sensitive to light and simple to use. Its preparative method is mentioned in Section 2.9.10.2.

Potassium ferrioxalate (0.15M solution 85ml) is added to the round bottomed flask, equipped with a filter solution consisting of three components: Ammonium hydroxide solution of cupric sulphate, carbontetrachloride solution of iodine and quinine hydrochloride solution. This filter is used for the isolation of the wavelength region around 400 nm.(47) as explained in Section 2.9.10. The ferrioxalate solution is irradiated through this filter for 80 minutes. 10ml of the resulting photolyte solution is then taken, diluted to 25ml with 0.1% of 1,10-phenanthroline solution and buffer solution. This gives a solution of $\left[\mathrm{Fe(Phen)_3}\right]^{2+}$. The procedure is explained in Section 2.9.10.2.

The experimental value of the molar extinction coefficient of $\left[\mathrm{Fe(Phen)_3}\right]^{2+}$ is 1.11×10^4 litres/mole - cm.(48)

The optical density obtained in my experiment = 1.187. In total solution we had produced : $\dfrac{1.187}{11{,}100} \times 2.5\ \mathrm{M\ Fe^{2+}}$ i.e.

$\dfrac{1.187 \times 2.5 \times 85}{11{,}100 \times 1000 \times 80}$ moles $\mathrm{Fe^{2+}}$/minute i.e.

2.84×10^{-7} moles/minute

Under our experimental conditions all light is absorbed, and the quantum yield for this reaction is ~ 1

$\therefore$ flux of light is $2.84 \times 10^{-7} \times 6.023 \times 10^{23}$

Repeating the same experiment with the filter solutions in place but now using a toluene solution of bis-p-phenetyl ditelluride with 20% ethanol, the curve in Figure (4) is obtained at 395nm, see Section 2.9.10.3.

As observed from Figure (4), the slope of the curve, and hence the quantum yield, varies with time, the instantaneous value of the quantum yield being always $\leqslant 0.7$ (the value at the maximum rate of reaction).

Concentrated solutions of the diaryl ditellurides in toluene with some added ethanol were allowed to react under radiation for a long time, about 24 hours. After such a period it is found that the reaction product is an oily-gel (see Section 2.10.1) which can be dried under vacuum.

The infrared spectra of the above reaction products were obtained using a KBr disc (Figures 5 and 6). From these spectra it can be seen that, in the case of diphenyl ditellurides the reaction product does not contain any aliphatic groups which normally absorb around 2900 cm^{-1}. Such groups could only have come from the alcohol that is present in the reaction mixture in this case. On the other hand, the tellurium-oxygen broad band between (750 - 550cm^{-1}) is clearly identifiable. Therefore, the final product does not contain incorporated alcohol.

Thin layer chromatography on silicagel was also used to study the reaction solution at different stages of irradiation. The solvents used were carbon tetrachloride, acetone, hexane, chloroform, toluene, toluene + acetone and toluene + chloroform. The following observations were made:-

Toluene solution of bis-p-phenetyl ditelluride has been studied before irradiation; when the irradiation reaction is half complete, and when the lamp is switched off after half completion, the reaction solution then being left in the dark for an hour. All of the above solvents give only one detectable spot.

In the case after all of the colour of the ditelluride has been bleached, some of the solvents, i.e. toluene, toluene + acetone, and toluene + chloroform give two detectable spots. The rest of the above solvents still give one spot only.

Lastly, when all of the colour of the ditelluride has been bleached, and the solution has then been left in the dark over night, some of the solvents, i.e. toluene, toluene + acetone and toluene + chloroform give two detectable spots. The rest of the above solvents give only one spot.

Results for the e.s.r. study of the bis-p-phenetyl ditelluride under different conditions are given below.

I Toluene solutions of the ditelluride were irradiated in the kinetic apparatus for 25 minutes under the following conditions:- presence of ethanol and oxygen, absence of ethanol but in presence of oxygen, and lastly in absence of oxygen but in presence of ethanol. The solution then transferred to an e.s.r. machine. Spectra obtained are shown in Figures (7 and 8) in Appendix 2.

II Experiments have also been carried out directly in the e.s.r. cavity by placing the capillary containing the toluene solution of the ditelluride in the cavity, and irradiating the sample by photographic lamp (275 watt) for 10 minutes, see Section 2.3.3, while the conditions were varied as before, i.e. in presence and absence of oxygen and ethanol. Spectra obtained are shown in Figure (9) in this Chapter, and Figure (10) in the Appendix 2.

III A THF solution of the bis-p-phenetyl ditelluride after treatment with lithium has also been studied, Section 2.9.7. Spectrum obtained shown in Figure (11) in this Chapter.

IV An e.s.r. study has also been done for a solution of butyl lithium and bromophenetol, Section 2.9.8. Figure (12) in this Chapter shows the spectrum of this solution.

The 'g' values obtained in the experiments are presented in Table 5.

It is interesting to note that when using ethanol and bis-p-ethoxy phenyl ditelluride, if the light irradiating this sample is switched off 30 minutes after the mixing of the reagents, the absorbance starts to increase with time slowly returning to its original level, as shown in Figure (13).

An experiment is also carried out in which the light is switched off when the original reaction appeared to be almost complete, no significant increase in the optical density takes place.

A 'H NMR investigation was carried out for the diphenyl ditelluride under different conditions **with** the follwing results.

When freshly prepared diphenyl ditelluride was dissolved in $CDCl_3$ and the NMR spectrum was measured, the expected two peaks belonging to the phenyl groups are observed as shown in Figure (14). The same spectrum is obtained when a range of different concentrations of the same ditelluride are used.

When the experiment is repeated with an aged sample of diphenyl ditelluride (stored for a few months), an unexpected spectrum with four peaks is observed as shown in Figure (15).

Condition	$10^{3}k/\mathrm{Mol}^{\frac{1}{2}}\mathrm{dm}^{-\frac{3}{2}}\mathrm{min}^{-1}$
Normal (Air)	0.36
Inert Atmosphere (Nitrogen)	0.20
Oxygen Atmosphere	0.47

Table 1 : The Rate of Reaction at 25°C Under Different Atmospheres.

10^3 K/T	$10^3 k$/mol$^{1/2}$ dm$^{-3/2}$ min^{-1}
3.41	0.38
3.36	0.35
3.30	0.41
3.25	0.40
3.19	0.39
3.14	0.40
3.09	0.40
3.05	0.34

Table 2 : Variation of the Rate of Reaction with Temperature.

EtOH %	10^3 k/mol$^{1/2}$ dm$^{-3/2}$ min^{-1}
7.5	0.10
10	0.13
12.5	0.17
15	0.23
17.5	0.27
20	0.32
22.5	0.33
25	0.35
27.5	0.39
30	0.45
32.5	0.47
35	0.52

Table 3 : Variation of the Value of Rate of Reaction With the Concentration of Alcohol.

Alcohol	$10^3k/\mathrm{mol}^{\frac{1}{2}}\,\mathrm{dm}^{-\frac{3}{2}}\,\mathrm{min}^{-1}$
Methanol	0.39
Ethanol	0.36
Propanol	0.36

<u>Table 4 : Rate of Reaction at 25°C in the Presence of Different Alcohols.</u>

Condition	'*g*' Value/Gauss
A Solution prepared in kinetic apparatus, irradiated for 25 minutes and then transferred to e.s.r. machine:	
1) + EtOH + O_2	2.014(b)
2) NO EtOH + O_2	2.017(b)
3) + EtOH, NO O_2	No signal
B Experiments carried out directly in e.s.r. cavity, irradiated for 10 minutes:	
1) + EtOH + O_2	2.017(b)
2) NO EtOH + O_2	2.017(b)
3) + EtOH,NO O_2	No signal
C THF solution of Ar_2Te_2 + Li with spin trap (a)	2.014(b)
D Butyl lithium + Bromophenetol; with spin trap (a)	The signal here is totally different than the above.

(a) The spin trap used is: N - tert - butyl - alpha - phenyl nitron

(b) Very broad signal.

Table 5 : '*g*' Values Obtained from e.s.r. Experiments.

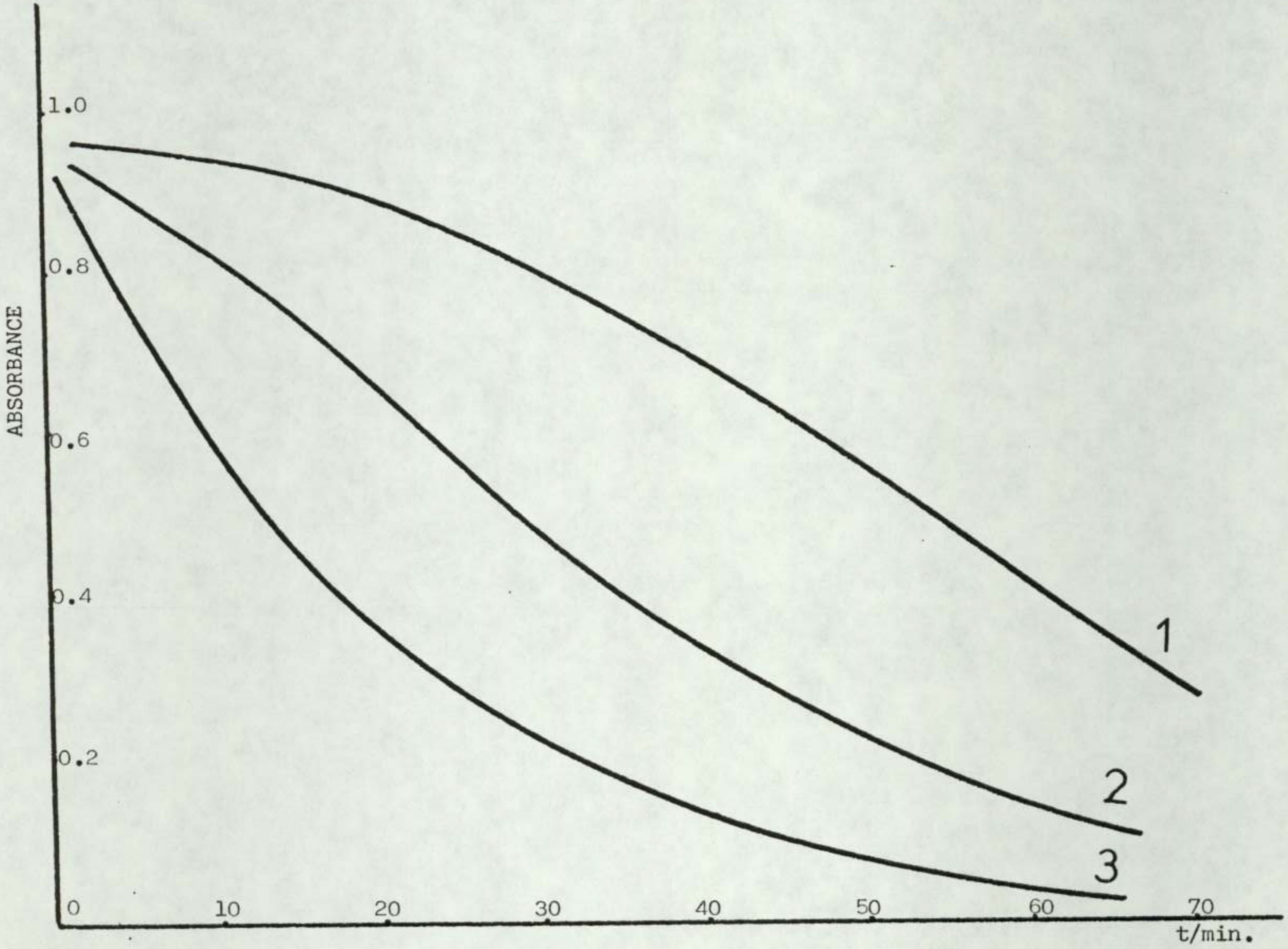


Figure 1 : Plot of Absorbance Versus Time of bis-p-ethoxyphenyl ditelluride with ethanol irradiated under the following atmosphere : 1 - Nitrogen, 2 - Air and 3 - Oxygen.

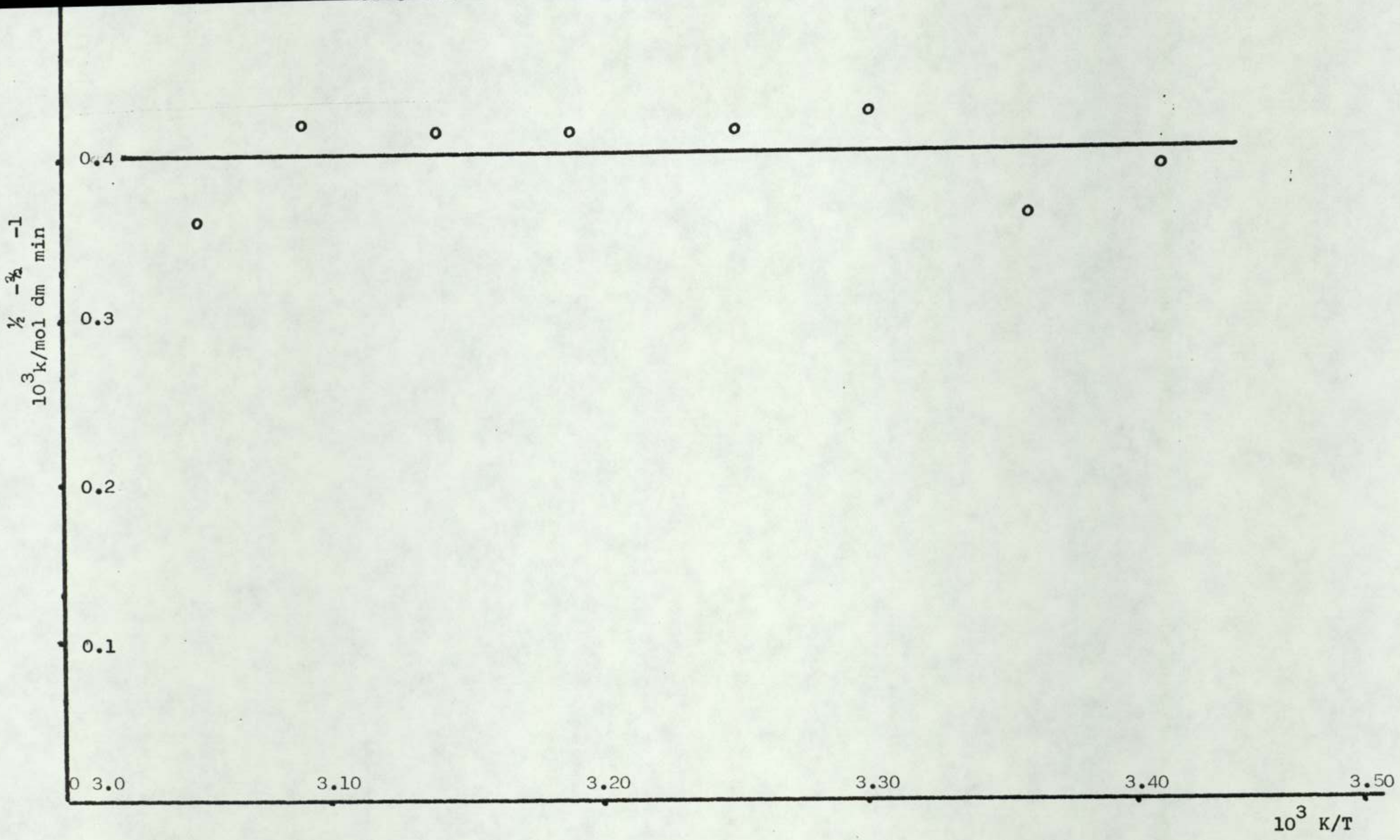


Figure 2 : Plot or Rate of Reaction of bis-p-ethoxyphenyl ditelluride with ethanol under irradiation versus temperature.

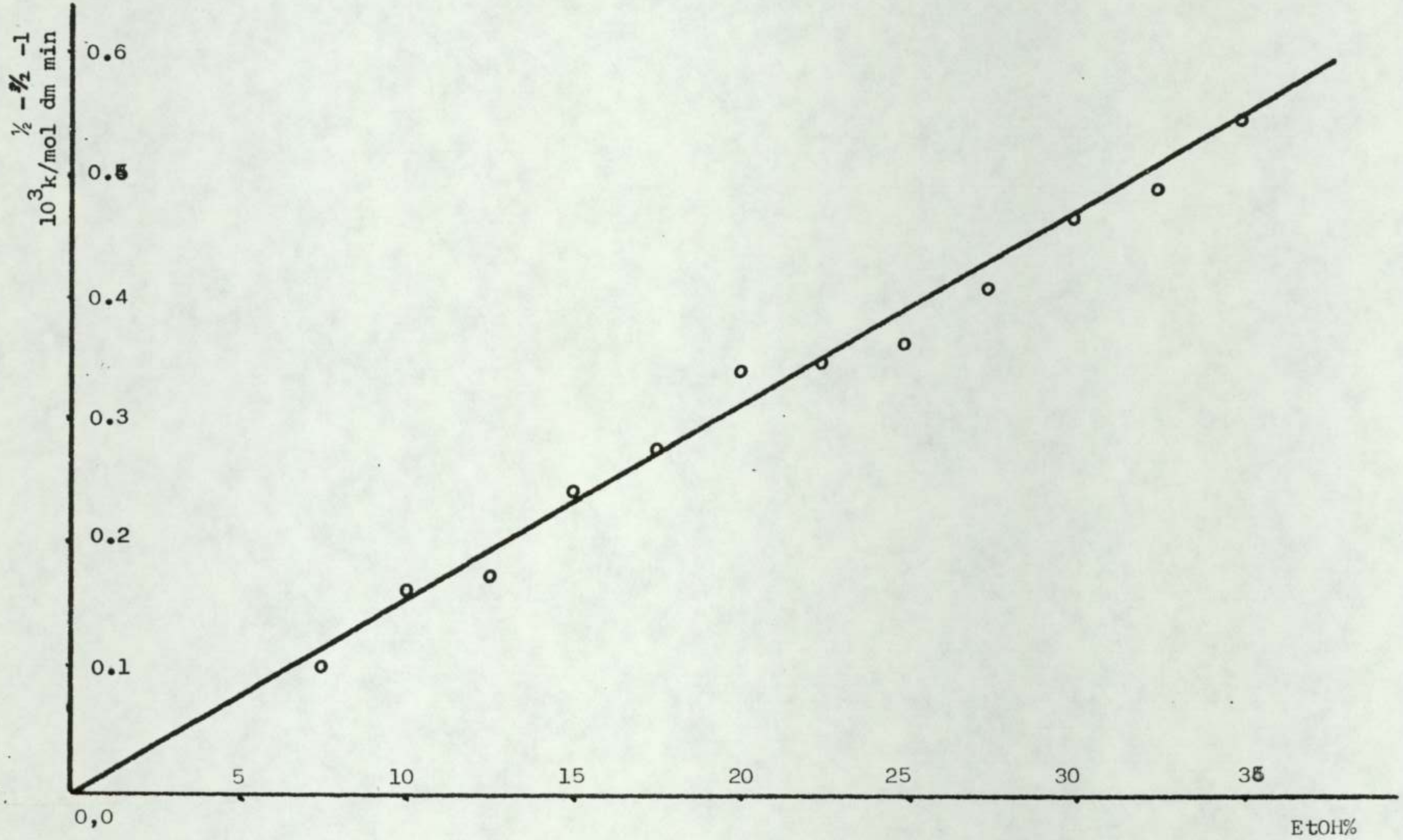


Figure 3 : Plot of Rate of Reaction of bis-p-ethoxyphenyl ditelluride under irradiation at different alcohol concentration and 25^{o}C.

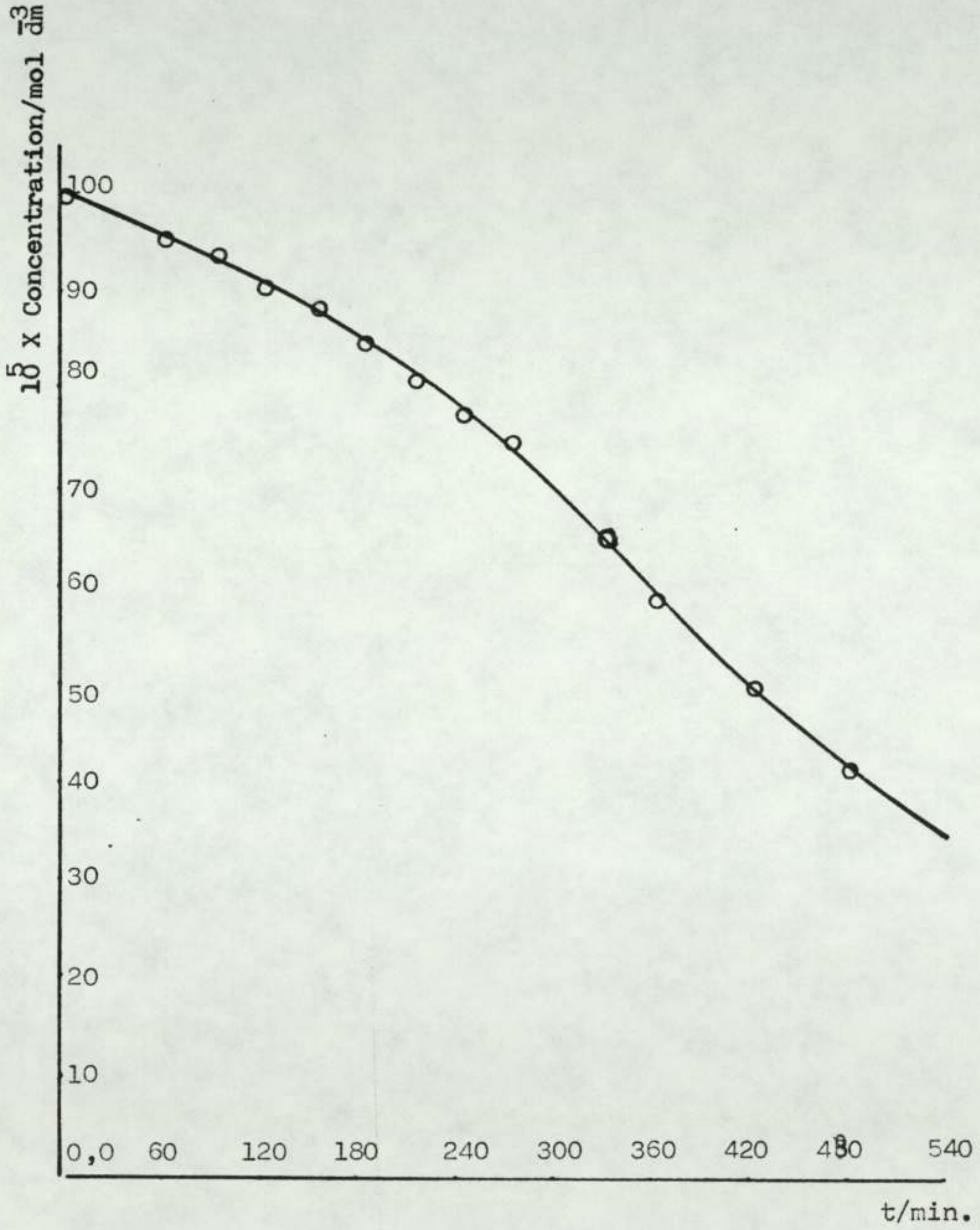
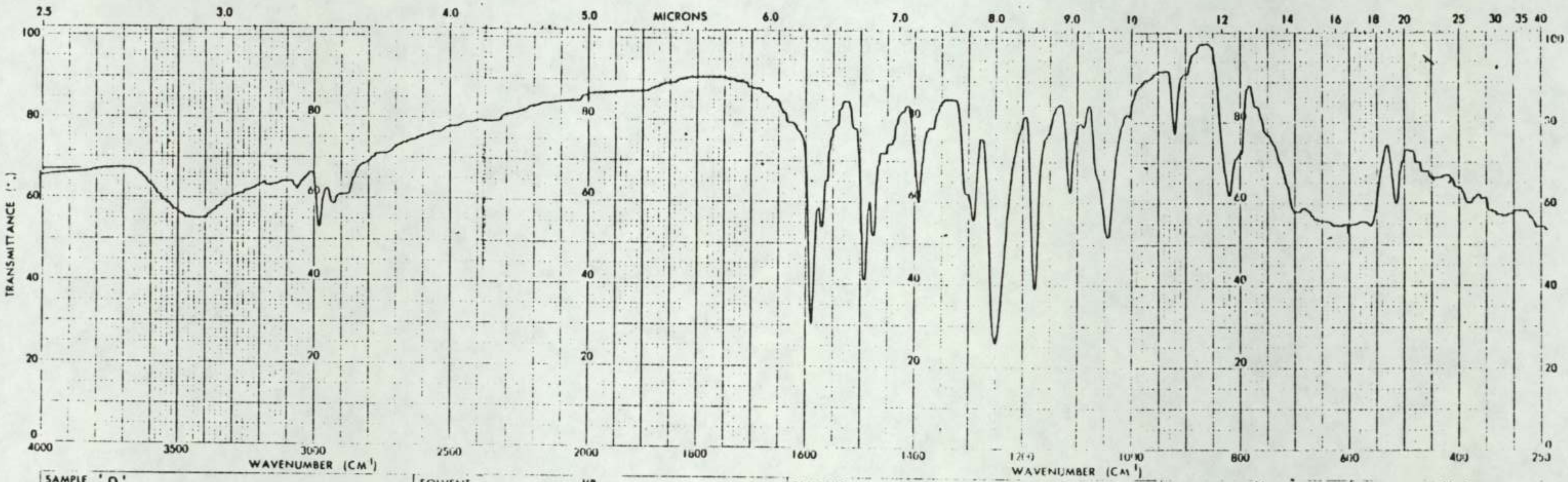


Figure 4 : Plot of Decrease in Concentration of bis-p-ethoxyphenyl ditelluride with time.



SAMPLE 'A'

ORIGIN R.T. Mehdi.

SOLVENT KBr.

CONCENTRATION approx. 1·0%

CELL PATH 13·0 m/m. dia. disc.

REFERENCE Air.

REMARKS

SCAN SPEED Medium.

SLIT Standard.

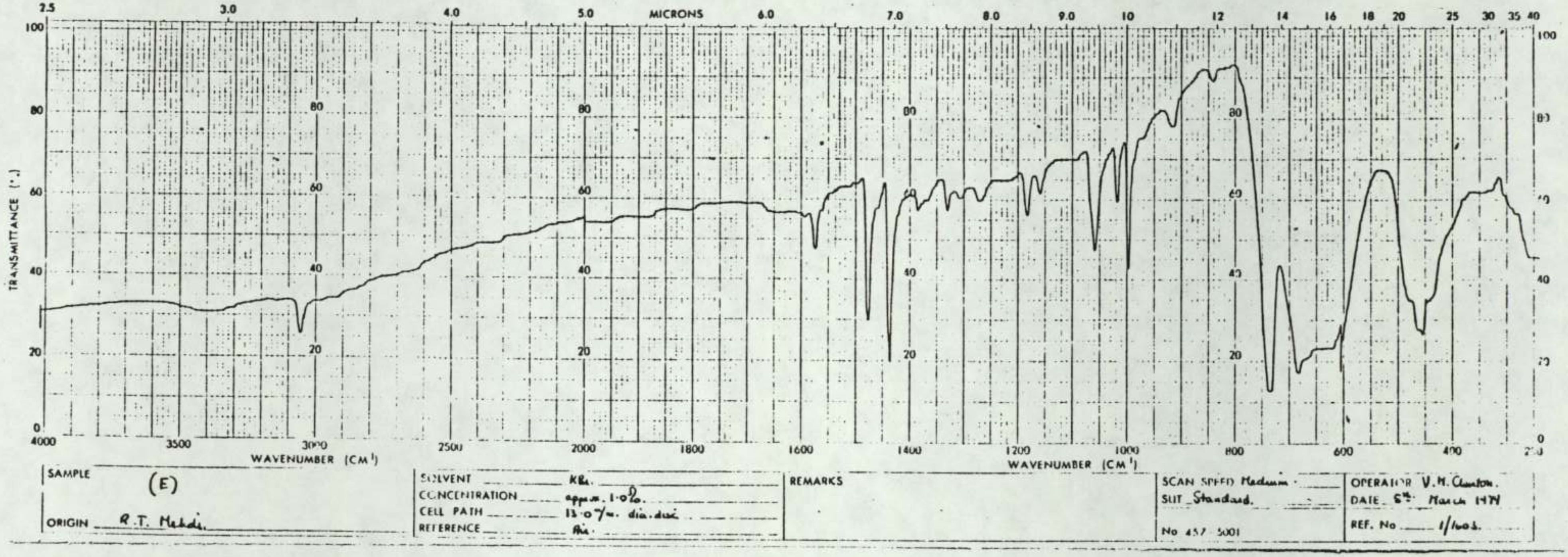
No 457 5001

OPERATOR V.H. Clenton.

DATE 24th October 1978

REF. No 1/926.

Figure 5 : Infrared spectrum of bis(p-ethoxyphenyl tellurenyl) oxide.



SAMPLE (E)

ORIGIN R.T. Mehdi.

SOLVENT KBr.

CONCENTRATION approx. 1·0%.

CELL PATH 13·0 m/m. dia. disc

REFERENCE Air.

REMARKS

SCAN SPEED Medium

SLIT Standard.

No 457 5001

OPERATOR V.H. Clanton.

DATE 5th March 1979

REF. No 1/lo03.

Figure 6 : Infrared spectrum of bis(phenyl tellurenyl) oxide.

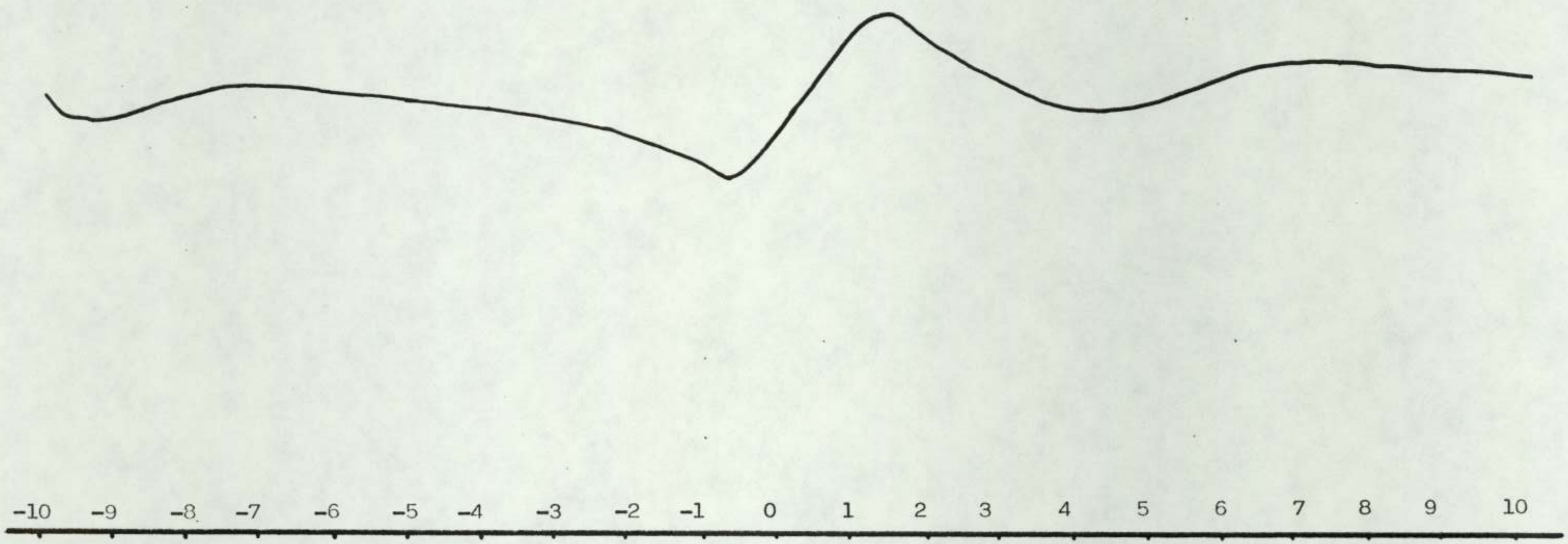


Figure 8 : E.S.R. spectrum of bis-p-ethoxyphenyl ditelluride without ethanol after 25 minutes irradiation outside the cavity. (arbitrary scale)

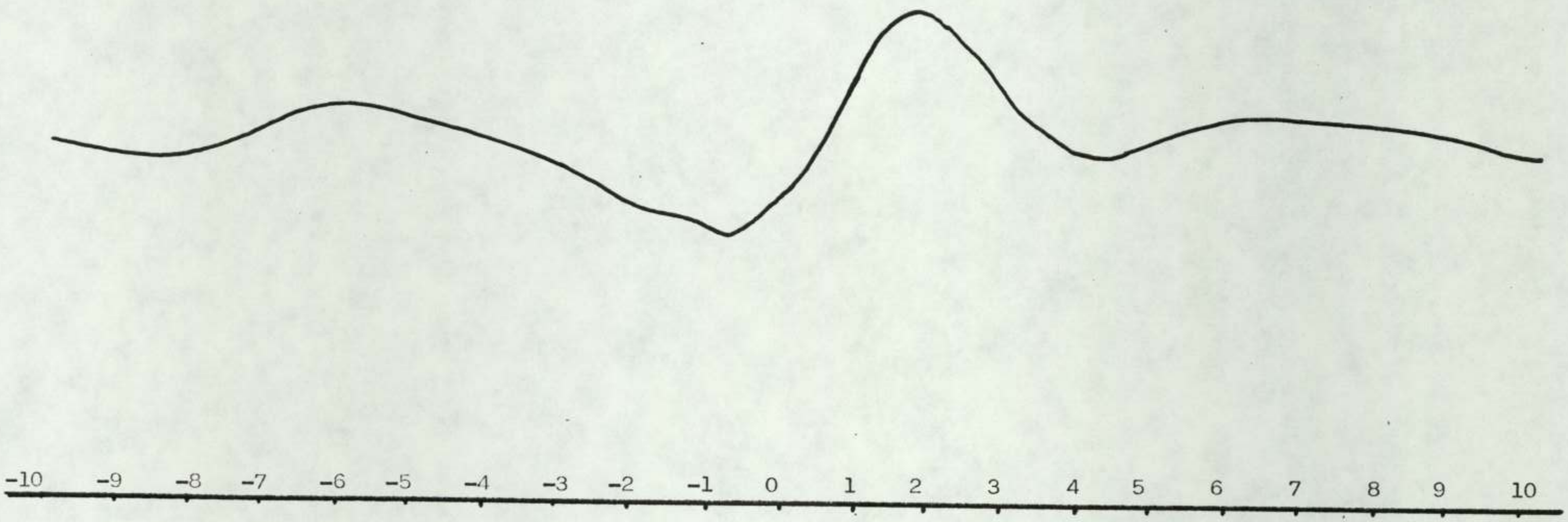


Figure 9 : E.S.R. spectrum of bis-p-ethoxyphenyl ditelluride with ethanol after irradiating the mixture within the cavity of the instrument for about 10 minutes. (arbitrary scale)

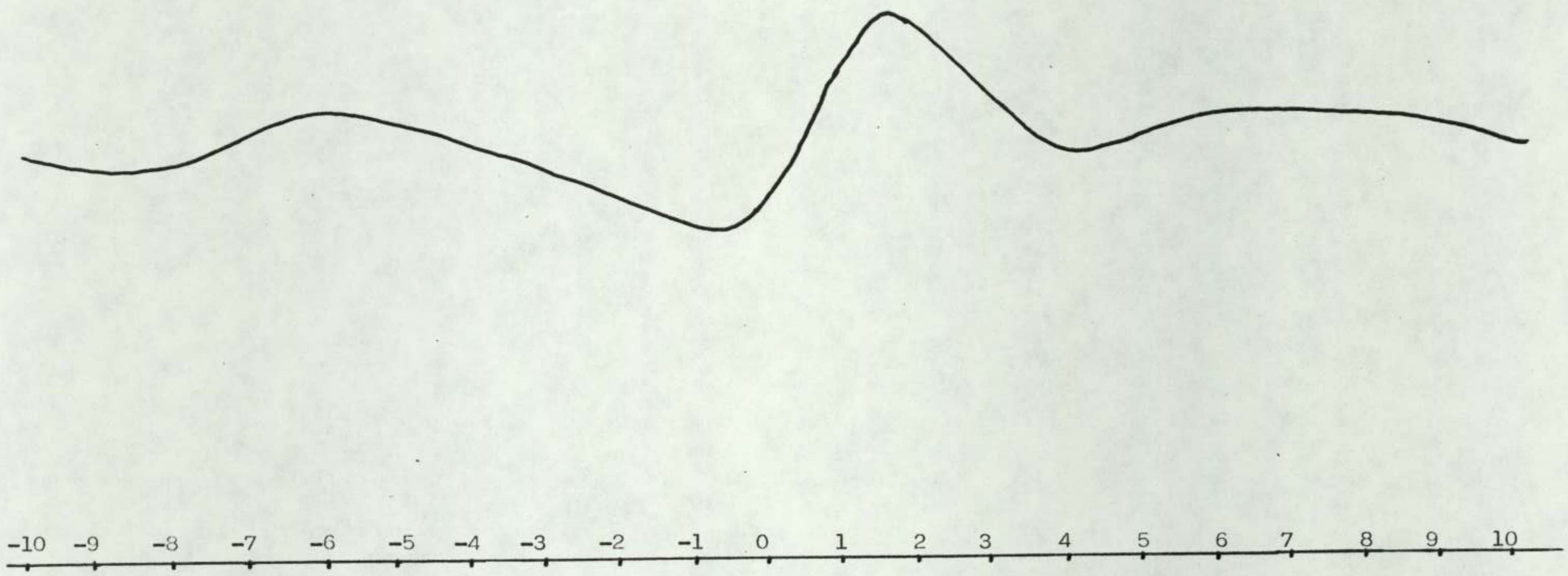


Figure 11 : E.S.R. spectrum of THF solution of bis-p-ethoxyphenyl ditelluride + Li with spin trap.

(arbitrary scale)

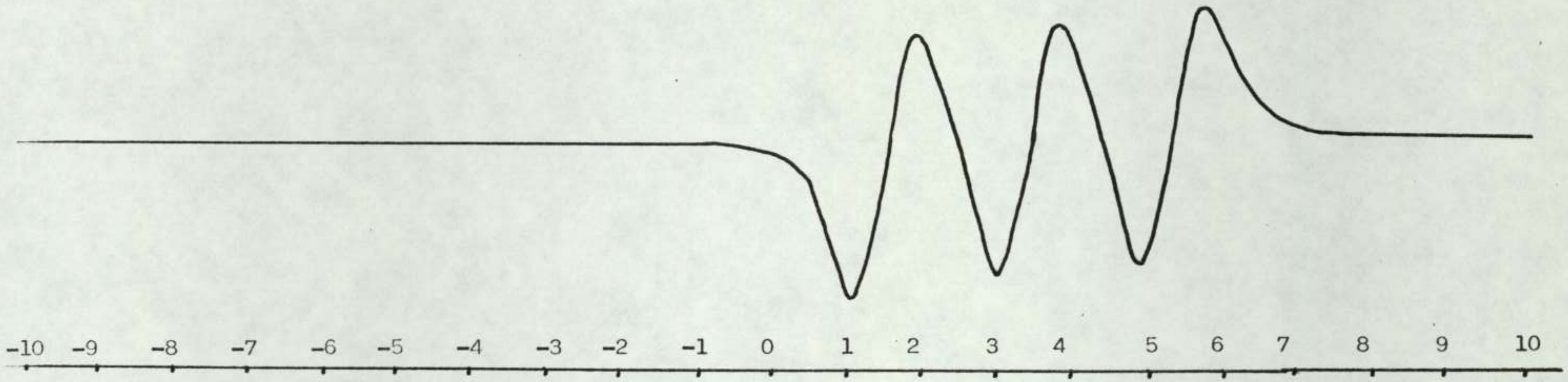


Figure 12 : E.S.R. spectrum of Butyl lithium + Bromophenetol, with spin trap.

(arbitrary scale)

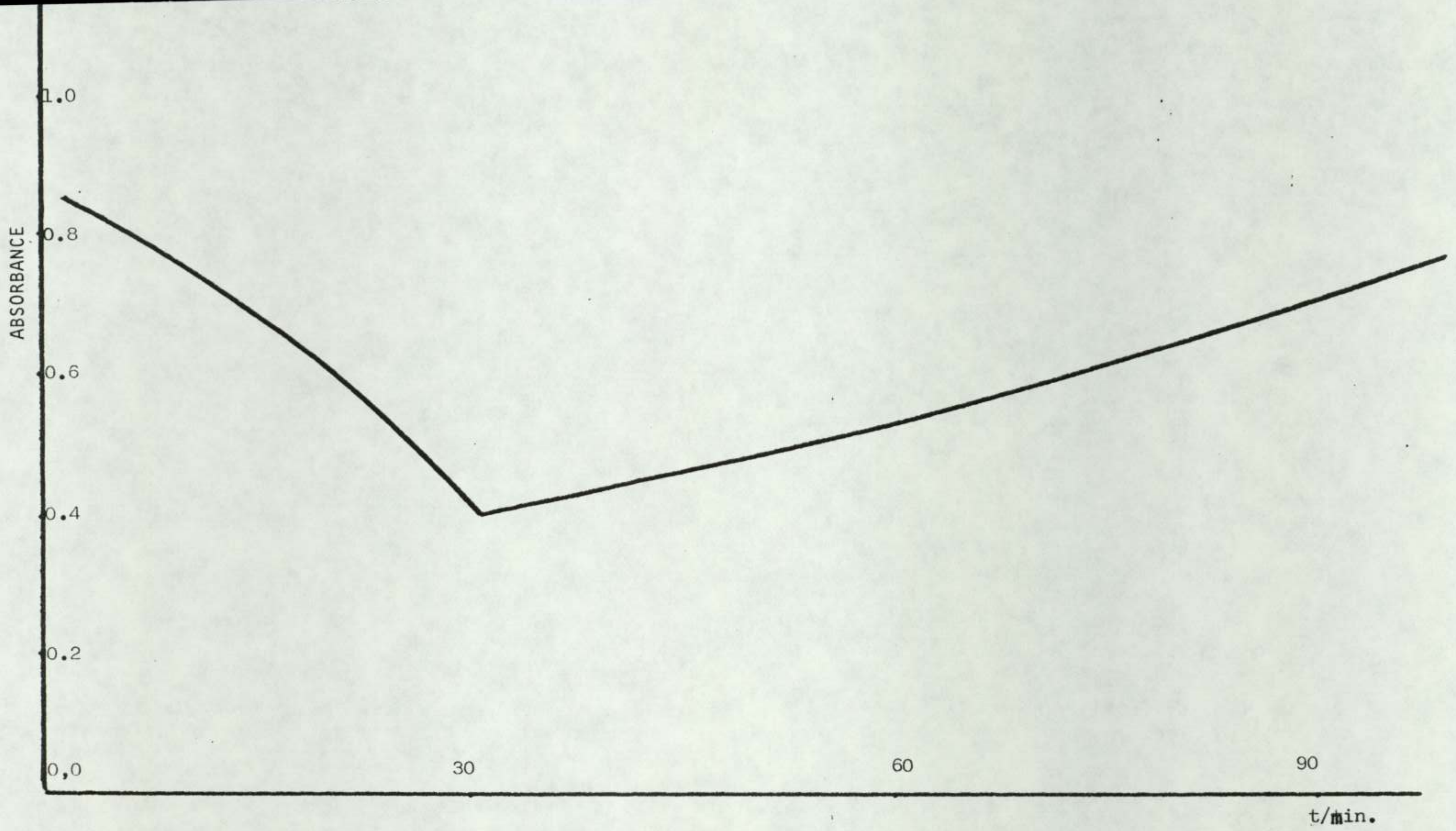


Figure 13 : Plot of Absorbance Against Time of bis-p-ethoxyphenyl ditelluride with ethanol under 30 minutes irradiation followed by a period of darkness.

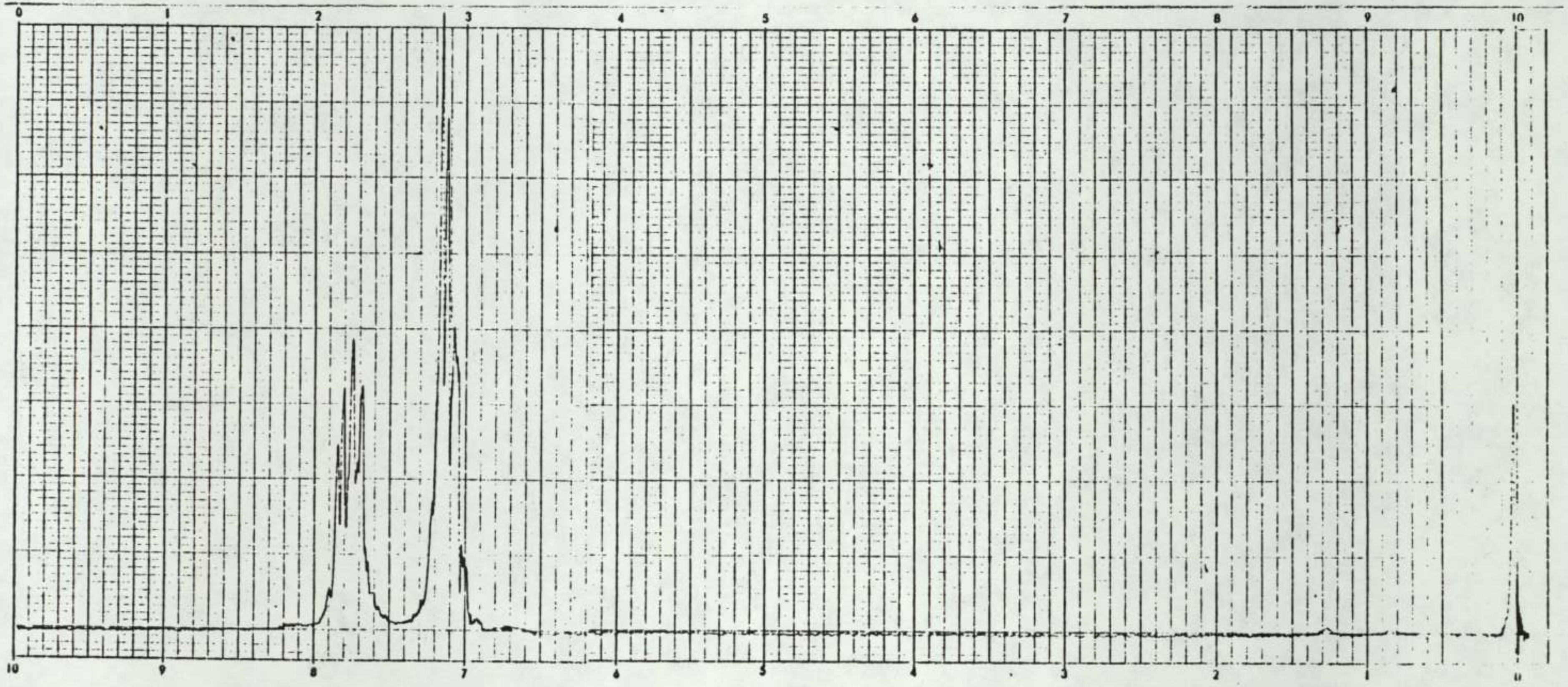


Figure 14 : 'Hnmr spectrum of freshly prepared diphenyl ditelluride.

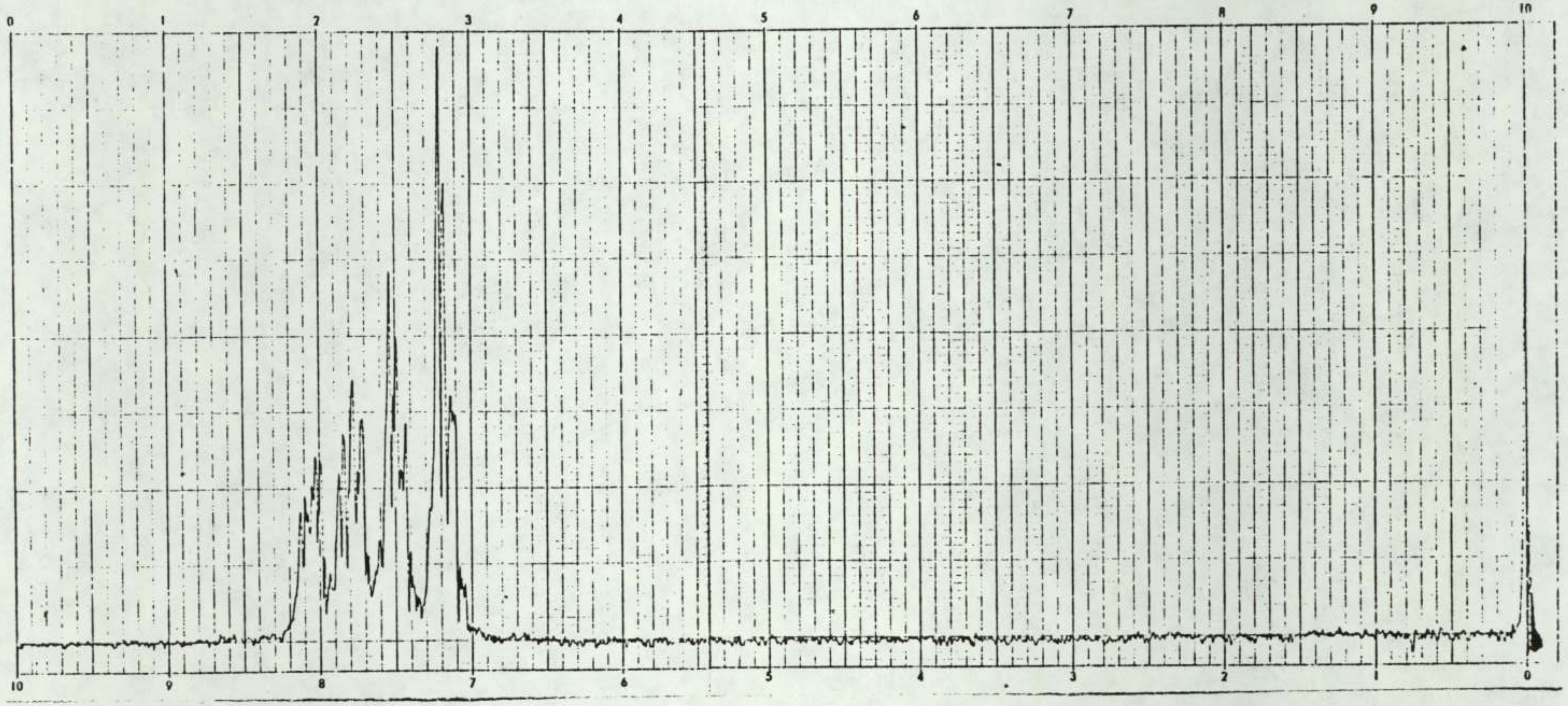


Figure 15 : 'Hnmr spectrum of an aged sample of diphenyl ditelluride.

DISCUSSION

The visible irradiation, under aerobic conditions, of a toluene solution of a diaryl ditelluride containing ethanol results in the bleaching of the orange/red colour due to the ditelluride. There is an initial induction period which may represent the reaction of the oxygen to build up an intermediate somehow. The induction period then is followed by a rate profile which is fitted by the equation:-

$$\sqrt{\left[Ar_2Te_2\right]} = k_{obs} \left[EtOH\right] t + C$$

The suitable concentration of the diaryl ditelluride solution used in the kinetic experiments is 10^{-3}M. The initial optical density of this solution is then approximately unity.

The depth of solution in the reaction vessel = 5cm

therefore $\log_{10} \frac{(Io)}{(I)} = 5.$

$\therefore \quad I \doteqdot 0$

$\therefore$ All light at $\lambda = 395$nm is absorbed.

When the ditelluride solution is irradiated through the filter solutions, Section 2.9.9, it shows that $\lambda = 395$ nm is activating, i.e. the optical density of the solution decreased with time. So that the depth of solution in the reaction vessel and the optical density of the solution at the absorption maximum of the ditelluride (395nm) are such that essentially all incident radiation of this wavelength is absorbed. That is, the rate of formation of the initial excited state will be zeroth order in ditelluride:

$$Ar_2Te_2 \xrightarrow{hv} Ar_2Te_2^{*} \qquad \text{zero order in } Ar_2Te_2$$

the observed kinetic equation means that:

$$-\frac{d\left[Ar_2Te_2\right]}{dt} \propto \left[Ar_2Te_2\right]^{\frac{1}{2}}$$

The exponent (½) does not depend on the light absorption so that the ditelluride molecule in the excited state, $Ar_2Te_2^{*}$, must react with another ditelluride molecule, and hence homolytic cleavage of at least one Te-Te bond takes place.

The experimental design means that it is impossible to exclude all traces of air. When the reaction is studied under almost pure nitrogen, the induction period lengthens and kobs drops. Under almost pure oxygen, the induction period disappears, see Figure 1 and kobs rises, Table 1. The values of kobs show that molecular oxygen is involved in the reaction, but not with a simple first order dependence.

The straight line passing through the origin obtained from the plot of rate of reaction against concentration of ethanol, Figure 3, indicates that the rate of reaction is directly proportional to the concentration of alcohol.

The constant, kobs, varies very little with temperature, see Figure 2. That means the activation energy is nearly zero. This fact, and the half order kinetic equation imply the involvement of radicals formed by the cleavage of a ditelluride. The e.s.r. data summarised below seems to confirm this deduction.

The maximum value of the quantum yield (i.e. at the maximum rate of reaction) is $\sim$ 0.7. This value does not prove that it is chain reaction, because the quantum yield value required for a chain reaction to take place is normally greater than one. But, for such a complicated photochemical process which involves reactions between the ditelluride solution with oxygen and ethanol, a chain reaction seems likely for such a high quantum yield.

A typical reaction solution of diaryl ditelluride in toluene, after irradiation for twenty five minutes under the usual reaction conditions, see Section 2.7.1, shows an e.s.r. signal. This indicates that free radical processes are involved in the reaction. The signal is a broad one; that may mean the free radical obtained contains tellurium. To identify the radical obtained a tetrahydrofuran solution of the same ditelluride has been treated with lithium, as explained in Section 2.9.7. This shows the same broad signal with the same 'g' value. On the other hand, butyl lithium and p-bromophenetole yield a totally different e.s.r. signal.

The same signal with the same 'g' value is also obtained when a solution of diaryl ditelluride in toluene, under aerobic conditions, is irradiated with visible light while in an e.s.r. cavity, see Section 2.3.3. The same signal is obtained whether or not ethanol is present, but no signal appears in the absence of molecular oxygen, (see Table 5 and Figures 7 - 12).

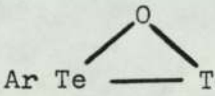
This clearly indicates that the presence of oxygen plays an important part in this reaction. Also, it indicates that ethanol is involved in the reaction but after the formation of radicals.

Irradiating a concentrated toluene solution of the diaryl ditelluride with some added ethanol for a long time, Section 2.10.1, can produce an oily-gel product, which can be dried under vacuum. The solid product obtained, which is insoluble in most of the organic solvents, appears in slightly different colours. This may depend upon the amount of some side products which appear during the irradiation reaction. That means the final product is impure, and it is not easy to purify.

Infrared spectra show that in the case of diphenyl ditelluride, the final product of reaction does not contain any aliphatic groups (Figure 6). Such groups could only have come from the alcohol that is present in the reaction mixture, it appears that the alcohol is not incorporated in the product although its presence is essential to the reaction.

The broad infrared band between 750 - 550 cm^{-1} indicates the presence of a tellurium oxygen bond,$^{(29)}$ Figures 5 and 6.

This observation, accompanied with the elemental analysis mentioned in Section 2.10.1, leads to the structure

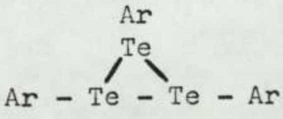

$\mathrm{Ar\,Te\overset{O}{\text{——}}Te\,Ar}$, for the product, bis(p-phenetyl tellurenyl)-oxide.

To study the source of the oxygen atom appearing in the product Ar_2Te_2O, an experiment was carried out by irradiating the ditelluride solutions in the presence and absence of water. The presence of water does not affect the course of the photolysis. Even with thoroughly dried materials, the irradiation reaction takes place as normal. This clearly indicates that the oxygen atom appearing in the product Ar_2Te_2O is not from traces of water in the system.

In the almost total absence of oxygen, using deoxygenated solvents, the reaction profile is different from that usually seen. The induction period is much longer, and the rate of reaction, when it commences, is much reduced, which demonstrates the involvement of molecular oxygen. If the abstraction of an oxygen atom from ethanol is excluded, then the only possibility is that molecular oxygen is cleaved and incorporated in the product.

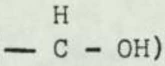
Thin layer chromatography shows only one major coloured compound early on, i.e. before irradiation, and when the ditelluride has been irradiated until the reaction is half complete. But, in the cases when all of the colour of the ditelluride solution has bleached, and also when the photolyte solution is left in the dark for a long time, two compounds can be detected. That means the product at this stage is not just one compound.

It was observed that when a photochemical experiment is allowed to proceed until the ditelluride concentration is halved (as measured by optical density) and the lamp then switched off, the ditelluride concentration slowly returns to its original level as shown in Figure 13. This does not happen when once the optical density has reached its final value. Taken in conjunction with the e.s.r. observations, this implies the original formation of a radical species which is then converted into a longer lived intermediate. On switching off the light at this stage, the long lived intermediate slowly yields a product, a new coloured material, perhaps:-



$\mathrm{Ar-Te\overset{\overset{\displaystyle Ar}{Te}}{\diagup\ \diagdown}Te-Ar}$, or by elimination of one of the aryl groups from the above compound $\mathrm{ArTe_3Ar}$.

In the absence of ethanol significant changes in optical density upon irradiation take much longer to occur.

Investigations have been made using various alcohols, some containing α- hydrogen ( $-\overset{H}{C}-OH$), and some not. It was found that alcohols with an α- hydrogen, e.g. CH_3OH, C_2H_5OH and C_3H_7OH, have the same effect on the irradiation reaction, but alcohols without an α- hydrogen, e.g. tertiary butanol and phenol do not effect the reaction. This probably indicates that the presence of an alcohol with an α- hydrogen is necessary for the reaction to take place.

From the 'H NMR observations of fresh diphenyl ditelluride the only two peaks appear in the spectrum, see Figure 14, indicating that the two phenyl groups are in the same environment, at least on an NMR timescale. While in the old sample of the same ditelluride the presence of the four peaks in the spectrum could indicate the different environment of the two phenyl groups (see Figure 15). This may arise as a result of the dioxygen's attacking the tellurium atoms and hence the phenyl positions could become non-equivalent.

Investigations by Granger(67) have proved that when the ditellurides are treated with solvents under normal conditions, the CIDNP effect is observed. This implies the existence of a radical process, while when the ditellurides are dissolved in deoxygenated solvents no CIDNP effect is observed.

From the above observations for the photochemical reaction the following plausible reaction mechanism can be suggested, where Te_2 represents the diaryl ditelluride.

$Te_2 \xrightarrow[ko]{hv} Te_2^*$ zeroth order in $[Te_2]$

$Te_2^* \xrightarrow{k1} Te_2$

$Te_2^* + O_2 \xrightarrow{k_2} Te_2O_2$

If the steady state hypothesis can be applied, i.e. assuming that the concentration of Te_2^* is small and constant;

$$[Te_2^*] = ko / (k_1 + k_2 [O_2])$$

$Te_2O_2 \xrightarrow{k3} Te_2 + O_2$

$Te_2O_2 + Te_2 \xrightarrow{k4} 2Te + Te_2 + O_2$

Steady state treatment gives:

$$[Te_2O_2] = k_o k_2 [O_2] / (k_1 + k_2 [O_2]) (k_3 + k_4 [Te_2])$$

$Te + EtOH \xrightarrow{k5} TeH + R$

$Te_2 + R \xrightarrow{k6} TeR + Te$

Steady state treatment for R gives, if k_8 and k_9 below are umimportant:

$$k_5 [Te][EtOH] = k_6 [Te_2][R]$$

$2Te \xrightarrow{k_7} Te_2$

$2R \xrightarrow{k_8} R_2$

$Te + R \xrightarrow{k_9} TeR$

Steady state treatment for Te therefore gives:

$2k_4 [Te_2O_2][Te_2] = 2k_7 [Te]^2$ if again k_9 is unimportant

$$\therefore [Te] = \sqrt{\frac{k_0k_2k_4 [O_2][Te_2]}{k_7(k_1 + k_2 [O_2])\ (k_3 + k_4[Te_2])}}$$

$$\frac{-d[Te_2]}{dt} = k_5 [Te][EtOH] + k_6 [Te_2][R]$$

$$= 2k_5 [Te][EtOH]$$

If $k_3 \gg k_4 [Te_2]$, then

$$\frac{-d[Te_2]}{dt} = 2k_5\left(\sqrt{\frac{k_0k_2k_4 [O_2]}{k_3k_7\ (k_1 + k_2[O_2])}}\right)[Te_2]^{1/2} [EtOH]$$

For the above scheme, the rate of reaction is half order with respect to the ditelluride, and first order with respect to ethanol concentrations. This is in agreement with what is found in the kinetic studies discussed previously.

The scheme also requires that the observed rate constant varies with the oxygen concentration in a non-linear manner.

$$k_{obs} = 2k_5 \left(\sqrt{\frac{k_0k_2k_4 [O_2]}{k_3k_7(k_1 + k_2[O_2])}}\right)$$

i.e. $$\frac{1}{kobs^2} = \frac{k_1k_3k_7}{4k_0k_2k_4k_5^2} \cdot \frac{1}{[O_2]} + \frac{k_3k_7}{4k_0k_4k_5^2}$$

But, as was mentioned above, the experimental method makes it impossible to exclude all traces of air. It is not possible to control the amount of oxygen involved sufficiently to test this relationship. Using two points, the equation

$$\left(\frac{1}{kobs^2}\right) \text{pure } O_2 - \left(\frac{1}{kobs^2}\right) \text{air} =$$

$$\frac{k_1k_3k_7}{4k_0k_2k_4k_5^2} \left\{ \frac{1}{[O_2]^{pure}} - \frac{1}{[O_2]^{air}} \right\}$$

could be used, but the reliability of the derived constant would be uncertain.

In this reaction it is not clear which of the following reactions takes place first : the dioxygen with the ditelluride, or the combination of two ditelluride molecules. In both cases the resultant kinetic equation is of the same form.

If the dioxygen reacts with the ditelluride first then the summary of the assumed mechanism could be written out fully as:-

$$Ar_2Te_2 \xrightarrow[k_0]{hv} Ar_2Te_2^* \quad \text{zeroth order in } \left[Ar_2Te_2\right] \qquad (1)$$

$$Ar_2Te_2^* \xrightarrow{k1} Ar_2Te_2 \qquad (2)$$

$$Ar_2Te_2^* + O_2 \xrightarrow{k\,2} Ar_2Te_2O_2 \qquad (3)$$

$$Ar_2Te_2O_2 \xrightarrow{k3} Ar_2Te_2 + O_2 \qquad (4)$$

$$Ar_2Te_2O_2 + Ar_2Te_2 \xrightarrow{k\,4} 2ArTe + Ar_2Te_2 + O_2 \qquad (5)$$

$$ArTe + CH_3CH_2OH \xrightarrow{k\,5} ArTeH + CH_3 - CHOH \qquad (6)$$

$$Ar_2Te_2 + CH_3CHOH \xrightarrow{k\,6} ArTeCHCH_3OH + ArTe \qquad (7)$$

$$2ArTe \xrightarrow{k7} Ar_2Te_2 \qquad (8)$$

$$2CH_3CHOH \xrightarrow{k\,8} CH_3CHOHCHOHCH_3 \qquad (9)$$

$$ArTe + CH_3CHOH \xrightarrow{k\,9} ArTeCH(OH)CH_3 \qquad (10)$$

A third indistinguishable possibility is that in which the excited molecule of the ditelluride combines with another ditelluride molecule before the reaction with dioxygen takes place. The above reaction mechanism could be adjusted by replacing equations (3), (4) and (5) in the above scheme by the following:-

$$Ar_2Te_2^* + Ar_2Te_2 \xrightarrow{k2'} Ar_4Te_4$$

$$Ar_4Te_4 \xrightarrow{k3'} 2Ar_2Te_2$$

$$Ar_4Te_4 + O_2 \xrightarrow{k4'} Ar_2Te_2 + 2ArTe + O_2$$

CHAPTER FOUR

REACTION OF IODINE WITH DIARYL DITELLURIDES

INTRODUCTION

One of the important routes which has been extensively employed to prepare the diaryl ditelluride is the reaction of tellurium tetrachloride with the appropriate aromatic compound. Aryl tellurium trichloride is then obtained. This can be reduced to the corresponding diaryl ditelluride, e.g. usually using sodium sulphide as a reducing agent.

Aryl tellurium trihalides can also be obtained easily by the well known method in which reaction can take place between elemental halogen and diaryl ditellurides as will be discussed later, the reverse of the first mentioned reaction.

Compounds of the type ArTeX (X = Cl, Br or I) are relatively unstable and few have been reported. Of this family 2-naphthyl tellurium iodide(68) and also some of the aromatic tellurimonohalides with a stabilising carbonyl group ortho to the tellurium atom, are the only tellurenyl derivatives which have been isolated without an additional Lewis base attached to Te. However, aromatic derivatives can be prepared in solution from diaryl ditellurides and an equimolar amount of elementary halogen.(69,70)

Petragnani(69) has found that a number of unstable and normally non-isolable tellurenyl halides can be prepared in solution,

from diaryl ditellurides and an equimolar amount of elementary halogen, and then treated with tetraorganyl phosphonium halides to yield dihalo (aryl) tellurates(II).
Products shown in the following equations have been obtained as stable crystalline solids.

$$ArTeTeAr + X_2 \longrightarrow 2ArTeX$$

$$ArTeX + [(C_6H_5)_3 PCH_3]X \longrightarrow [(C_6H_5)_3PCH_3][ArTeX_2]$$

Ar = $(p\text{-}CH_3OC_6H_4)$, $(p\text{-}EtOC_6H_4)$

Hange$^{(70)}$ has found that diphenyl ditelluride dissolved in methanol reacts with halogen (chlorine or bromine), and ligands containing sulphur or selenium to form complexes of divalent tellurium:

$$C_6H_5TeTeC_6H_5 + X_2 + 2L \longrightarrow 2\ C_6H_5TeLX$$

L = thiourea, selenourea, triphenyl phosphine selenide, or trimorpholyphosphineselenide.

$$C_6H_5TeTeC_6H_5 + Br_2 + 4L' \longrightarrow 2C_6H_5TeL'_2 + 2Br^-$$

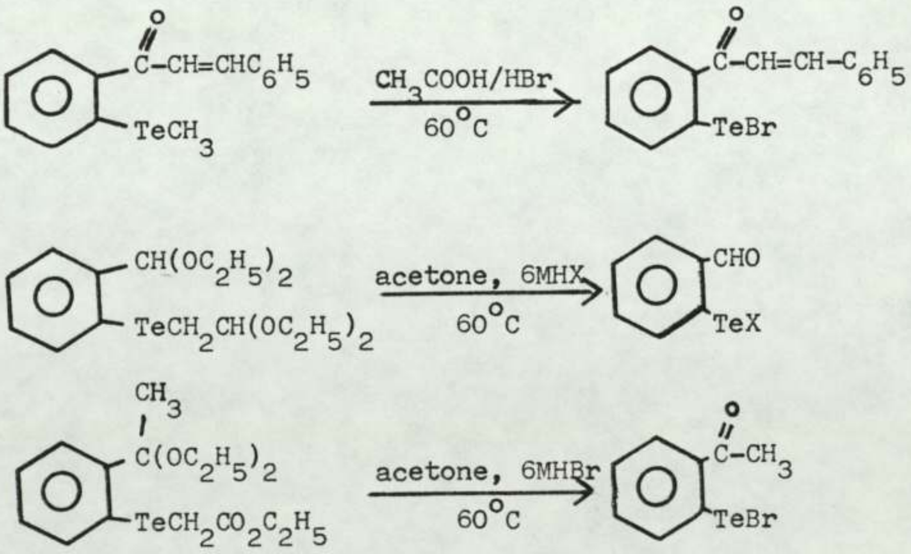
L' = thiocyanate or selenocyanate

The anionic complexes formed have been isolated as tetramethyl ammonium salts.

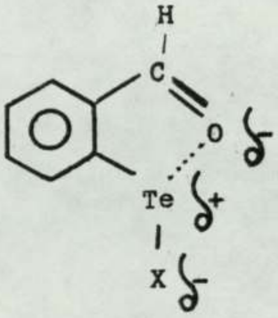
When potassium selenocyanate instead of tetramethylammonium selenocyanate(70) was present during the halogenolysis of diphenyl ditelluride with bromine, bis(phenyltellurium) selenide instead of the expected phenyl bis(selenocyanato) tellurate(II) was obtained. The suggested reaction sequence shown as follows:-

$$\begin{tikzcd}
\mathrm{RTeBr} \arrow[r, "\mathrm{KSeCN}"] & \mathrm{RTeSeCN} \arrow[r, "\mathrm{SeCN}^-"] & \mathrm{RTeSe}^- + \mathrm{Se(CN)_2} \arrow[d, "\mathrm{RTeSeCN}"] \\
 & & \mathrm{RTeSeTeR} + \mathrm{SeCN}^-
\end{tikzcd}$$

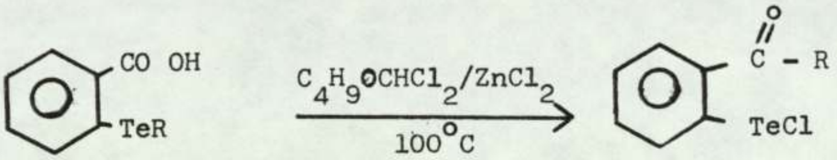
When a carbonyl group is present in the ortho-position to the tellurium atom, then the isolation of aryl tellurium halides is possible. The following tellurium monohalides were prepared by Piette and co-workers as described by equations below:(71,72)



The formation of these tellurium monohalides seems to be facilitated by the presence of a carbonyl function in the aliphatic group bonded to the tellurium atom. This interaction sufficiently stabilises the tellurium halide, which is now co-ordinatively less unsaturated, to allow the isolation of these compounds.(73)

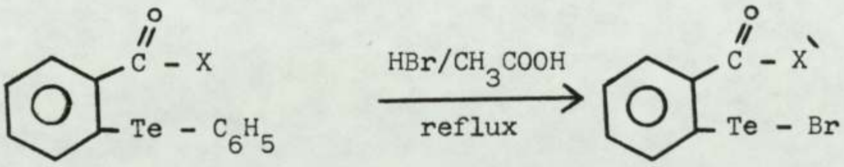


The ortho-substituted aryl tellurenyl halides were prepared from aryl 2-carboxyphenyl tellurides upon treatment with butyl dichloromethyl ether/$ZnCl_2$.(74)



R = (C_6H_5 , 4-$CH_3C_6H_4$, 3-thienyl)

When 2-alkoxycarbonylphenyl phenyl tellurides were refluxed for 24 hours in a mixture of hydrobromic and acetic acid, the tellurium - C (phenyl) bonds were cleaved and 2- alkoxyphenyl tellurium bromides formed.(74)



(X,X` = Cl , OH : CH_3O , CH_3O : C_2H_5O , C_2H_5O)

The chlorocarbonyl group in the above compound is hydrolysed to the acid during the reaction.

Subsequently it has been found(75) that aryl tellurenyl bromide and iodide can be obtained according to the general equation (1) below from diaryl ditellurides and equimolar portions of halogens, if the conversion is carried out in a solvent in which the starting materials but not the tellurenyl compound are soluble. In this way, equation (2), the further reaction of aryl tellurenyl halide to aryl tellurium trihalide, is avoided.

$$Ar_2Te_2 + X_2 \longrightarrow 2ArTeX \qquad (1)$$

$$ArTex + X_2 \longrightarrow ArTeX_3 \qquad (2)$$

(X = Br,I): Ar = C_6H_5 , 4 - (CH_3O) C_6H_4 , 4 - (C_6H_5) C_6H_4 ,

, 3 , 4 - $(CH_3O)_2$ C_6H_3

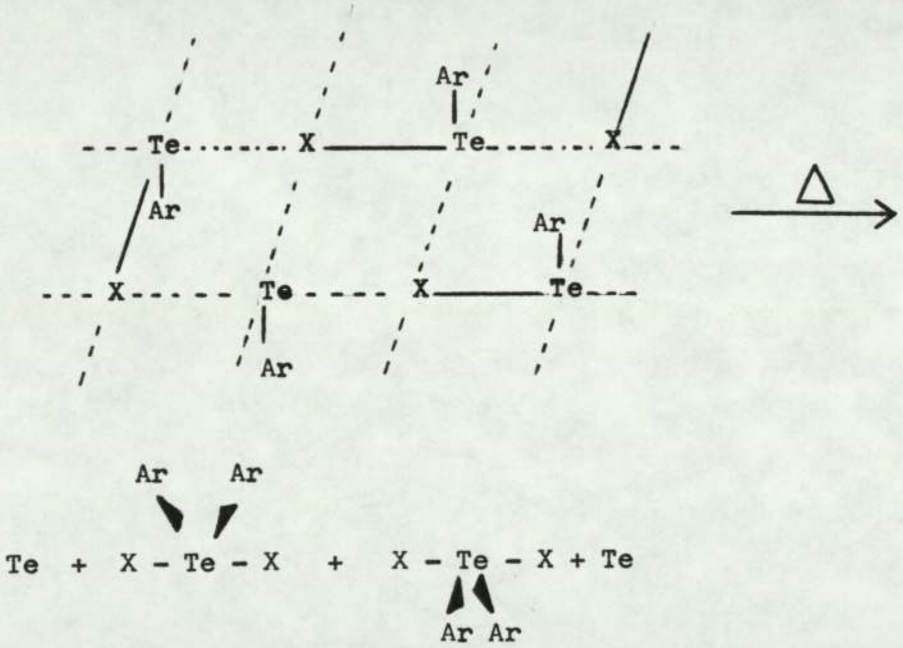
The aryl tellurenyl halides were synthesised according to the general recipe, with moisture excluded and using nitrogen as an inert atmosphere. Suitable solvents for the preparation have been shown to be nonpolar solvents, e.g. petroleum ether, benzene, toluene and CCl_4.

The aryl tellurenyl bromides are coloured red to brown. The corresponding iodides blue - violet to black. They are obtained in a partially crystalline form. The aryltellurenyl bromides are not very stable and change colour after standing for a day. On the other hand, the aryl tellurenyl iodides can remain in a stable form for weeks, unaffected and are also stable when stored under dry air. The aryl tellurenyl halide can be reduced with sodium sulphide to the corresponding diaryl ditelluride and can be oxidised to the corresponding aryl tellurium trihalide with halogens.(75) On hydrolysis the starting materials, diaryl ditellurides, are formed together with aryl tellurium trihalides as the secondary products.

The preparation of aryl tellurium halides, RTex, from equimolar amounts of diaryl ditellurides and aryl tellurium trihalides(76) in refluxing organic solvents has been attempted according to the equation:

$$R_2Te_2 \quad + \quad RTeX_3 \xrightarrow[\text{reflux}]{\text{solvent}} 3RTeX$$

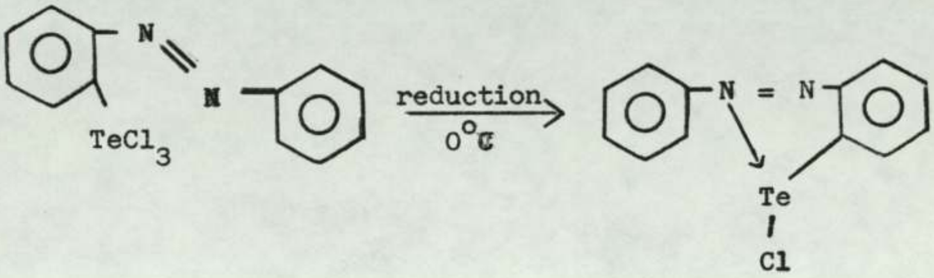
These reactions led to the desired products only with the 2- biphenyl (X = Br, in petroleum ether), and phenyl (X = I, in $ClCH_2CH_2Cl$) derivatives. All other compounds investigated [R,X: C_6H_5 , Cl; C_6H_5 , Br ; 4-$CH_3OC_6H_4$, Cl and I ; 3,4 - $(CH_3O)_2$ C_6H_3 , Cl] produced only diaryl tellurium dihalides and tellurium. Phenyl tellurium iodide and 4 - methoxyphenyl tellurium iodide subjected to the conditions employed above for the reactions between R_2Te_2 and $RTeX_3$ generated the same products as were obtained from the ditellurides and aryl tellurium trihalides. These observations and the results of experiments with ^{123}Te - labelled starting materials suggest strongly that aryl tellurium halides, RTeX are intermediates in all these reactions. Whether or not the aryl tellurium halide can be isolated, depends on the thermal stability of the compound. It was postulated that instability is caused by the easy migration of aryl groups in the associated aryl tellurium halides solids, as shown below:



$$\mathrm{Te} + \mathrm{X-\overset{Ar\ \ Ar}{Te}-X} + \mathrm{X-\underset{Ar\ \ Ar}{Te}-X} + \mathrm{Te}$$

Such a migration should be facilitated by small halogen atoms, which allow the tellurium atoms to be close to each other and by substituents in the benzene ring such as CH_3O-.(76)

(Phenylazophenyl - 2C,N^1) tellurium (II) chloride was recently obtained$^{(77)}$ by reducing an aqueous solution of (phenylazophenyl - 2C,N^1) tellurium (IV) trichloride by potassium metabisulphite at 0°C.



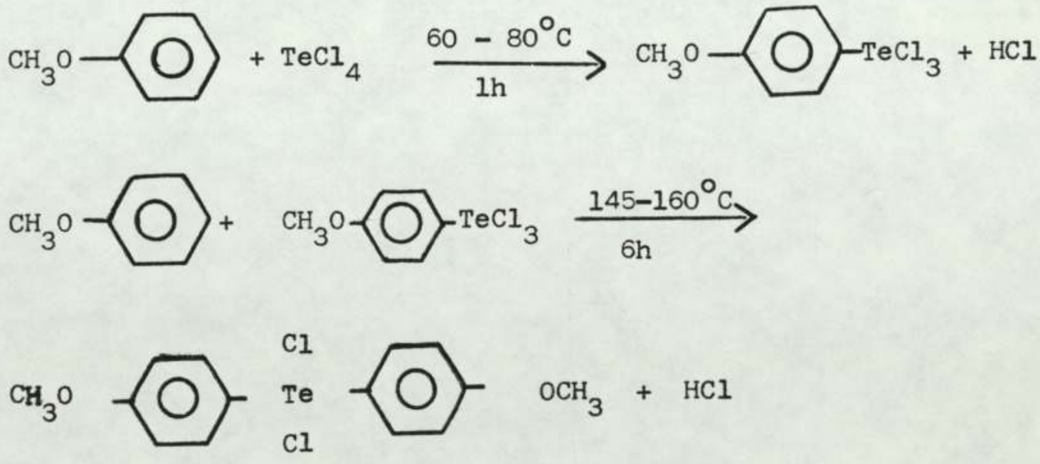
A fair number of organyl tellurium trihalides have been prepared by established methods, such as the halogenolysis of ditellurides in organic medium, the condensation of tellurium tetrachloride with aromatic hydrocarbons containing an activating substituent, or the reaction of aryl mercury chlorides with tellurium tetrachloride.

Preparation of phenyl tellurium triiodide from the ditelluride and iodine must be carried out at low temperatures (10 - 15°C).$^{(78)}$ At higher temperatures intractable mixtures may be obtained. In the addition of iodine to diphenyl ditelluride, a black, benzene soluble material is obtained. This may be a mixture of $PhTeI_3$ and a second substance. It was found that there is no suitable solvent for the separation of these two substances.

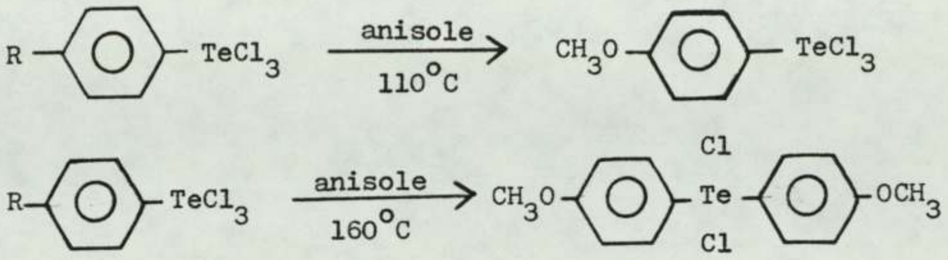
Lastly, it has been suggested that the black material may be the intermediate phenyl tellurenyl iodide PhTeI.(78)

The addition of chlorine to 2-formylphenyl tellurium chloride produces the trichloride. This reaction is not of importance for $RTeCl_3$ compounds, since the conversion of ditellurides to tellurium trichlorides can be effected in one step. The monohalides which can be isolated only in special cases, as was mentioned above, would, however, be useful as starting materials for $RTeXY_2$ derivatives.(71)

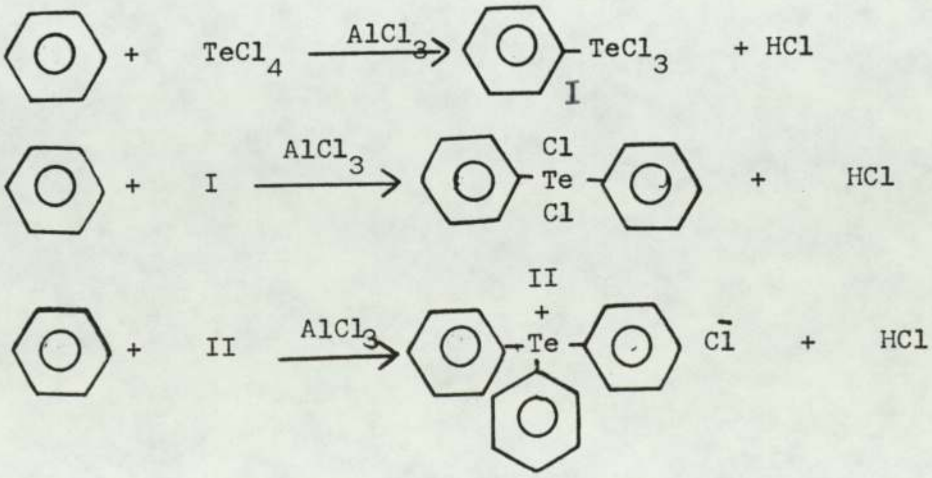
Tellurium tetrachloride behaves as an electrophilic reagent towards aromatic compounds bearing activating substituents (e.g. RO–) giving aryl tellurium trichlorides or bis(Aryl) tellurium dichlorides,(79) as exemplified:



An exchange of organic groups has been observed(80) when the aryl tellurium trichlorides, $4\text{-}RC_6H_4TeCl_3$ ($R = CH_3$, Br, C_2H_5O), are heated with anisole at 110°C. Under these conditions the 4 - methoxyphenyl tellurium trichloride and bis(4-methoxyphenyl) tellurium dichloride are obtained:



Guenther$^{(81)}$ found that the combination of tellurium tetrachloride with aluminium chloride at 1:2 molar mixture respectively, constitutes an efficient process for the introduction of tellurium into aromatic molecules. Kinetic control of the reaction with benzene (a substance inert to $TeCl_4$ alone) selectively yielded the products of successive substitution on tellurium as follows:- diphenyl ditelluride (i.e. to facilitate the isolation of the organic tellurium compound it was reduced to the ditelluride), diphenyl tellurium dichloride and triphenyl tellurium chloride after evolution of 1, 2 and 3 equivalents HCl respectively.



It has been observed(82) that for the process

$$2RC_6H_4TeCl_3 \rightleftharpoons (R\ C_6H_4)_2\ TeCl_2 + TeCl_4$$

the forward reaction goes in

good yields in the organotellurium series. The equilibria can be shifted to the right by using copper powder which removes the tellurium tetrachloride by reducing it to tellurium:

$$2ArTeCl_3 + 4Cu \longrightarrow Ar_2TeCl_2 + 4CuCl + Te$$

The reverse reaction, leading to the synthesis of aryl tellurium trichloride, occurs when diaryl tellurium dichlorides are refluxed in toluene with an equimolar amount (or an excess) of tellurium tetrachloride. The reaction mixture, after the removal of solvent, may be reduced with $Na_2S \cdot 9H_2O$, to the corresponding diaryl ditellurides. These can be reconverted into aryl tellurium trichlorides by the action of thionyl chloride.

Pant(83) has prepared aryl tellurium trichlorides by the treatment of triaryl lead chloride and tellurium tetrachloride in dioxane. The mixture is then stirred for four hours, at room temperature:

$$(C_6H_5)_3\ PbCl + TeCl_4 \xrightarrow{\text{dioxane}} C_6H_5TeCl_3 + (C_6H_5)_2\ PbCl_2$$

Phenyl tellurium trichloride is obtained by stirring together equimolar amounts of triphenyl tin chloride or tetra phenyl tin and tellurium tetrachloride in toluene for two hours at room temperature:(84)

$$(C_6H_5)_3SnCl + TeCl_4 \xrightarrow{toluene} (C_6H_5)_2SnCl_2 + C_6H_5TeCl_3$$

$$(C_6H_5)_4Sn + TeCl_4 \xrightarrow{toluene} (C_6H_5)_3SnCl + C_6H_5TeCl_3$$

Petragnani(85) has reported that when (ArTe SeAr) is treated with bromine, the Te-Se bond is cleaved to give a mixture of aryl tellurium tribromide and areneselenenyl bromide:

$$ArTeSeAr + 2Br_2 \longrightarrow ArTeBr_3 + ArSeBr$$

The two bromides are easily separated by their differential solubility in organic solvents.

In view of the ease of the cleavage of the C(aryl) - $SiMe_3$ bond under the action of electrophilic agents and also of the relative accessibility of aryl trimethyl silanes, these compounds have been applied(86) in the synthesis of some aryl tellurium trihalides. For example, by boiling aryl trimethyl silanes with equivalent amounts of tellurium tetrachloride in toluene:

$$RC_6H_4Si(CH_3)_3 + TeCl_4 \longrightarrow RC_6H_4TeCl_3 + (CH_3)_3SiCl$$

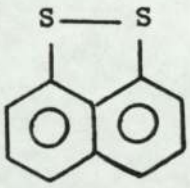
(R = 4-CH_3 , H , 3-CH_3 and 4-Br)

4-Fluorophenyl tellurium trichloride and 3-fluorophenyl tellurium tribromide were obtained in 100% yield from the ditellurides and SO_2Cl_2 and bromine in benzene, respectively.(87)

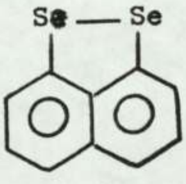
3-Fluorophenyl tellurium trichloride has also been obtained quantitatively from the ditelluride and SO_2Cl_2 in benzene.(87) This had also been synthesized previously from tellurium tetrachloride and the aryl mercury chloride.(88)

$$R\ C_6H_4HgCl + TeCl_4 \longrightarrow R\ C_6H_4TeCl_3 + HgCl_2$$

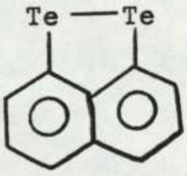
A new series of electron donor compounds (I - VI) have been studied(89) : Peri-bridged naphthalene dichalogenides (NDC's).



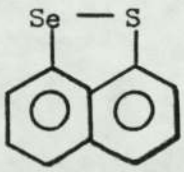
I



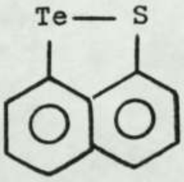
II



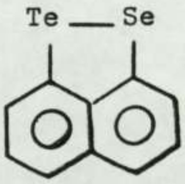
III



IV



V



VI

These compounds are expected to function as electron donors in charge - transfer complexes. The three symmetrical chalcogen-bridged naphthalenes were all found to form 1 : 1 donor-acceptor complexes with tetracyanoquinodimethane.

All six NDC's form complexes with elemental iodine as an acceptor. The complexes are formed by mixing solutions of the NDC and iodine in a suitable solvent and allowing the complexes to crystallize. All these complexes are shiny crystalline solids with colours ranging from silvery grey to black. Large crystals have been produced in the case of NDSe - iodine. These shiny metallic grey crystals were found to correspond to a stoichiometry of $NDSe_1 - I_{1.82}$. Elemental microanalysis revealed that this ratio of NDSe to iodine is reproducible over a number of independently prepared samples.

Recently Pritzkow$^{(90)}$ has studied the crystal and molecular structure of dimethyltellurium tetraiodide $(CH_3)_2\ TeI_4$. He has determined the intermolecular bonding between $(CH_3)_2\ TeI_2$ and I_2. It was proved that the structure is built up by $(CH_3)_2\ TeI_2$ and I_2 molecules and does not contain Te(VI). The compound should be formulated as dimethyltellurium diiodide-diiodine $(1/_1)$. The iodine molecules are on both sides bound to iodine atoms of $(CH_3)_2\ TeI_2$ molecules, and not to the central tellurium. Figure 1.

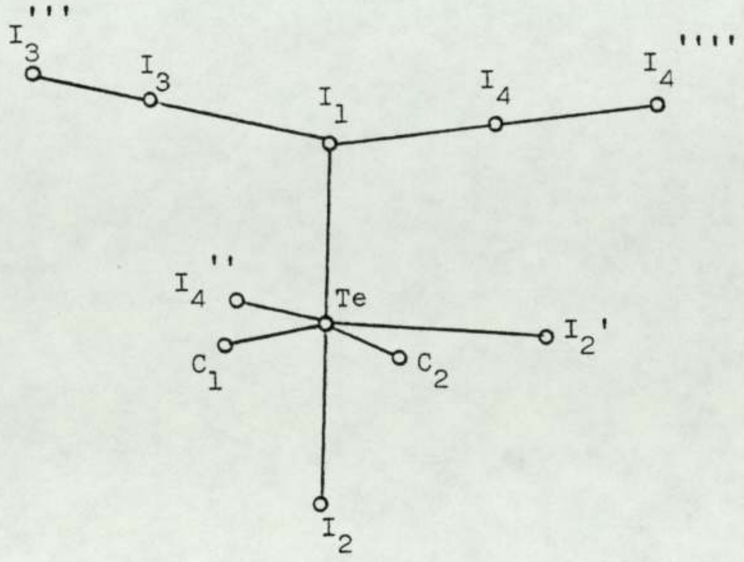


Figure 1 : Molecular Structure and Labelling of $(CH_3)_2\ TeI_4$.

The I_2 molecule and the two other iodine atoms form a linear chain, only one of the iodine atoms bound to tellurium, I(1), is connected with the I_2 molecules. The connection of the I_2 molecules via I(1) leads to zigzag chains. Besides this chain the tellurium forms weak intermolecular bonds, one to I(2)', which is directly bound to another tellurium, and one to I(4)" which belongs to one of the bridging iodine molecules.

In the present work it has been observed that when toluene solution of iodine added to the bis-p-ethoxyphenyl ditelluride, a dark blue substance appears within a very short time. This may be an intermediate product. A specially designed apparatus was used (see Section 2.8) to investigate the possibility of the rapid appearance of an intermediate product. But, this apparatus seems too crude to control this reaction.

Chemical equilibrium investigations have been carried out by monitoring optical density changes at three different wavelengths, 500nm, 318nm and 284nm. The iodine is mixed with the ditelluride and the absorbance then measured from the reaction mixture two minutes after mixing, as a sufficient time for the equilibrium to be reached at room temperature.

The wavelength 500nm was found to be the best for studying the equilibrium constants for the formation of the intermediate complexes, $Ar_2Te_2.I_2$ and $Ar_2Te_2.2I_2$. The absorbance was monitored at this wavelength for a range of concentrations at different temperatures (see Tables 1, 2 and 3). The data obtained was then analysed by computer (see Appendix 3). The results from the computer analysis fitted the observed data very well, Tables 1A in this Chapter, 2A and 3A in Appendix 6.

It was observed that there were two main stages in the overall reaction between I_2 and Ar_2Te_2. The initial reaction is fast. This is followed by a slower subsequent stage. The fast stage involves the formation of the 1:1 and 1:2 donor acceptor complexes, that is $Ar_2Te_2.I_2$ and $Ar_2Te_2.\ 2I_2$, respectively. The subsequent dissociation of the complex $Ar_2Te_2.2I_2$ to form the intermediate compound, p-ethoxyphenyl telluronium iodide, ArTeI occurs during the slow stage. This is borne out by the results of the kinetic investigations described below.

Table 1 shows that the absorbance of a reaction solution shortly after mixing is very low when the concentrations of the reactants (the iodine and the ditelluride) are equal. This is due to the formation of the $Ar_2Te_2.I_2$ complex. The absorbance increase with the increment of the iodine concentration, indicates the formation of the $Ar_2Te_2.2I_2$ complex. These two species have markedly different spectral properties.

The spectrophotometric studies show that two peaks appear rapidly at the wavelengths of 318nm and 284nm after mixing iodine with the ditelluride. The peak at 318nm disappears after a short time, while the other keeps growing during this time.

Kinetic investigations show that at the wavelength of 284nm the absorbance-time curve obtained after mixing the reactants contains two parts. The absorbance increases rapidly in a few minutes, but then decreases slowly. These observations may indicate the fast stage and the slower subsequent stage mentioned above.

Kinetic data obtained for these reactions prove that the fast process is a second order reaction, and the slower is a first order reaction.

'HNMR studies of equimolar amounts of iodine and bis-p-ethoxyphenyl ditelluride in $CDCl_3$, carried out just after mixing show an obvious difference in the proton chemical shifts from the pure bis-p-ethoxyphenyl ditelluride.

These observations confirm that intermediate products are formed in the reaction.

RESULTS

The reaction between iodine and bis-p-ethoxyphenyl ditelluride in toluene has been investigated. It was observed that the iodine colour disappeared when the reactants mixed together and a dark blue substance appeared within a very short time.

The length of time for the disappearance of the iodine colouration depends on the temperature of the reaction mixture and the concentration of the reactants. When the reaction is carried out at 0°C, the reaction mixture appears to be dark blue to the human eye within ten seconds, at reagent concentrations of the order of 10^{-2}M.

The possibility of the appearance of an intermediate product in the above reaction, was investigated by the use of the spectrophotometric technique using a dual syringe system in conjunction with an **SP** 8 - 100 UV-visible spectrophotometer. By this technique the attempted control of the fast (complete within 1 or 2 minutes) reaction between the iodine and the ditelluride solutions (using toluene as solvent) was carried out. The two cylindrical parts of the apparatus are enclosed in a jacket through which water at constant temperature, (normally low temperature) is continuously passed to keep reactant solutions at a constant temperature, as was explained in Section 2.8.

The absorbance is monitored with respect to time, firstly at 500nm, and in later experiments at 395nm. The wavelength of 500nm was used to monitor the disappearance of the iodine, while the wavelength of 395nm was used to observe the rate of disappearance of the bis-p-ethoxyphenyl ditelluride. This equipment proved to be too crude to follow any reaction with a half life less than approximately 5 seconds.

An equilibrium study of the reaction between the iodine and bis-p-ethoxyphenyl ditelluride was investigated as follows: 2ml of iodine solution (4×10^{-3} M) were transferred by the help of a 2ml pippette to the 1cm spectrophotometric cell containing 2ml of the ditelluride (10^{-3}M). The absorbance of the resulting solution was measured against a purified toluene blank in two cases, firstly immediately after mixing and secondly when the absorbance becomes almost constant.

It was observed that there were two stages in the reaction. An initial stage which takes place rapidly, and a subsequent slow reaction which starts a few minutes after mixing. It has been observed that the fast reaction involves the formation of two donor acceptor complexes, which are 1 : 1 ($Ar_2Te_2.I_2$) and 1 : 2 ($Ar_2Te_2.2I_2$) complexes under equilibrium conditions. The formation of p-ethoxyphenyl tellurenyl iodide then takes place in the slower stage.

When reaction mixtures are left at room temperature, it is observed that two minutes are sufficient for the equilibrium to be reached. If the reaction mixture is left for a longer period the slow stage of the reaction forming ArTeI commences.

Investigations of the equilibrium were carried out at three wavelengths, 500nm, 318nm and 284nm at room temperature. Data obtained for the absorbance of the reaction mixture at three wavelengths (for a range of different concentrations of the reactants) was then analysed using the computer program explained in Appendix 3.

It has been found that 500nm is the best wavelength to study the equilibrium constant of the reaction between the iodine and the ditelluride.

Typical data obtained for the absorbance of the reaction mixture at the wavelength of 500nm and room temperature ($25^{\circ}C$) is shown in Table 1.

The good agreement between the calculated and experimental results suggests that the reaction scheme described above is correct, Table 1A.

Finally, the experiment was repeated at the wavelength of 500nm and at another two temperatures, $10^{\circ}C$ and $40^{\circ}C$. Data obtained are presented in Tables 2 and 3 respectively. All of the results obtained were then treated with the computer as above, and similar results have been obtained. Tables 2A and 3A in Appendix 6.

A spectrum of a mixture of equimolar amounts of the iodine and the ditelluride shows almost no absorbance at the wavelength of 500nm at this stage of the total reaction sequence.

Values for K_1, E_1, K_2 and E_2 have been calculated by using the above mentioned program, where K_1, E_1 are the equilibrium constant and the extinction coefficient of the 1 : 1 complex ($Ar_2Te_2.I_2$). K_2 and E_2 are the equilibrium constant and the extinction coefficient of the 1 : 2 complex ($Ar_2Te_2.2I_2$). The values of these parameters for the wavelengths of 500nm, 318nm and 284nm at room temperature (25°C), are presented in Table 4, together with the sum of the square differences (SSD) between the observed and the calculated absorbances.

Table 5 shows the data obtained for K_1,E_1,K_2 and E_2 at the temperatures 10°C, 25°C and 45°C at the wavelength of 500nm. From the data it can be seen that the value of K_2 is in a reliable range and should therefore be reasonably accurately determined. However, it seems that the experiment is not sufficiently accurate to calculate ΔH from the three sets of data obtained without a very large error being involved.

e.g. $\Delta H = -60.3 \pm 39.25\ k\,J.mol^{-1}$

The spectrophotometric trace showed that there are two peaks appearing at the wavelengths of 318nm and 284nm, as shown in Figure 2. The peak at 318nm disappears after a short time, this time could be extended by lowering the temperature of the reaction mixture. The other peak (at 284nm) continues to increase at 7°C for about 10 minutes, after which it starts to decrease slowly.

The reaction was followed kinetically at the wavelength of 284nm, which shows that the course of the reaction involved two stages : fast stage and slow stage. The course of the fast stage reaction could be observed at low temperatures. This reaction was studied at 7°C. At this temperature the reaction is completed within 10 minutes. The curve of the absorbance with respect to time was monitored, and the following results have been obtained.

The data obtained from the above curve fits the second order equation:

$$A + B \xrightarrow{k} C$$

where A, B and C represent diaryl ditelluride, iodine and the product, respectively. The following equations can be obtained when $A_o = B_o$.

$$\left(\frac{1}{(D - D\infty} - \frac{1}{Do - D\infty)}\right) = \text{kobs } t \text{ - - - - - - - - - - - - } (1)$$

where D is the absorbance at any time, D_o is the initial absorbance, and D_∞ is the absorbance at $t = \infty$

It was found that a plot of:

$\left(\frac{1}{(D - Doo} - \frac{1}{Do - Doo)} \right)$ VS t is a straight line with

gradient = kobs

where kobs ; the observed rate constant, can be used to calculate the true rate constant as follows:

$$kobs = \frac{k}{E_A + E_B - E_C}$$

(for more details see Appendix 4).

The other equation which has been used for the same reaction when Ao $\neq$ Bo is

$$\ln \left\{ \frac{r \Delta_{\infty} - \Delta}{r(\Delta_{\infty} - \Delta)} \right\} = k'obs\ t \text{ - - - - - - - - - - - (2)}$$

where Δ = D - Do , $r = \frac{Bo}{Ao}$

It has been observed that a plot of:

$\ln \left\{ \frac{r \Delta_{\infty} - \Delta}{r(\Delta_{\infty} - \Delta)} \right\}$ against t is a straight line with gradient =

$k'obs$, where

$$k'obs = k\ (Bo - Ao)$$

The derivations of the above two equations are explained in Appendix 4.

The previously determined values of K_1 and K_2 show that the main product in the equilibria at these concentrations will be the 1 : 1 adduct $Ar_2Te_2.I_2$. Therefore it seems likely that we are following here the setting up of this equilibrium. Since K_1 is very large, k_{-1} is small compared to k_1 therefore within experimental error this is the rate constant being determined here. The rate constants obtained are shown in Table 6.

The slow stage of the reaction was then studied, and the data obtained from the curve of absorbance as function of time fits the first order equation explained below:

Now:-

$$I_2 + Ar_2Te_2.I_2 \underset{}{\overset{K_2}{\rightleftharpoons}} Ar_2Te_2.2I_2$$

$$Ar_2Te_2.2I_2 \xrightarrow{k_3} 2ArTeI + I_2$$

The equilibrium values of K_1 discussed above show that the formation of $Ar_2Te_2.I_2$ can be regarded as being essentially complete, hence the use of $Ar_2Te_2.I_2$ in this scheme. The following equation can be obtained:

$$\ln\ (\text{Doo} - \text{D}) = \overset{''}{k}\text{obs}\ t \text{ - - - - - - - - - - - - - } (3)$$

It has been found that a plot of:

$\ln\ (\text{Doo} - \text{D})$ VS t is a straight line with gradient $= - \overset{''}{k}\text{obs}$, where

$$\text{kobs}'' = \frac{K_2 k_3 y}{1 + K_2 y}$$

where $Y = [I_2]_o - [Ar_2 \, Te_2]_o$

K_2, k_3, y and the derivations of the above equation are explained in Appendix 5.

The experiment was studied using different ratios of the reactant concentrations. The values obtained for kobs are shown in Table 7. From these values it can be seen that the equation:

$$\frac{1}{\text{kob}''\text{s}} = \frac{1}{k_3} + \frac{1}{K_2 k_3} \left(\frac{1}{[I_2]_o - [Te]_o} \right)$$ (see Appendix 5)

should hold.

A plot of:

$\left(\frac{1}{\text{kob}''\text{s}} \right)$ VS $\frac{1}{[I_2]_o - [Te]_o}$ is a straight line as shown in Figure 3.

The treatment of the data at 25°C give values of:

$$\frac{1}{K_2 k_3} = 1.03 \text{ mol dm}^{-3} \text{ S}$$

and $\frac{1}{k_3} = 1,620 \text{ S}$

that is,

$k_3 = 6.17 \times 10^{-4} \text{ S}^{-1}$

and $K_2 = 1570 \text{ mol}^{-1} \text{ dm}^{3}$

This kinetically determined value of K_2 is in very good agreement with the value of 1500 $\text{mol}^{-1}\ \text{dm}^{3}$ obtained from the equilibrium studies.

The experiment of the slow stage of the reaction was repeated at different temperatures in the range of (25 - 55°C) with 5°C intervals. The results obtained for kobs from equation 3 are presented in Table 8. The plot of **ln kobs against** temperature is obtained as a straight line shown in Figure 4, with gradient = 29.5 kJ mol^{-1}

Another kind of experiment has been carried out, a study of the behaviour of p-ethoxyphenyl tellurium triiodide (prepared from the ditelluride and iodine as was mentioned in Section 2.9.3) in toluene solution. When $ArTeI_3$ dissolved in toluene a purple colour formed within a few minutes, followed by the appearance of the yellow brown colour which is the normal colour of the p-ethoxyphenyl triiodide.

Finally, 'HNMR investigations have been carried out as follows: Equimolar amounts of bis-p-ethoxyphenyl ditelluride and iodine were mixed together rapidly in $CDCl_3$, the NMR spectrum was then measured immediately after mixing. The protonchemical shifts of this mixture shows clear differences from the individual pure bis-p-ethoxyphenyl ditelluride. The NMR spectra of the ditelluride and the 1 : 1 ratio mixture are presented in Figures 5 and 6 respectively. δ values (referred to TMS as internal reference) are summarised in Table 9.

$[I_2]$ \ $[Ar_2Te_2]$	5×10^{-4} M	4×10^{-4} M	3×10^{-4} M	2×10^{-4} M	1×10^{-4} M	5×10^{-5} M	2.5×10^{-5} M
1×10^{-3} M	1.265	1.381	1.426	1.292	1.135	1.053	1.035
5×10^{-4} M	0.080	0.215	0.413	0.532	0.529	0.509	0.514
4×10^{-4} M	0.090	0.058	0.187	0.350	0.408	0.396	0.406
3×10^{-4} M	0.106	0.073	0.043	0.176	0.280	0.294	0.303
2×10^{-4} M	0.125	0.091	0.060	0.028	0.137	0.174	0.193
1×10^{-4} M	0.144	0.107	0.078	0.044	0.014	0.064	0.084
5×10^{-5} M	0.163	0.114	0.085	0.058	0.019	0.009	0.030

Table 1 : Typical data for the absorbance of mixture of bis-p-ethoxyphenyl ditelluride with iodine at the wavelength of 500nm and at room temperature (25°C).

$[I_2]$ \ $[Ar_2Te_2]$	5×10^{-4} M	4×10^{-4} M	3×10^{-4} M	2×10^{-4} M	1×10^{-4} M	5×10^{-5} M	2.5×10^{-5} M
1×10^{-3} M	1.162	1.227	1.238	1.199	1.116	1.060	1.029
5×10^{-4} M	0.071	0.258	0.421	0.515	0.538	0.525	0.513
4×10^{-4} M	0.058	0.059	0.227	0.358	0.414	0.415	0.408
3×10^{-4} M	0.083	0.051	0.047	0.191	0.285	0.301	0.302
2×10^{-4} M	0.109	0.077	0.045	0.035	0.149	0.185	0.195
1×10^{-4} M	0.136	0.103	0.071	0.038	0.023	0.065	0.085
5×10^{-5} M	0.149	0.116	0.084	0.052	0.019	0.017	0.030

Table 1A : Calculated absorbance of the mixture of bis(p-ethoxyphenyl) ditelluride with iodine at the wavelength of 500nm at 25°C.

$[Ar_2Te_2]$ / $[I_2]$	5×10^{-4} M	4×10^{-4} M	3×10^{-4} M	2×10^{-4} M	1×10^{-4} M	5×10^{-5} M
5×10^{-4} M	0.09	0.244	0.500	0.67	0.63	0.55
4×10^{-4} M	0.098	0.068	0.244	0.44	0.51	0.44
3×10^{-4} M	0.11	0.078	0.048	0.22	0.35	0.32
2×10^{-4} M	0.13	0.096	0.062	0.03	0.15	0.190
1×10^{-4} M	0.15	0.115	0.080	0.05	0.018	0.056

Table 2 : Absorbance of mixture of bis-p-ethoxyphenyl ditelluride with iodine at the wavelength of 500nm and at 10°C.

$[I_2]$ \ $[Ar_2Te_2]$	5×10^{-4} M	4×10^{-4} M	3×10^{-4} M	2×10^{-4} M	1×10^{-4} M	5×10^{-5} M
5×10^{-4} M	0.080	0.16	0.25	0.340	0.43	0.45
4×10^{-4} M	0.090	0.05	0.15	0.240	0.32	0.36
3×10^{-4} M	0.11	0.08	0.04	0.130	0.23	0.26
2×10^{-4} M	0.14	0.10	0.06	0.030	0.12	0.16
1×10^{-4} M	0.16	0.12	0.08	0.054	0.02	0.054

Table 3 : Absorbance of mixture of bis-p-ethoxyphenyl ditelluride with iodine at the wavelength of 500nm and at 45°C.

λ nm	K_1	K_2	E_1	E_2	SSD
500	1.0×10^7	1.43×10^3	59	4960	0.047
318	5.0×10^8	1.1×10^3	6575	25250	0.022
284	1.5×10^8	1.5×10^3	6650	24180	0.075

Table 4 : Values of the equilibrium constants and the extinction coefficient of the complexes, $Ar_2Te_2 \cdot I_2$ and $Ar_2Te_2 , 2I_2$ at the wavelengths of 500nm, 318nm and 284nm and at 25°C.

T ^{o}C	K_1	K_2	E_1	E_2	SSD
10	1.65×10^7	2.8×10^3	93	4900	0.02
25	1.0×10^7	1.43×10^3	59	4960	0.047
45	1.48×10^7	0.21×10^3	90	4660	-

Table 5 : Values of the equilibrium constants and the extinction coefficient of the complexes, $Ar_2\,Te_2 \cdot I_2$ and $Ar_2\,Te_2 \cdot 2I_2$ at the wavelength of 500nm and at different temperatures.

$Ar_2 Te_2$	I_2	$kobs/min^{-1}$	$k/dm^3 mol^{-1} min^{-1}$
2.5×10^{-5} M	2.5×10^{-5} M	1.627	3429
2.5×10^{-5} M	5×10^{-5} M	0.09	3600
2.5×10^{-5} M	8×10^{-5} M	0.282	3760
2.5×10^{-5} M	1.25×10^{-4} M	0.33	3300
2.5×10^{-5} M	1.5×10^{-4} M	0.321	2568
2.5×10^{-5} M	2×10^{-4} M	0.481	2748
5×10^{-5} M	2.5×10^{-5} M	0.081	3240
1×10^{-4} M	2.5×10^{-5} M	0.236	3146

Table 6 : Rate constant of the fast stage of the reaction of bis(p-ethoxyphenyl) ditelluride with iodine at 7 °C.

$[Ar_2Te_2]$	$[I_2]$	kobs/min^{-1}	1/kobs/min	$1/([I]_o - [Te]_o)$
5×10^{-5} M	1×10^{-4} M	0.00267	374.5	20000
5×10^{-5} M	1.5×10^{-4} M	0.005	200	10000
5×10^{-5} M	2×10^{-4} M	0.0067	149.3	6666.7
5×10^{-5} M	2.5×10^{-4} M	0.009	111.1	5000
5×10^{-5} M	3×10^{-4} M	0.010	100	4000

Table 7 : Rate of the slow stage of the reaction of bis(p-ethoxyphenyl) ditelluride with iodine at 25°C.

kobs/min^{-1}	ln kobs/min^{-1}	K/T
0.0067	$\bar{6}.994$	0.00336
0.0088	$\bar{5}.267$	0.00330
0.0108	$\bar{5}.472$	0.00325
0.0123	$\bar{5}.602$	0.00319
0.0148	$\bar{5}.787$	0.00314
0.0167	$\bar{5}.908$	0.00310
0.0193	$\bar{4}.052$	0.00305

Table 8 : Rate of the slow stage of the reaction of bis(p-ethoxyphenyl) ditelluride at different temperatures.

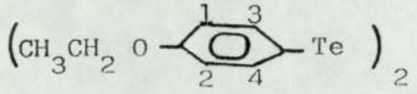
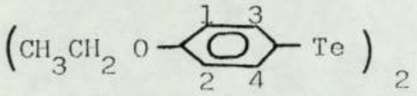
Compound	Chemical Shift (δ) ppm, TMS = 0 ppm
	CH_3 : 1.39(t) ; CH_2 : 3.97 (q) ; H(1,2) : 6.61 (d) ; H(3,4) : 7.59 (d).
 · I_2	CH_3 : 1.40(t) ; CH_2 : 4.07(q) ; H(1,2) : 6.80 (d) ; H(3,4) : 7.38 (d).

Table 9 : Chemical shift obtained from the 'HNMR spectra of pure bis(p-ethoxyphenyl) ditelluride and mixture of equimolar amounts of bis(p-ethoxyphenyl) ditelluride and iodine; (d) for doublet, (t) for triplet and (q) for quartet.

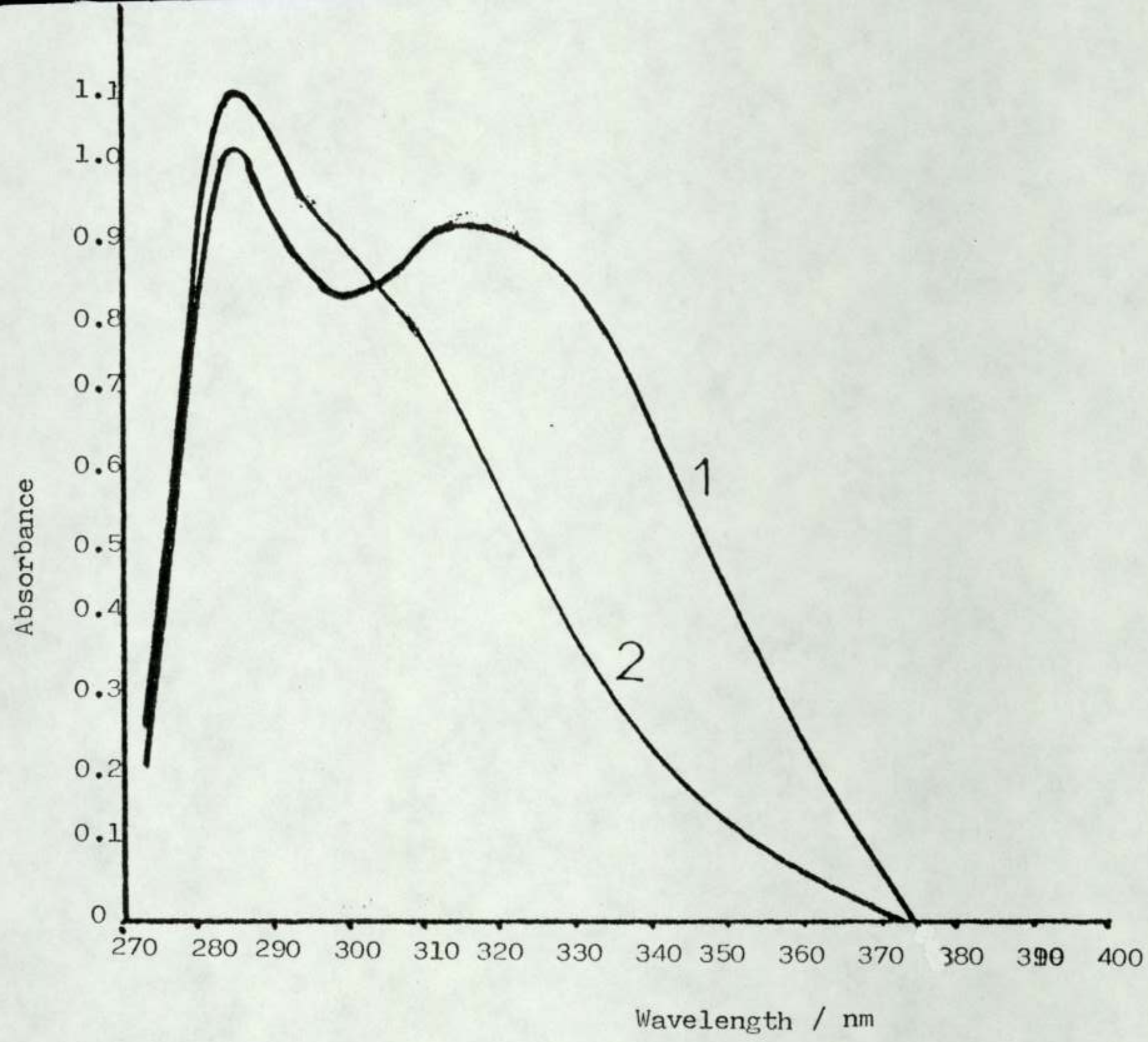


Figure 2 : The absorbance with respect to time of mixture of equimolar amounts of bis(p-ethoxyphenyl) ditelluride and iodine in solution at 7°C : 1 - just after mixing, 2 - five minutes later.

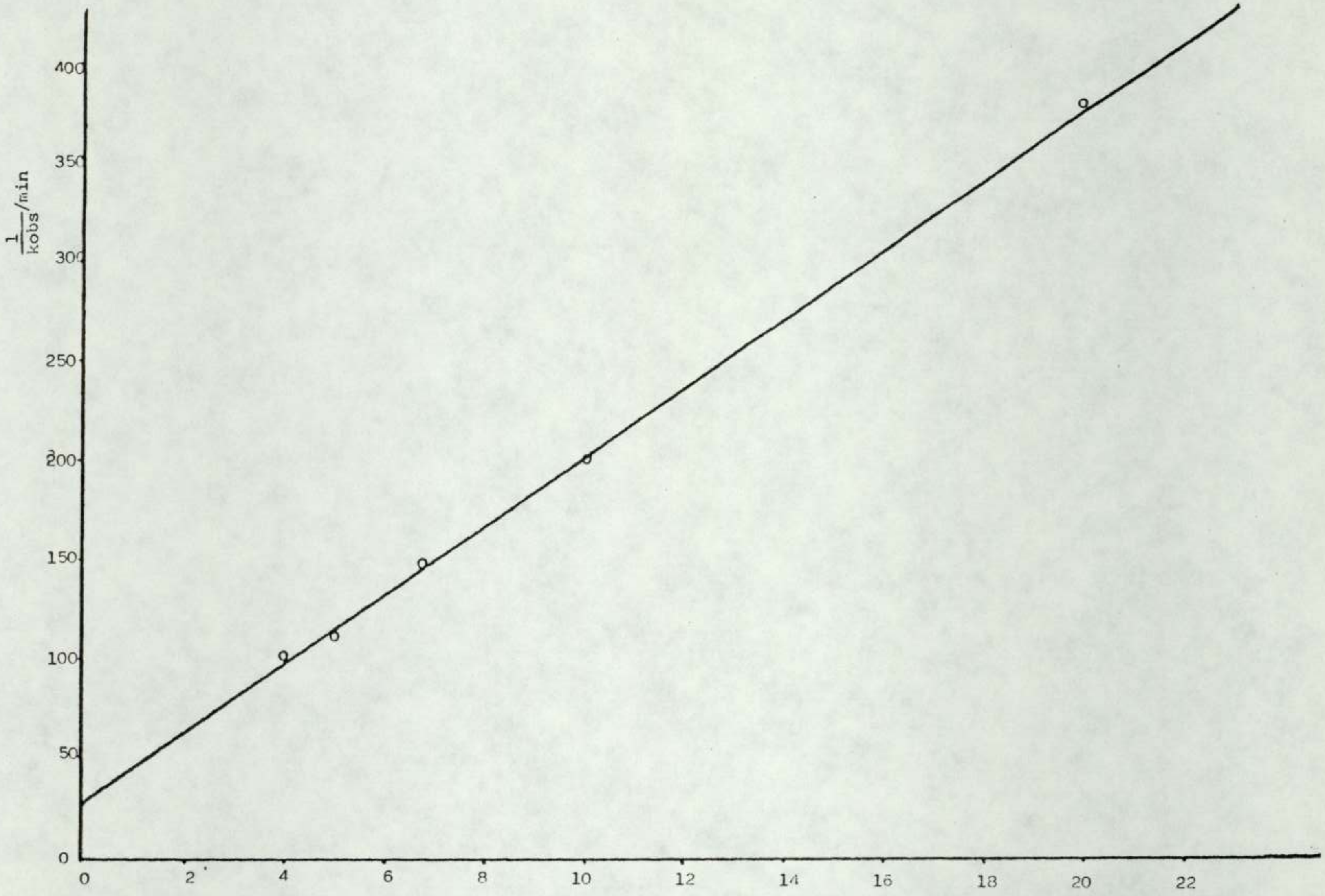


Figure 3 : Plot of the reciprocal of the rate of the slow stage of the reaction of bis(p-ethoxyphenyl) ditelluride with iodine against $10^{-3}/([I]_o - [Te]_o)$ at 25°C.

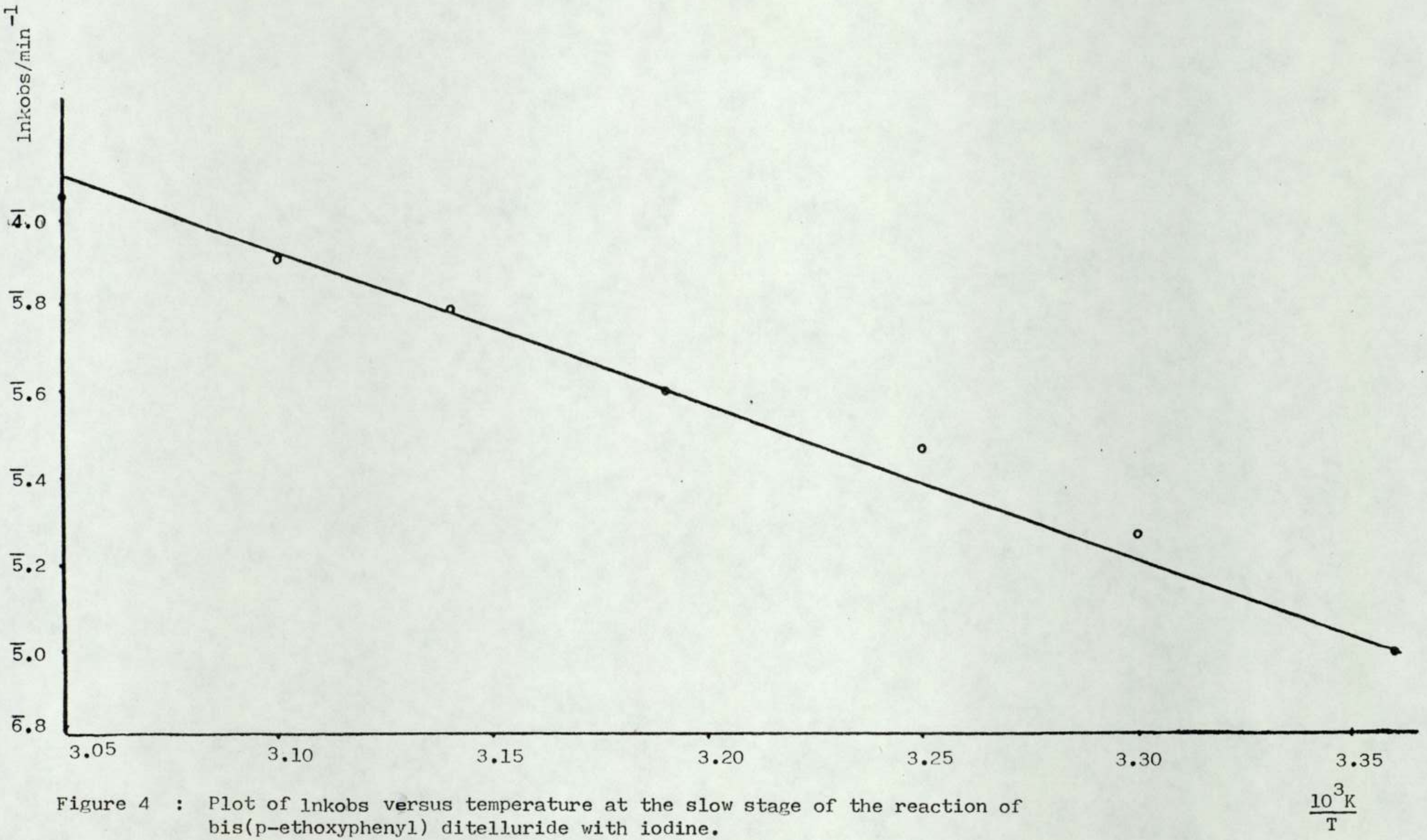


Figure 4 : Plot of lnkobs versus temperature at the slow stage of the reaction of bis(p-ethoxyphenyl) ditelluride with iodine.

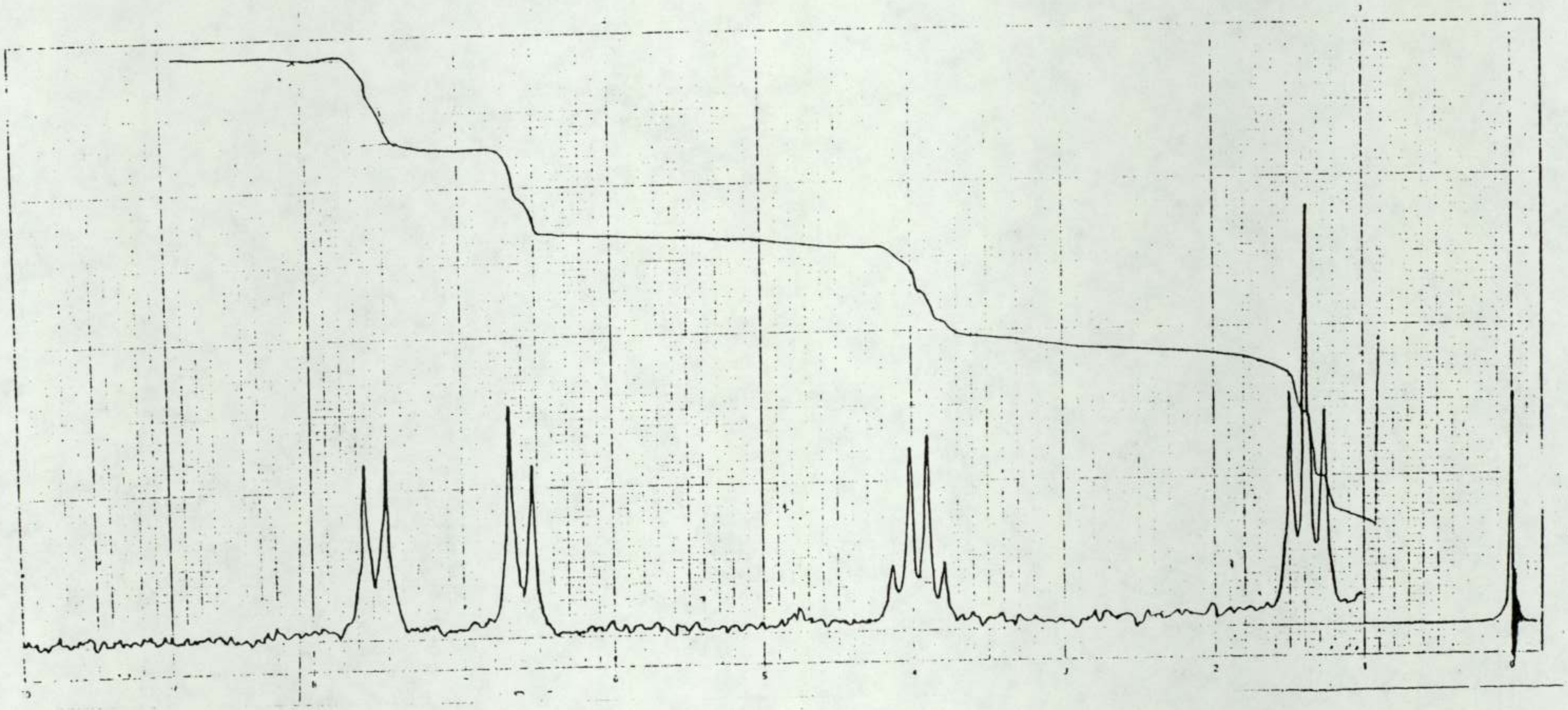


Figure 5 : 'HNMR spectrum of bis(p-ethoxyphenyl) ditelluride.

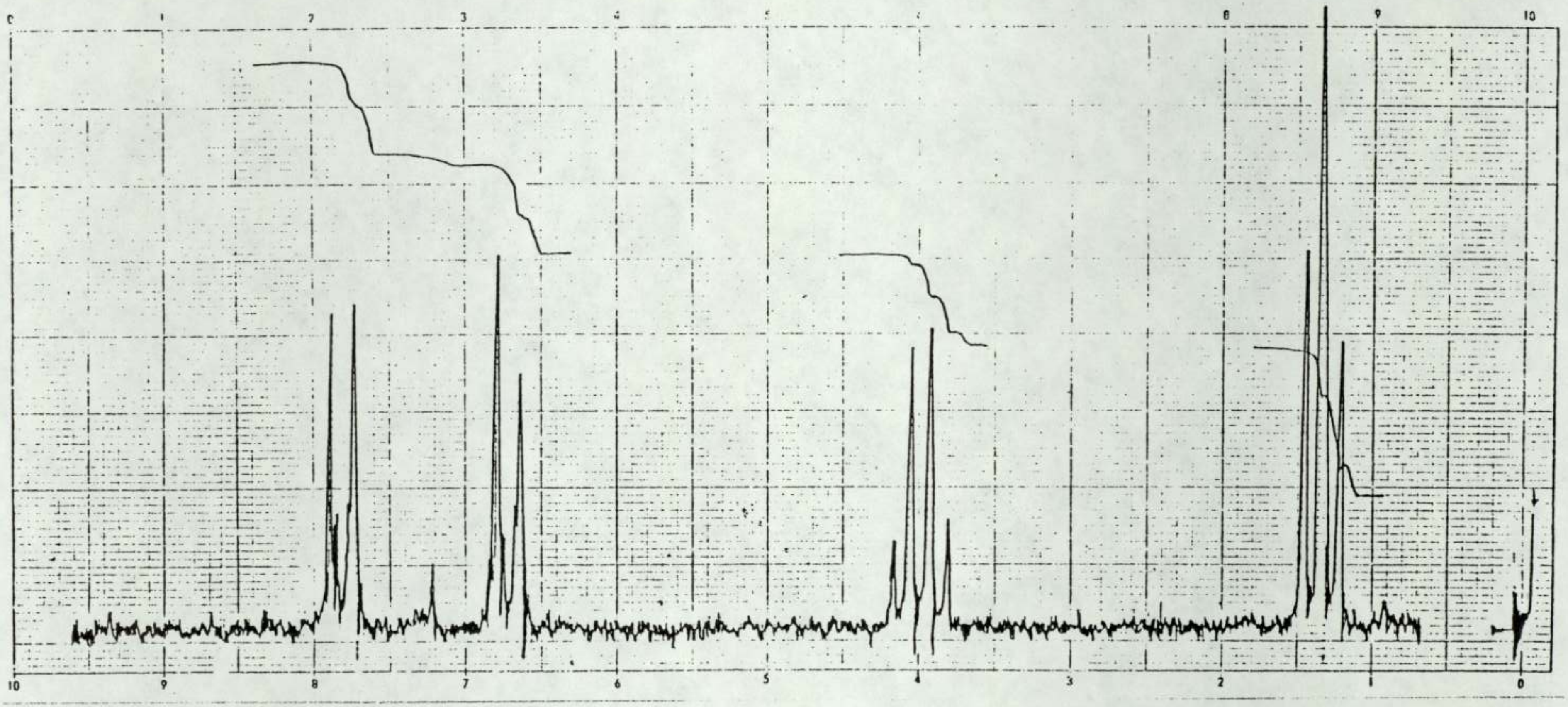


Figure 6 : 'HNMR spectrum of mixture of equimolar amounts of bis(p-ethoxyphenyl) ditelluride and iodine.

DISCUSSION

The purple colour of a toluene solution of iodine or the violet colour of iodine in carbon tetrachloride, is due to the formation of a donor acceptor complex, e.g. $CH_3C_6H_5{\cdot}I_2$. The reaction is readily reversible because there is no full chemical bond between a ring carbon atom and the iodine. This charge transfer complex has an intense absorbance at the wavelength of 500nm.

This purple colour disappears after mixing with the toluene solution of bis-p-ethoxyphenyl ditelluride. A dark blue substance appears clear to the human eye within a very short time. This probably indicates the formation of an intermediate product.

Experiments have been carried out to study the possibility of the appearance of an intermediate product in the above reaction, by using a dual syringe system connected to an SP8 - 100 UV visible spectrophotometer, explained in Section 2.8. That is, a simple rapid mixing device.

No definite conclusions could be drawn from the results of these experiments. There might be an initial reaction, essentially complete within say 10 seconds at room temperature, but no evidence of such a reaction was observed. It seems that a more efficient system is required which involves a much shorter delay between the mixing of the ditelluride and iodine, their passage through the tube to the spectrophotometer cell and the measurement of the absorbance, to seek for such evidence. This equipment is not suitable for following such fast reactions. It has proved to be too crude for following any reaction with a half life around 5 seconds.

McWhinnie and Thavornyutikarn(91) have observed that the black benzene-soluble material obtained by mixing solutions of iodine with diphenyl ditelluride, may be a mixture of $PhTeI_3$ and phenyltellurenyl iodide, PhTeI an intermediate product. No suitable solvent for the separation of the two substances has been found. Subsequently, Schulz(75) has been able to separate ArTeX (Ar = C_6H_5 , 4-(CH_3O) C_6H_4 , 4-(C_6H_5) C_6H_4 , 3,4-$(CH_3O)_2$ C_6H_3; X = Br , I) from diaryl ditellurides and equimolar portions of halogens, if the reaction is carried out in a solvent in which the starting materials, but not the tellurenyl compound, are soluble.

Two peaks at the wavelength of 318nm and 284nm have been observed to appear rapidly after mixing iodine with the ditelluride. These studies show that the peak at 318nm disappears after a short time, approximately 2 minutes, while the other keeps growing. These observations may indicate the formation of an intermediate product.

Equilibrium investigations of this reaction have been carried out at three wavelengths, 500nm, 318nm and 284nm. It has been observed that 500nm is the most suitable wavelength to study the equilibrium constant of the reaction between the iodine and the ditelluride, in contrast with the other wavelengths:- 318nm and 284nm - which are not suitable for studies using a wide range of different concentrations of the reactants.

At this wavelength (500nm) it is observed that when reaction mixtures are left at room temperature (1 - 2) minutes are sufficient for equilibrium to be reached. A casual inspection of the data obtained in Table 1 shows that the absorbance of a reaction solution shortly after mixing, is very low when the concentrations of the iodine and the ditelluride are equal. This indicates the formation of a 1 : 1 complex. On the other hand, the absorbance increases as the iodine concentration increases, indicating the formation of the 1 : 2 complex. The energy levels of the two species are different.

The possibility of the formation of 1 : 1 and 1 : 2 donor acceptor complexes in the reaction of (NDC's) with an electron acceptor, has been suggested,(89) (see Compounds I - VI in the introduction of this Chapter). These compounds are expected to function as electron donors in charge-transfer complexes. Compounds I - III were found to form 1 : 1 complexes with tetracyanoquinodimethane. All six NDC's are expected to form 1 : 2 complexes with elemental iodine as an acceptor.

Furthermore Pritzkow(90) has determined the intermolecular bonding between $(CH_3)_2$ TeI_2 and I_2 in dimethyltellurium tetraiodide $(CH_3)_2 Te I_4$. It was proved that the structure is built up by $(CH_3)_2$ $Te I_2$ and I_2 molecules and does not contain Te(VI). The compound should be formulated as dimethyltellurium diiodide-diiodine $(1/_1)$.

These observations can support the possibility of the formation of $Ar_2 Te_2 \cdot I_2$ and $Ar_2 Te_2 . 2I_2$ (the 1 : 1 and 1 : 2 complexes respectively) explained above.

The spectrum of a mixture of equimolar amounts of the iodine and the ditelluride obtained at this stage of the total reaction sequence, shows essentially no absorbance at the wavelength of 500nm. This can confirm the above observations of the formation of $Ar_2Te_2.I_2$.

The data of Table 1 have been analysed using the computer program, shown in Appendix 3. The results calculated give a very good agreement with the observed data. This suggests that the scheme described above is correct, Tables 1A, 2A and 3A.

In the reaction between iodine and the ditelluride, it has been observed that there are two main stages in the overall reaction. The initial reaction is fast and is followed by a slower subsequent reaction.

The fast stage of the reaction involves the formation of two different species, which are the two donor acceptor complexes, 1 : 1 ($Ar_2\ Te_2 \cdot I_2$) and 1 : 2 ($Ar_2\ Te_2 \cdot 2I_2$) under equilibrium conditions. These two species have markedly different spectral properties.

It has been found that the value of the equilibrium constant at the formation of the 1 : 1 complex (K_1) is very large, see Table 4. This indicates that this reaction lies essentially completely over to the complex side. Also, it is almost complete before any subsequent reaction occurs. It may also mean that the value obtained for K_1 is not very accurate. In order to determine K_1 accurately, very small and accurately known concentrations of the reactants are required to give significant concentrations of all the species involved.

$$Ar_2\ Te_2 + I_2 \xrightleftharpoons{K_1} Ar_2\ Te_2 \cdot I_2 \qquad (1)$$

The value of the equilibrium constant of the 1 : 2 complex (K_2) is reproducible and reasonably constant at the different wavelengths. It can be seen that the value of K_2 is very sensitive to the input data. The 1 : 2 complex is produced from the interaction between $Ar_2Te_2.I_2$ and the iodine.

$$Ar_2Te_2.I_2 + I_2 \xrightleftharpoons{K_2} Ar_2Te_2.2I_2 \qquad (2)$$

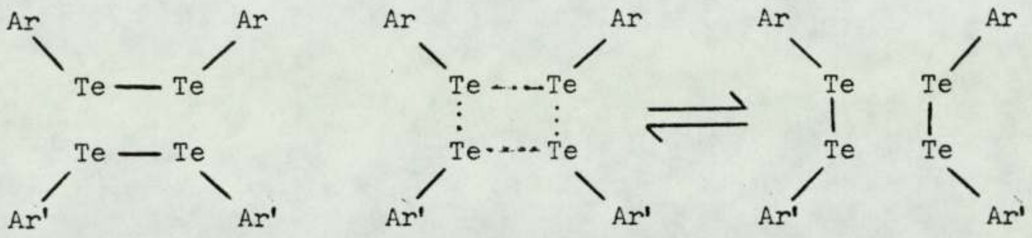
The values of the extinction coefficients E_1 and E_2 of the 1 : 1 and 1 : 2 complexes respectively should also be reliable. At the wavelength of 500nm the E_1 value is very small compared with the extinction coefficient of the reactants EI_2 and EAr_2Te_2. While at the wavelength of 318nm the value of E_1 is nearly equal to the sum of the EI_2 and EAr_2Te_2. At the wavelength of 284nm the value of E_1 is equal to the value of EAr_2Te_2. On the other hand, the values of E_2 at all the wavelengths of 500nm, 318nm and 284nm are very much greater than E_1, EI_2 and EAr_2Te_2.

Taken together with the determined equilibrium constant, the above results suggest that the 1 : 1 complex is unlikely to be simply a charge transfer complex, while the 1 : 2 complex is probably a charge transfer complex.

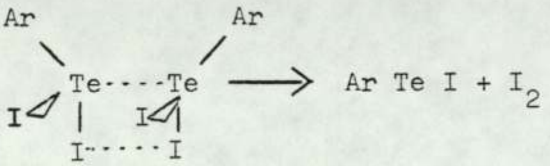
The fast stage of the reaction discussed above is followed by a slower subsequent reaction which starts a few minutes after mixing, to form p-ethoxyphenyltelluronium iodide from the 1 : 2 complex ($Ar_2Te_2.2I_2$), equation (2).

$$Ar_2\,Te_2\,,\,2I_2 \longrightarrow 2Ar\,Te\,I + I_2$$

Dance$^{(92)}$ explains the possibility of the cleavage of Te – Te bonds in the formation of unsymmetrical ditellurides by a non-radical reaction, as follows:-



Therefore, it is possible that the formation of Ar Te I can take place by the breaking of the Te - Te bond at the $Ar_2\ Te_2\ ,\ 2I_2$.



In fact the alternative of a radical reaction is unlikely because there is evidence that radicals are not present under these conditions (see Chapter 3).

The two stages of the reaction discussed above are shown to occur by the results of the kinetic investigations described below.

Kinetic studies show that there are two distinct parts of the absorbance - time curve obtained at the wavelength of 284nm after mixing the reactants. The rapid increase of the absorbance takes place first followed by a slower decrease of absorbance. These two different parts of the curve indicate the fast stage and the slower subsequent stage of the reaction which are observed in the equilibrium investigations discussed above.

It has been found kinetically that the course of the fast reaction (the first part of the curve) can be observed at low temperatures, e.g. 7°C . This temperature was used to study this reaction kinetically.

Kinetic investigations under second order conditions of concentration, prove that the rapid stage is a second order reaction.

$$Ar_2\ Te_2 + I_2 \xrightleftharpoons{K_1} Ar_2\ Te_2\cdot I_2$$

Since the equilibrium constant values (K_1) discussed above proves that the formation of $Ar_2\ Te_2\cdot I_2$ can be regarded as being almost complete. The permanent complex which appears in the rapid stage is obviously $Ar_2\ Te_2\cdot I_2$ rather than $Ar_2\ Te_2\cdot 2I_2$ under the conditions used in these experiments.

The equations used to calculate the rate constant are:-

$$\left(\frac{1}{(D - D_\infty} - \frac{1}{D_o - D_\infty)}\right) = \text{kobs}\ t$$

when $[Ar_2Te_2]_o = [I_2]_o$

and

$$\ln \frac{(r\Delta_\infty - \Delta)}{(r\ (\Delta - \Delta_\infty)\ )} = \text{k}'\text{obs}\ t$$

when $[Ar_2Te_2]_o \neq [I_2]_o$

For details about the derivation of these equations see Appendix 4.

The values obtained for the rate constant, Table 6, are large, indicating that the formation of $Ar_2\ Te_2 \cdot I_2$ takes place very fast in comparison to the formation of the intermediate Ar Te I.

The other part of the absorbance-time curve obtained at wavelength of 284nm has also been studied kinetically. It was observed that in this part of the curve the absorbance decreases slowly.

Data obtained from this part of the curve shows that the slow stage of the reaction is first order.

$$Ar_2\ Te_2 \cdot 2I_2 \xrightarrow{k_3} 2Ar\ Te\ I + I_2$$

The following equation is used to calculate the rate constant:

$$\ln (D\infty - D) = - k''obs\ t$$

k''obs has been obtained for different ratios of the reactant concentrations, Table 7.

In the slow stage of the reaction there are two ways in which the intermediate Ar Te I may be formed, by the dissociation of either of the complexes - $Ar_2\ Te_2 \cdot I_2$ or $Ar_2\ Te_2 \cdot 2I_2$:

$$Ar_2\ Te_2 \cdot I_2 \longrightarrow 2Ar\ Te\ I \qquad (3)$$

$$Ar_2\ Te_2 \cdot 2I_2 \longrightarrow 2Ar\ Te\ I + I_2 \qquad (4)$$

If the dissociation takes place according to equation (3) then it can be seen from Appendix 5 that:

$$k''_{obs} = \frac{k_3}{1 + K_2Y}$$

where $Y = [I]_o - [Te]_o$

$$\therefore \left(\frac{1}{k''_{obs}}\right) = \frac{1}{k_3} + \frac{K_2}{k_3}\left([I]_o - [Te]_o\right) \text{ ------ (A)}$$

But, if it takes place due to equation (4), then:

$$k''_{obs} = \frac{K_2k_3Y}{1 + K_2Y}$$

$$\therefore \frac{1}{k''_{obs}} = \frac{1}{k_3} + \frac{1}{K_2k_3}\left(\frac{1}{[I]_o - [Te]_o}\right) \text{ ----- (B)}$$

The value of $K_2 = 1570$ mol dm^{-3} determined kinetically by employing equation (B) is in very good agreement with the value of 1500 mol dm^{-3} found in the equilibrium study. This clearly indicates that the formation of the intermediate p-ethoxyphenyl tellurenyl iodide is due to the dissociation of $Ar_2Te_2 , 2I_2$ rather than of Ar_2Te_2 , I_2.

From the above observations the following reaction mechanism can be suggested:

$$Ar_2Te_2 + I_2 \overset{K_1}{\rightleftharpoons} Ar_2Te_2\cdot I_2$$

$$Ar_2Te_2\cdot I_2 + I_2 \overset{K_2}{\rightleftharpoons} Ar_2Te_2 , 2I_2$$

$$Ar_2Te_2\cdot 2I_2 \xrightarrow{k_3} 2ArTeI + I_2$$

The formation of Ar Te I could be followed by a subsequent interaction between iodine and Ar Te I to produce p-ethoxyphenyl tellurium triiodide, e.g.

$$\text{Ar Te I} + \text{I}_2 \longrightarrow \text{Ar Te I}_3$$

But, this has not been investigated.

Another study has been done by preparing p-ethoxyphenyl tellurium triiodide according to the literature,(41) from the reaction between bis-p-ethoxyphenyl ditelluride and iodine section 2.9.3. When Ar Te I_3 powder is dissolved in toluene a purple colour is formed within a few minutes followed by the appearance of the yellow colour which is the normal colour of Ar Te I_3 - this may be due to an equilibrium between Ar Te I_3 , Ar Te I and iodine in solution:

$$\text{Ar Te I}_3 \rightleftharpoons \text{Ar Te I} + \text{I}_2$$

or most probably, the following reaction sequence takes place during the dissolution:

$$\begin{tikzcd}
\begin{matrix}\text{Ar Te I}_3 \\ \text{(solid)}\end{matrix} \arrow[r, "\text{fast}", "\text{Toluene}"'] & \begin{matrix}\text{Ar Te I} & + & \text{I}_2 \\ \text{(solid)} & & \text{(solution)}\end{matrix} \arrow[d] \\
\begin{matrix}\text{Ar Te I}_3 \\ \text{(solution)}\end{matrix} & \begin{matrix}\text{Ar Te I} & + & \text{I}_2 \\ \text{(solution)} & & \text{(solution)}\end{matrix} \arrow[l]
\end{tikzcd}$$

The results of some preliminary N.M.R experiments which have not been pursued in detail are relevant to this material.

In my work equimolar amounts of bis-p-ethoxyphenyl ditelluride and iodine were mixed together rapidly in deuterochloroform. 'HNMR spectrum was then measured immediately after mixing. The proton chemical shifts of this equimolar mixture show clear differences from that of pure bis-p-ethoxyphenyl ditelluride. This is another clear indication of the formation of the intermediate product discussed above.

CHAPTER FIVE

Oxidative-Addition Reactions of Transition Metal Complexes With The Diaryl Ditellurides

INTRODUCTION

The term 'oxidative addition' has come to be used to designate a rather widespread class of reactions. In general, it describes a process which results in an increase in both the oxidation state and co-ordination number of a metal ion. One of these is that the oxidations of certain classes of complexes; notably those with nearly filled d shells, i.e. d^7 - d^{10}; are accompanied by increases in the preferred co-ordination numbers of the metal atoms and hence by the incorporation of additional ligands into their co-ordination shells.

Three classes of reactions have attracted particular attention in recent years, namely the oxidative addition reactions of five co-ordinate d^7, four co-ordinate d^8, and four co-ordinate d^{10} complexes. In each of these cases the driving force for reaction is associated with the increase in stability in going from the initial open shell configuration (containing 17, 16 and 18 valence electrons, respectively) to the closed shell configuration of the product.

The principal studies on the mechanisms of oxidative addition reactions of d^7 complexes, which have been concerned with $Co(CN)_5^{3-}$ are exemplified by the equation:

$$2\left[Co^{II}(CN)_5\right]^{3-} + X - Y \longrightarrow \left[Co^{III}(CN)_5 X\right]^{3-} + \left[Co^{III}(CN)_5 Y\right]^{3-}$$

$X - Y = H_2$, Br_2, HOOH, CH_3I, etc.

These reactions have been shown to proceed through free-radical stepwise mechanisms illustrated by the reaction with H_2O_2 as shown below:

$$Co(CN)_5^{3-} + H_2O_2 \longrightarrow Co(CN)_5OH^{3-} + OH\cdot \text{ rate determining step}$$

$$Co(CN)_5^{3-} + OH\cdot \longrightarrow Co(CN)_5OH^{3-}$$

The evidence(93) for this mechanism includes the second-order kinetic behaviour

(rate $= k\left[Co(CN)_5^{3-}\right]\left[H_2O_2\right]$)

as well as detection of the intermediate $OH\cdot$ radical through its reaction with added I^-.

The $Co(CN)_5^{3-}$ ion reacts slowly with solvent water, thus:

$$2Co(CN)_5^{3-} + H_2O \longrightarrow Co(CN)_5H^{3-} + Co(CN)_5OH^{3-}$$

and also directly with hydrogen, thus:

$$2Co(CN)_5^{3-} + H_2 \longrightarrow 2Co(CN)_5H^{3-}$$

possibly through the intermediacy of the $\left[Co_2(CN)_{10}\right]^{6-}$ ion(94), which forms according to the equation:

$$2Co(CN)_5^{3-} \rightleftharpoons Co_2(CN)_{10}^{6-}$$

followed by a rate-determining reaction between $Co_2(CN)_{10}^{6-}$ and H_2. The rapid reversible transformation of the green $Co(CN)_5^{3-}$ to the intensely violet dimer $Co_2(CN)_{10}^{6-}$ is readily detected visually as the concentrations of aqueous $Co(CN)_5^{3-}$ solutions are increased, particularly at low temperatures ($\sim 0^{\circ}C$). Attempts to study this reaction quantitatively were unsuccessful, because of the instability of the solutions with respect to decomposition by the reaction with solvent water shown above.

The $Co(CN)_5^{3-}$ ion also undergoes bimolecular oxidative insertion reactions(95) with C_2F_4, C_2H_2, SO_2, or $SnCl_2$ to give for example:

$[(NC)_5\,Co\,SnCl_2\,Co(CN)_5]^{6-}$.

The relationship between species existing in solutions of d^{10} complexes notably complexes of Ni^{o}, Pd^{o} and Pt^{o}, is not completely understood, but it has been shown that equilibria can occur between the co-ordinatively saturated complex ML_4 and species formed by dissociation of L.(96)

$$M\,(PPh_3)_4 \rightleftharpoons M\,(PPh_3)_3 \rightleftharpoons M\,(PPh_3)_2$$

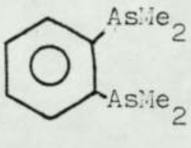
It appears that the main species formed on dissolving $Pt\,(PPh_3)_4$ is the complex $Pt\,(PPh_3)_3$. Nevertheless, even though a certain species may predominate under certain conditions in solution, it is sometimes difficult to establish the actual reactive species in a particular reaction. This complication has made an examination of oxidative addition difficult, but it is probable that both one and two step mechanisms occur as for d^8 – complexes (which will be mentioned later).

One of the most reactive compounds which undergoes the oxidative addition reaction is $Pt^o (PPh_3)_4$, which has been found to add oxidatively a large number of small molecules such as alkyl halides, acyl halides, carbon disulphide,(97) etc., to form $Pt^{11} (PPh_3)_2$ (X) (Y) complexes (X – Y = RX, RCOCl, CS_2, etc.).

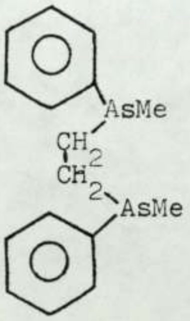
The addition of the oxidant to $Pt^o (PPh_3)_4$ is accompanied or more usually preceded, by the loss of one or more ligands from the transition metal complex, e.g.

$$Pt^o (PPh_3)_4 + X\,Y \xrightarrow{\qquad} Pt^{11} (X)(Y)(PPh_3)_2 + 2PPh_3$$

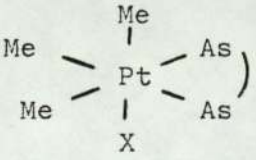
The stereochemistry of oxidative addition to the platinum (11) complexes $Pt\,Me_2$ (LL) has been determined for LL = the bidentate arsenic ligands(98):



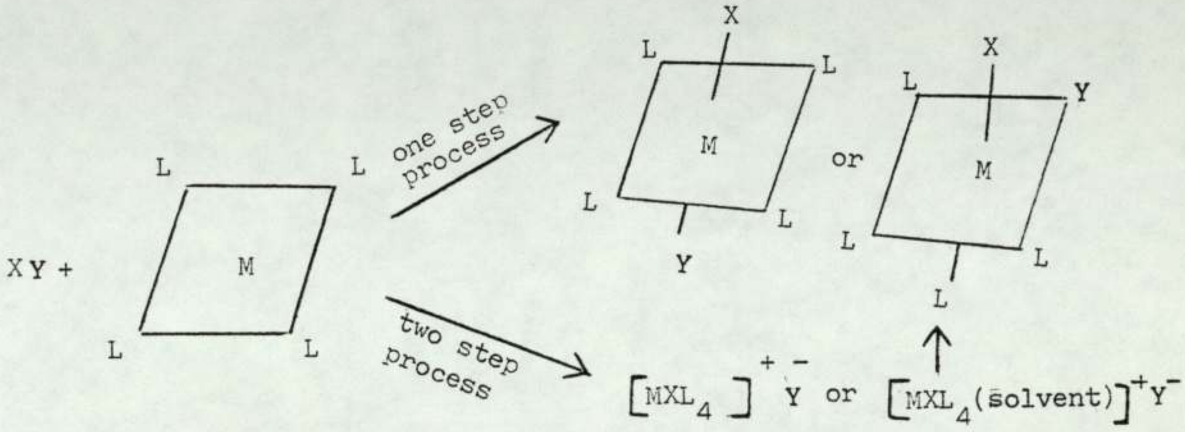
and



The oxidative addition of methyl halides gives the 1, 2, 3 or fac-trimethyl platinum (IV) as shown below. It is not possible to choose between cis and trans addition from this observation.



A brief outline of possible types of oxidative addition will now be given for the oxidation of d^8 to d^6 complexes. It is Vaska's compound $[Ir\ Cl\ (CO)\ (PPh_3)_2]$ that most readily comes to mind in this context, and oxidative addition of molecules X Y to complexes of the type $[ML_4]$ may occur by one of the two limiting mechanisms shown below, resulting in cis or trans adducts of the type $[ML_4\ XY]$.



If X Y is H_2(99) the process is of the one step type, but for other molecules the problem is largely unsolved:

$$[Ir^{I}\ (CO)\ (PPh_3)_2\ Cl] + X - Y \longrightarrow [Ir^{III}\ (X)\ (Y)\ (CO)\ (PPh_3)_2\ Cl]$$

$X - Y = H_2$, HCl, CH_3I, Ar S S Ar' etc.

The kinetics of the reaction between trans-$[Ir\ Cl\ (CO)\ (PPh_3)_2]$ and the disulphides p - YC_6H_4 S - S C_6H_3 - 2,4 - $(NO_2)_2$ (Y = Br, F, H, Me, or MeO) follow simple second order kinetics. The overall mechanism is considered to be:(100)

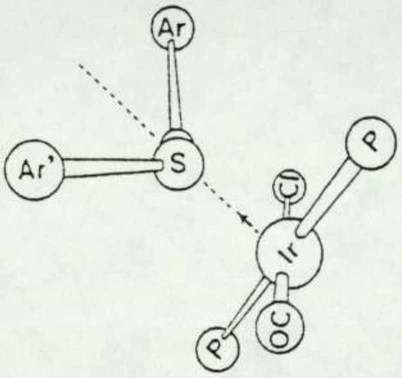
$$\text{trans-}\left[\mathrm{IrCl(CO)(PPh_3)_2}\right] + \mathrm{ArS\text{-}SAr'} \xrightarrow[\text{slow}]{k_2} \left[\mathrm{IrCl(SAr)(SAr')(CO)(PPh_3)_2}\right]$$

$$\left[\mathrm{IrCl(SAr)SAr')(CO)(PPh_3)_2}\right] \xrightarrow{\text{fast}} \left[\mathrm{IrCl(SAr)(SAr')(CO)(PPh_3)}\right]$$

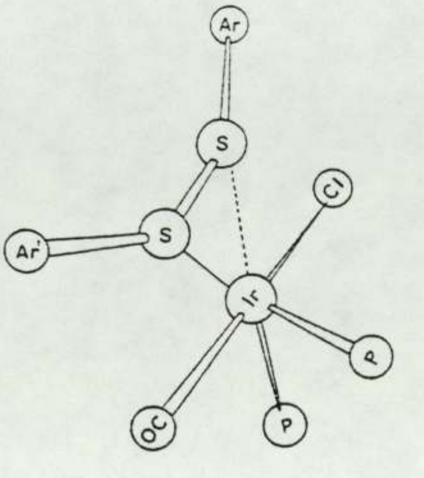
$$+ \mathrm{PPh_3}$$

$$\left[\mathrm{IrCl(SAr)(SAr')(CO)(PPh_3)}\right] \xrightarrow{\text{fast}} \tfrac{1}{2}\left[\mathrm{IrCl(SAr)(SAr')(CO)(PPh_3)}\right]_2$$

It is probably the iridium complex acting as a nucleophile which initially attacks the sulphur - sulphur bond from the back side as shown below:



This will give rise to a three-centred activated complex in which there is formation of two iridium sulphur bonds with concomitant weakening of the sulphur - sulphur bond. This activated complex is shown below:



The cleavage of the sulphur - sulphur bond promoted by triphenyl phosphine complexes of palladium (o) and platinum (o) to produce $[M(PPh_3)_2\ (SR)_2]$ have been explained by Zanella et al$^{(101)}$. When a mixture of equimolar amounts of $[Pt(PPh_3)_4]$ and Ph ss Ph were kept overnight, a yellow solid $[Pt(PPh_3)_2\ (SR)_2]$ is obtained.

Diorgano ditellurides often undergo tellurium - tellurium bond cleavage when reacted with transition metal compounds to afford materials in which RTe groups bridge metal centres. However, some instances are known where the bond remains intact.$^{(102)}$

It has been noticed that when elemental mercury is shaken with a benzene solution of diphenyl ditelluride, bis(phenyltelluro) mercury is formed in 83 percent yield.$^{(103)}$

$$Hg + Ph_2\ Te_2 \longrightarrow Ph\ Te - Hg - Te\ Ph \qquad (a)$$

The mercury compound is stable at room temperature, but decomposes to the parent ditelluride and metallic mercury in refluxing benzene.

$$Ph - Te - Hg - Te - Ph \xrightarrow[\text{Benzene}]{\text{Reflux}} \underset{\underset{\text{to step (a)}}{\downarrow}}{Ph_2\ Te_2} + Hg \qquad (b)$$

The reaction of the diorgano ditellurides with mercuric halides has been investigated by Dance$^{(104)}$. From this reaction there appear to be two distinct classes of compounds. The majority are light yellow solids of stoichiometry $R\ Te\ Hg\ X_2$ or

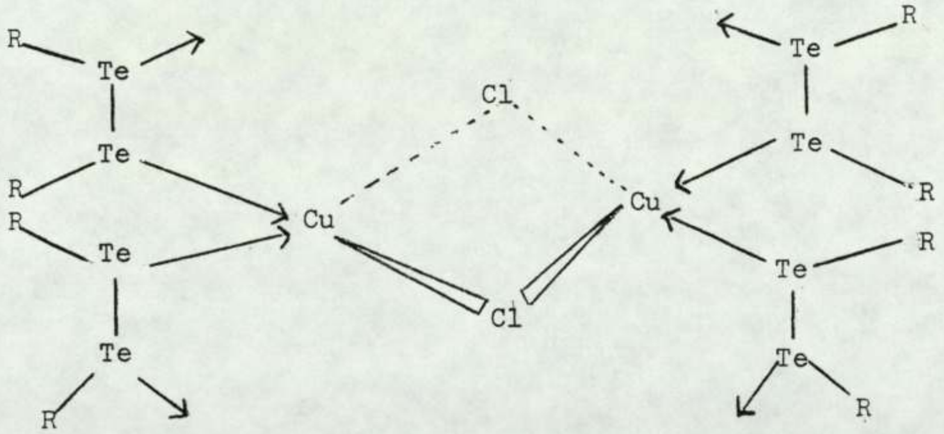
$R_2 Te_2 Hg X_2$ (R = p-Et O $C_6 H_4$, X = Cl, Br,I). There is no evidence of a strong Te - Te bond in the Raman spectrum, but ν(Te - Te) would be affected by co-ordination of tellurium to another atom and it is possible that there still exists a Te - Te bond within the complexes.

The second group of ditelluride mercuric halide complexes are dark brown. In these complexes the R Te - Te R molecule can be considered to be either very weakly bonded to the mercuric halide, remaining essentially two co-ordinate, or cleavage of the Te - Te bond has taken place to give R Te - M groups. In the latter case the presence of R Te - Hg - Te R groups would not be consistent with the observed stoichiometry and therefore it is probable that these complexes are best formulated as $R_2 Te_2 \cdot Hg X_2$, in which both Te - Te and Hg - X bonds remain essentially similar to those present in the reactants.

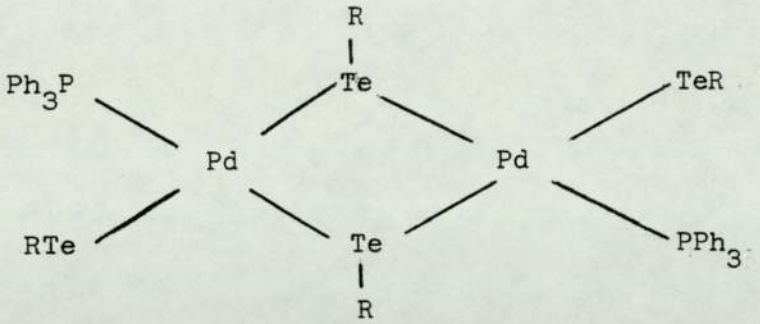
The reaction of $M_3(CO)_{12}$ (M = Fe, Ru) with diphenyl diselenide and diphenyl ditelluride has been studied.$^{(105)}$ The dinuclear complexes $[M(CO)_3EPh]_2$ (E = Se,Te) are the first products to be isolated from the reactions of the dodecacarbonyls with the diphenyl dichalcogenides. However, when M = Ru, the dinuclear complexes react further with $Ph_2 E_2$ to form two series of polymeric materials $[Ru(CO)_2 (EPh)_2]_n$ where n is approximately seven in one series and approximately fourteen in the other.

It has been reported that ditelluride complexes of copper (I) may be readily prepared by reaction of copper (I) chloride or bromide stirred in acetonitrile under nitrogen to which an etherial solution of the ditelluride is slowly added. Precipitates of $R_2\ Te_2 \cdot CuX$ are obtained by cooling the warm solution of the reaction mixture (R = p - EtO C_6H_4 , $C_6\ H_5$, Et, Bu, Pentyl).(102)

Investigations have subsequently been carried out on the complex $R_2'\ Te_2 \cdot CuCl$.(106) They lead to the conclusion that both tellurium atoms are weakly co-ordinated to copper (I) and that the halide ligands are bridging (the complexes are not electrolytes, hence ionic formulations may be eliminated). A possible structure has been assumed as shown schematically below:



The oxidative addition of two diorganoditellurides (di-2-thienyl ditelluride and bis-p-ethoxyphenyl ditelluride) to Pd $(PPh_3)_4$ has been demonstrated.(107) In both cases brown materials are produced which molecular weight studies indicate to be dimers. The compounds are non-electrolytes in DMF and are reasonably formulated involving both bridging and terminal R Te groups, as shown overleaf:



There is no information showing whether the oxidative addition goes via a radical or concerted pathway, but both have been regarded as possible.

In the present work the oxidative-addition reactions of some transition metal complexes, with some diaryl ditellurides have been studied.

Three classes of reactions of transition metal complexes have been chosen, namely the oxidative-addition reactions of five co-ordinate d^7, four co-ordinate d^8 and four co-ordinate d^{10} complexes.

The reaction between $Co(CN)_5^{3-}$ and diaryl ditellurides takes place rapidly. The peak at the wavelength of 967nm associated with the complex $Co(CN)_5^{3-}$, disappears rapidly after mixing methanol-water solutions of $Co(CN)_5^{3-}$ and bis-p-phenetyl ditelluride. Both the flow system apparatus (Section 2.7) and the stopped-flow system (Section 2.8) have been used to study the reaction kinetically. It seems that this reaction may proceed either by the free radical stepwise mechanism, or by a bimolecular oxidative insertion reaction.

Vaska's compound $IrCo(PPh_3)_2Cl$ reacts with the diaryl ditellurides ($Ar_2\ Te_2$, Ar = p-EtOC_6H_4 , C_6H_5 , p-$CH_3C_6H_4$, p-ClC_6H_4) by an oxidative addition reaction. Kinetic studies using a uv-visible spectrophotometer show that the kinetics in each case obey the second order rate law,

$$\text{rate} = k_2 \left[IrCO(PPh_3)_2Cl\right]\left[Ar_2Te_2\right].$$

I.R investigations have been carried out for a mixture of a concentrated solution of an equimolar amount of Vaska's compound and bis-p-phenetyl ditelluride (using carbon tetrachloride as solvent), by studying the absorption peak associated with the carbonyl group. This peak first of all shifted from 1955 cm^{-1} to 2065 cm^{-1} with some reduction in strength immediately after mixing. It then increases in strength over a period of 30 minutes. The shape of the peak starts to change within 90 minutes, with the appearance of a new shoulder. Within 3 - 4 hours a new peak is clearly seen at 2080 cm^{-1} (see Figure 10).

^{125}Te NMR investigations on the product $Ir(PPh_3)_2\ CO(ArTe)_2Cl$, show a spectrum with a single line which may indicate that there is a very small Te - Ir coupling constant. The expected four lines in the spectrum are not seen.

When bis-p-phenetyl ditelluride is added to the toluene solution of $Pt(PPh_3)_4$ and stirred for 24 hours (see Section 2.9.11), no reaction seems to take place between the reactants. This is not surprising because the tendency of (triphenyl phosphine) platinum(o) complexes to undergo oxidative addition is limited to fairly reactive molecules,$^{(99)}$ unlike the d^7 and d^8 complexes discussed above.

RESULTS

On addition of a methanolic solution of bis-p-ethoxyphenyl ditelluride to a water-methanol solution containing $CoCl_2$ and KCN (which react together to form $Co(CN)_5^{3-}$ as explained in Section 2.9.6) in the absence of air, a compound which we hoped would be pentacyano p-ethoxyphenyl telluride cobaltate (111) is rapidly formed by the reaction:

$$2\left[Co^{11}(CN)_5\right]^{3-} + Ar\,Te - Te\,Ar \longrightarrow 2\left[Ar\,Te\,Co^{111}(CN)_5\right]^{3-}$$

In order to study this reaction kinetically, the disappearance of the peak at the wavelength of 967nm, associated with the ion $Co(CN)_5^{3-}$, has been carried out. For this purpose the flow system apparatus (Section 2.7) was used first of all. Then the reaction was followed using the stopped-flow apparatus (Section 2.8). In both cases it has not been possible to draw any conclusion about the kinetics of the reaction, because of the very rapid disappearance of the peak at the wavelength of 967nm. The reaction is too rapid to be controlled by the present technique.

Another kind of an oxidative addition reaction has been carried out between the diaryl ditellurides and trans-chlorocarbonyl bis (triphenyl phosphine) iridium; Vaska's compound; which is prepared by reacting a mixture of iridium (111) chloride and triphenylphosphine in dimethyl formamide solution (Section 2.9.5).

The reaction between diaryl ditellurides and Vaska's compound has been studied kinetically using a uv-visible spectrophotometer. It has been observed that when toluene solutions of bis-p-ethoxyphenyl ditelluride and Vaska's compound are mixed together at room temperature ($25^{\circ}C$), a gradual change from the spectra of the starting materials takes place as shown in Figure 1.

It was found that the best wavelength to study this reaction is at $\lambda = 364$nm. At this wavelength the absorbance of the reaction mixture increases with time.

The curve of the absorbance with respect to time was monitored, and the following results have been obtained. First of all the data obtained from this curve fits the second order equation:

$$A + B \longrightarrow C \qquad (1)$$

where A, B, and C represented diaryl ditelluride, Vaska's compound and the product respectively. The following equations can be obtained:

When $A_o = B_o$

$$\frac{1}{D_\infty - D_t} = kobs\ t - \frac{1}{D_o - D_\infty} \qquad (2)$$

where Dt is the absorbance at any time, $D\infty$ is the absorbance at $t = \infty$, and kobs is the observed rate constant. It was found that a plot of:

$$\frac{1}{D_\infty - D_t} \text{ VS } t$$

is a straight line with gradient = kobs.

The observed rate constant can be used to calculate the true rate constant as follows:

$$\mathrm{kobs} = \frac{k}{El}$$

where E is the extinction coefficient, and l is the path length.

When $A_o \neq B_o$ in the above equation (1), the following equation can be obtained:

$$\log\left(\frac{D\infty - Dt}{nD\infty - Dt}\right) = -\mathrm{kobs}\ t - \log n \qquad (3)$$

where Dt, D∞ and kobs are the same as those explained above in equation (2). n is dependent upon the ratio of the reactants, e.g. when the ratio is 1 : 2 , n = 2 ; 1 : 3 , n = 3 etc.

It was found that a plot of:

$\log\left(\frac{D\infty - Dt}{nD\infty - Dt}\right)$ against t

is a straight line with gradient = kobs. The true rate constant can be calculated from:

$$\mathrm{kobs} = k\ (B_o - A_o)$$

Typical graphs obtained when equations (2) and (3) were employed, are shown in Figures 2 and 3 respectively.

The experiment was studied using different ratios of the reactant concentrations. A ½cm spectrophotometer cell was used in all the experiments. The reactants were transferred to the cell using 2ml graduated syringes, a separate syringe being used for each solution. After each experiment the syringes and the cell were cleaned first of all with acetone and then with toluene. They were finally dried by passing compressed air through them. The results obtained for the rate constant at room temperature (25°C) are shown in Table 1.

The experiment was then repeated at different temperatures in the range of (25 - 50°C) with 5°C intervals. The values obtained for the rate constant are presented in Table 2.

After studying the reaction between bis-p-ethoxyphenyl ditelluride and Vaska's compound, investigations have been carried out with some other diaryl ditellurides, e.g. $(Cl\,C_6H_4)_2Te_2$, $(CH_3C_6H_4)_2Te_2$ and Ph_2Te_2 , and the results obtained are explained below.

The temperature range used during these investigations was (25 - 50°C) with 5°C intervals, when bis-p-chlorophenyl ditelluride was used. The results obtained for the rate constant are shown in Table 3.

When bis-p-tolyl ditelluride, and / or diphenyl ditelluride are used, the temperature range used was (40 - 60°C) with 5°C intervals. The results of the rate constants obtained are given in Tables 4 and 5 respectively.

Using the above results of the rate constants at different temperatures, the activation parameters, Ea (the activation energy), ΔH^{*} , and ΔS^{*} , can be calculated as follows:

Transition state theory gives

$$kr = \left(\frac{k_B \ T}{h} \right) e^{-\Delta G^{*}/RT} \qquad (4)$$

where kr is the rate constant in seconds, k_B is Boltzmann constant = 1.38×10^{-23} J K^{-1}, h is planck constant = 6.63×10^{-34} J Hz^{-1}, and R is the gas constant = 8.314 J K^{-1} $mole^{-1}$.

$$\ln kr = \left(\ln \frac{k_B}{h}\right) + \ln T - \frac{\Delta H^{*}}{RT} + \frac{\Delta S^{*}}{R} \qquad (5)$$

$$\frac{\partial \ln kr}{\partial(\frac{1}{T})} = \frac{-\Delta H^{*}}{R} + \frac{\partial \ln T}{\partial(\frac{1}{T})} \qquad (6)$$

$$\ln T = -\ln\left(\frac{1}{T}\right)$$

$$\therefore \frac{\partial \ln T}{\partial(\frac{1}{T})} = -\frac{1}{(\frac{1}{T})} = -T$$

A plot of ln kr VS $\frac{1}{T}$ gives a straight line as shown in Figures 4, 5, 6 and 7 with gradient G,

$$G = \frac{-Ea}{R}$$

from which Ea can be obtained.

But from the above gradient (equation 6) G,

$$G = \frac{-(\Delta H^{*} + RT)}{R}$$

from which ΔH^{*} can be calculated.

The values of ΔS^{*} can be calculated by employing equation (5) above.

The results for these activation parameters are presented in Table 6.

Infra red spectrophotometric investigations have also been carried out following the position of the carbonyl group. The strong absorption peak associated with the carbonyl group in Vaska's compound appears at 1955 cm^{-1} (see Figure 8). Equimolar amounts of a high concentration of bis-p-ethoxyphenyl ditelluride and trans $[Ir\ CO\ (PPh_3)_2\ Cl]$ solutions were mixed together (using carbon tetrachloride as solvent). The mixture was then injected into an I R spectrophotometric cell (using 1mm cell spacing and NaCl windows, see Section 2.3.2) immediately after mixing.

It is observed that directly after mixing the peak at 1955 cm^{-1} is shifted to 2065 cm^{-1} with some reduction in strength. The strength of the band then increases with time over a period of about 30 minutes. After a period of about 90 minutes, it is observed that the shape of the band starts to change, with the appearance of a new shoulder within the band. Within 3 - 4 hours a new peak has developed which can be seen clearly at 2080 cm^{-1}. These variations of the carbonyl band are shown in Figure 10.

ESR investigations on the reaction between the ditellurides and Vaska's compound give a spectrum with a broad signal. This may indicate the involvement of free radical processes during the course of the reaction.

^{125}Te NMR studies on the product $Ir\ (PPh_3)_2\ CO\ (Ar\ Te)_2\ Cl$, give a spectrum with a single line which may mean that the Te - Ir coupling constant is very small. The $\delta^{125}Te$ obtained is 453.6 ± 1 ppm using Me_2Te as an external reference. Neither $^1J_{Te-Ir}$, nor $^2J_{P-Te}$ are yet known.

^{31}P NMR studies on the product mentioned above give a spectrum with a single line. This is the same as the signal that appears in Vaska's compound, but in a different position in the spectrum. The $\delta^{31}P$ values obtained for Vaska's compound is 16.45 ppm, and that of the product $Ir(PPh_3)_2CO(ArTe)_2Cl$ is 116.22 ppm.

^{13}C NMR spectrum of the product shows multiplet in the aromatic range as can be seen in Figure 11. ^1H NMR studies on the same product also show multiplet in the region of (6.8 - 7.5 ppm), Figure 12. These observations may be assigned to the involvement of different aromatic groups in the molecule.

Finally, attempts have been carried out to study another kind of oxidative addition reaction, between the diaryl ditellurides and tetrakis (triphenyl phosphine) platinum(o); $Pt(PPh_3)_4$. The last compound is prepared according to the literature by adding potassium tetrachloroplatinate (11) solution slowly to an alkaline triphenyl phosphine solution while stirring at 65°C (see Section 2.9.4).

Bis-p-ethoxyphenyl ditelluride is added to the toluene solution of Pt $(PPh_3)_4$ and the mixture then stirred for about 24 hours under nitrogen at room temperature (25^oC) (see Section 2.9.11). It seems that no reaction takes place between the two compounds under these conditions. The unchanged ditelluride can be obtained by evaporating the solvent and subsequently separating the components of the solid.

$[Ar_2Te_2]$	$[IrCO(PPh_3)_2Cl]$	k_{obs}/min^{-1}	$k/dm^3 mol^{-1} min^{-1}$
$5 \times 10^{-4}M$	$5 \times 10^{-4}M$	0.0161	30.0
$2.5 \times 10^{-4}M$	$5 \times 10^{-4}M$	0.00336	30.9
$1.5 \times 10^{-4}M$	$4.5 \times 10^{-4}M$	0.00391	30.0
$1 \times 10^{-4}M$	4×10^{-4}	0.00427	32.8
$1 \times 10^{-4}M$	5×10^{-4}	0.00532	30.6

Table 1 : Rate constant of the reaction of bis-p-ethoxyphenyl ditelluride with Vaska's compound at 25°C.

K/T	kobs/min^{-1}	k/dm^{3} mol^{-1} min^{-1}	ln k
0.00309	0.00336	30.9	3.4312
0.00314	0.00314	28.9	3.3642
0.00319	0.00285	26.3	3.2678
0.00324	0.00259	23.8	3.1705
0.00330	0.00236	21.8	3.0800
0.00335	0.00206	19.0	2.9435

Table 2 : Rate constant of the reaction of bis-p-ethoxyphenyl ditelluride with Vaska's compound at different temperature.

10^3K/T	kobs/min^{-1}	k/dm^3 mol^{-1} min^{-1}	ln k
3.356	0.00699	14.3	2.6574
3.300	0.0084	17.7	2.8725
3.247	0.00868	19.2	2.9540
3.195	0.0119	25.7	3.2481
3.145	0.0130	27.7	3.3210

Table 3 : Rate constant of the reaction of bis-p-chlorophenyl ditelluride with Vaska's compound at different temperature.

10^3K/T	kobs/min^{-1}	k/dm^3 mol^{-1} min^{-1}	ln k
3.247	0.00224	4.23	1.4418
3.195	0.00381	7.08	1.9577
3.145	0.00675	12.5	2.5231
3.096	0.0104	19.5	2.9728
3.049	0.0233	42.5	3.7490

Table 4 : Rate constant of the reaction of bis-p-methylphenyl ditelluride with Vaska's compound at different temperature.

10^3K/T	kobs/min^{-1}	k/dm^3 mol^{-1} min^{-1}	ln k
3.247	0.00404	6.45	1.8640
3.195	0.00657	10.6	2.3594
3.145	0.0104	16.5	2.8059
3.096	0.0192	30.5	3.4183
3.049	0.0407	61.0	4.111
3.003	0.0511	78.0	4.3568

Table 5 : Rate constant of the reaction of diphenyl ditelluride with Vaska's compound at different temperature.

Reaction	$k/dm^3 mol^{-1} sec^{-1}$	$\Delta H^*/kcal mol^{-1}$	$\Delta S^* cal deg^{-1} mol^{-1}$
$Ir(CO)(PPh_3)_2Cl + (p\text{-}C_2H_5OC_6H_4Te)_2$	0.44	3.1	-47
$Ir(CO)(PPh_3)_2Cl + (p\text{-}ClC_6H_4Te)_2$	0.43	5.8	-38
$Ir(CO)(PPh_3)_2Cl + CH_3I^{(a)}$	3.5×10^{-3}	5.6	-51
$Ir(CO)(PPh_3)_2Br + CH_3I^{(a)}$	1.6×10^{-3}	7.6	-46
$Ir(CO)(PPh_3)_2I + CH_3I^{(a)}$	0.91×10^{-3}	8.8	-43
$Ir(CO)(PPh_3)_2Cl + (p\text{-}CH_3C_6H_4Te)_2$	0.12	21.9	13
$Ir(CO)(PPh_3)_2Cl + (C_6H_5)_2 Te_2$	0.177	19.9	5

Table 6 : Activation parameters for the oxidative addition of some diaryl ditellurides to Vaska's compound at 40°C. (a) data obtained from ref (110) at 25°C.

$\Delta(\Delta H^*)$/k cal mol^{-1}	$\Delta(\Delta S^*)$/cal mol^{-1} deg^{-1}	$\Delta(T\Delta S^*)$/k cal mol^{-1}
2.7	9	2.8
18.8	60	18.8
16.8	52	16.3

Table 7 : The compensation between the values of ΔH^* and Δs^* for the reaction of some diaryl ditellurides with Vaska's compound at 40°C.

Where $\Delta(\Delta H^*) = \Delta H^*$ of a particular diaryl ditelluride $-$ ΔH^* of bis-p-ethoxyphenyl ditelluride .

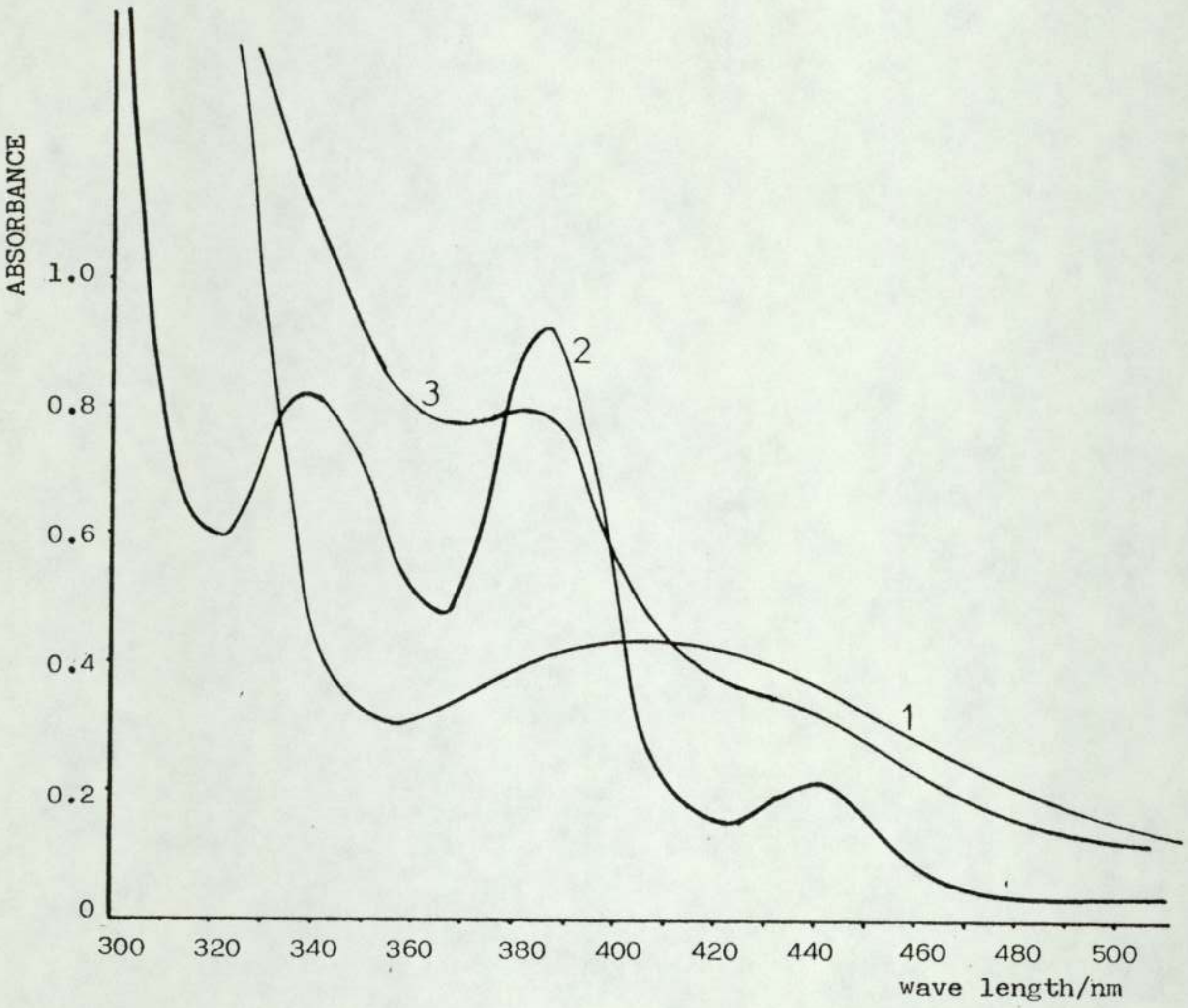


Figure 1 : UV-visible spectra of solutions of 1-bis-p-ethoxyphenyl ditelluride, 2-Vaska's compound, and 3-the reaction mixture of compounds 1 and 2 after 20 minutes.

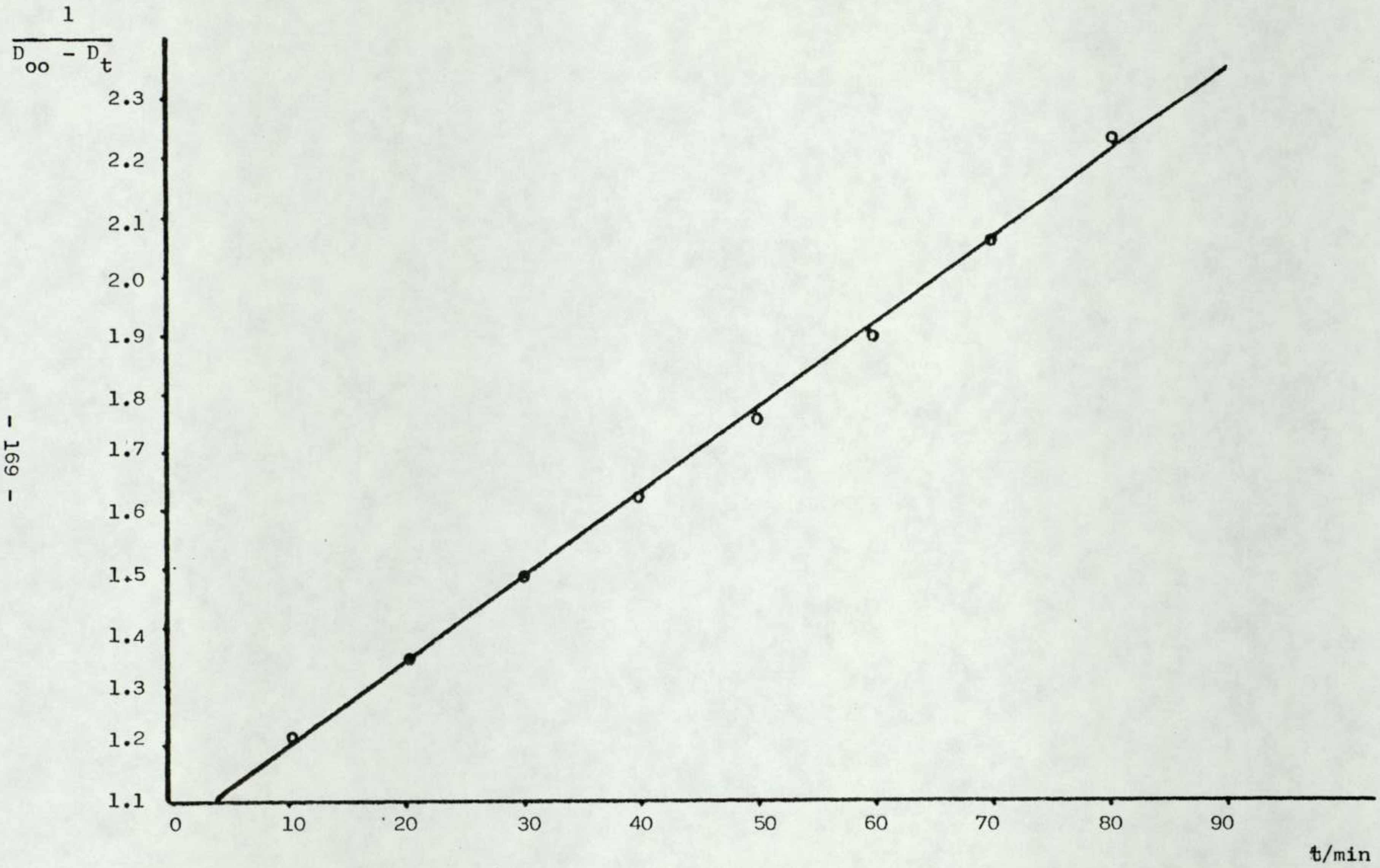


Figure 2 : Plot of $\frac{1}{D_{oo} - D_t}$ versus time at 364nm of the reaction of Ar_2Te_2 ($Ar = p\text{-}EtOC_6H_4$) with Vaska's compound at concentration of 5 X 10^{-4}M each and at 50^oC.

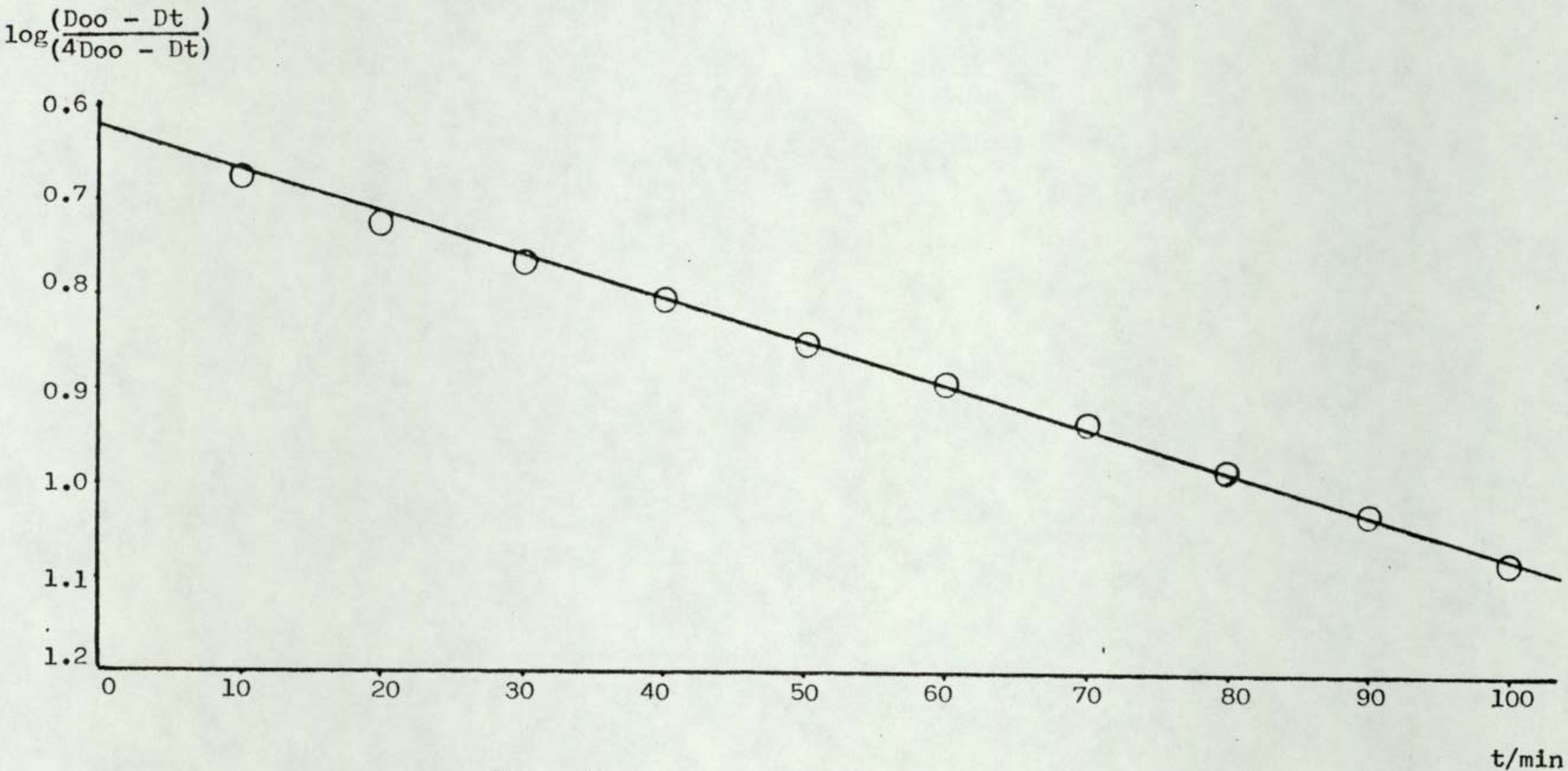


Figure 3 : Plot of log $\frac{Doo - Dt}{4D_{oo} - D_t}$ versus time at 364nm of the reaction of Ar_2Te_2 ($Ar = p\text{-}EtOC_6H_4$) with Vaska's compound at concentrations of 10^{-4}M and 4 X 10^{-4}M respectively, and at 50°C.

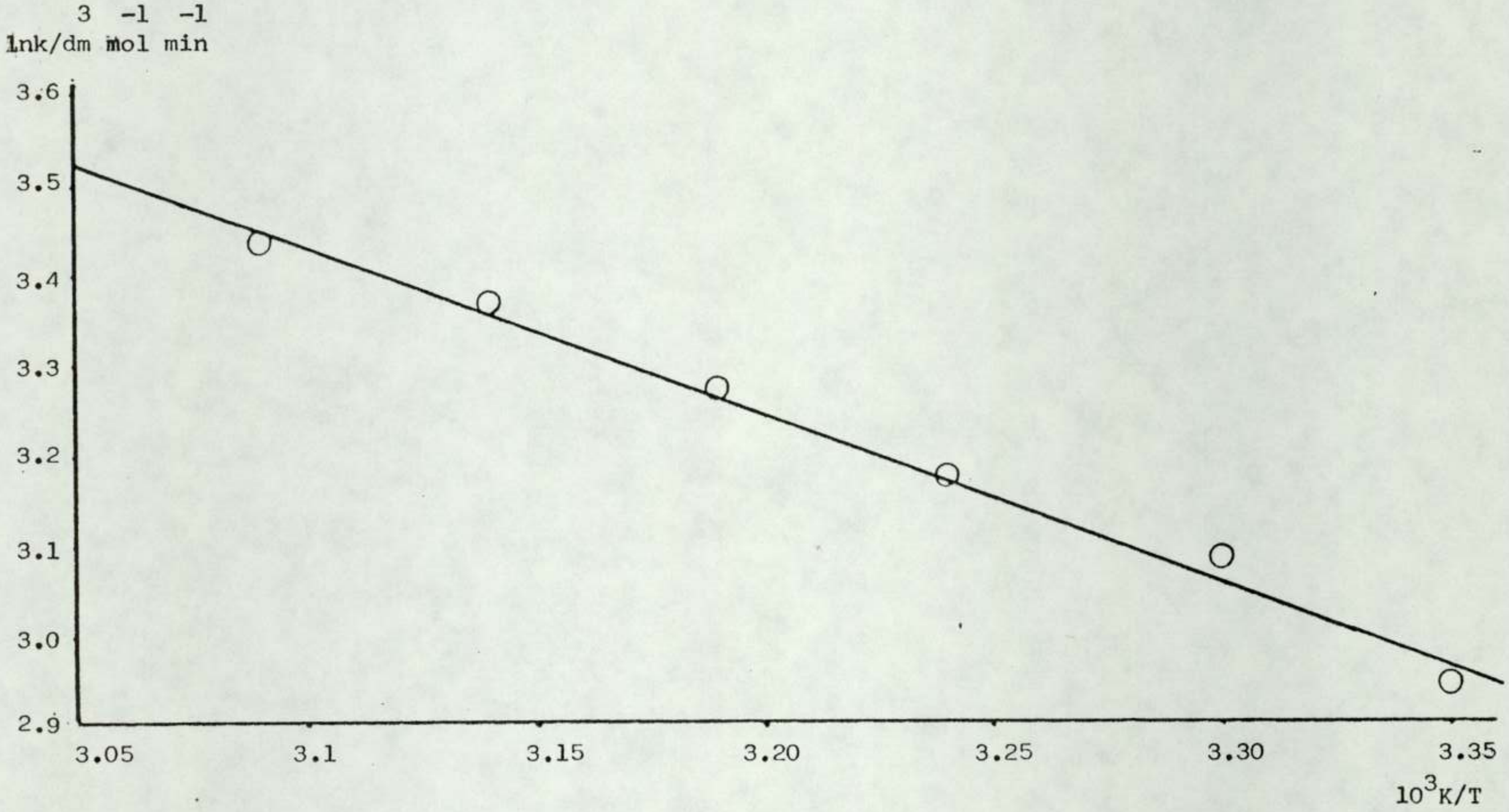


Figure 4 : Plot of Ink versus $\frac{1}{T}$ of the reaction of bis-p-ethoxyphenyl ditelluride with Vaska's compound.

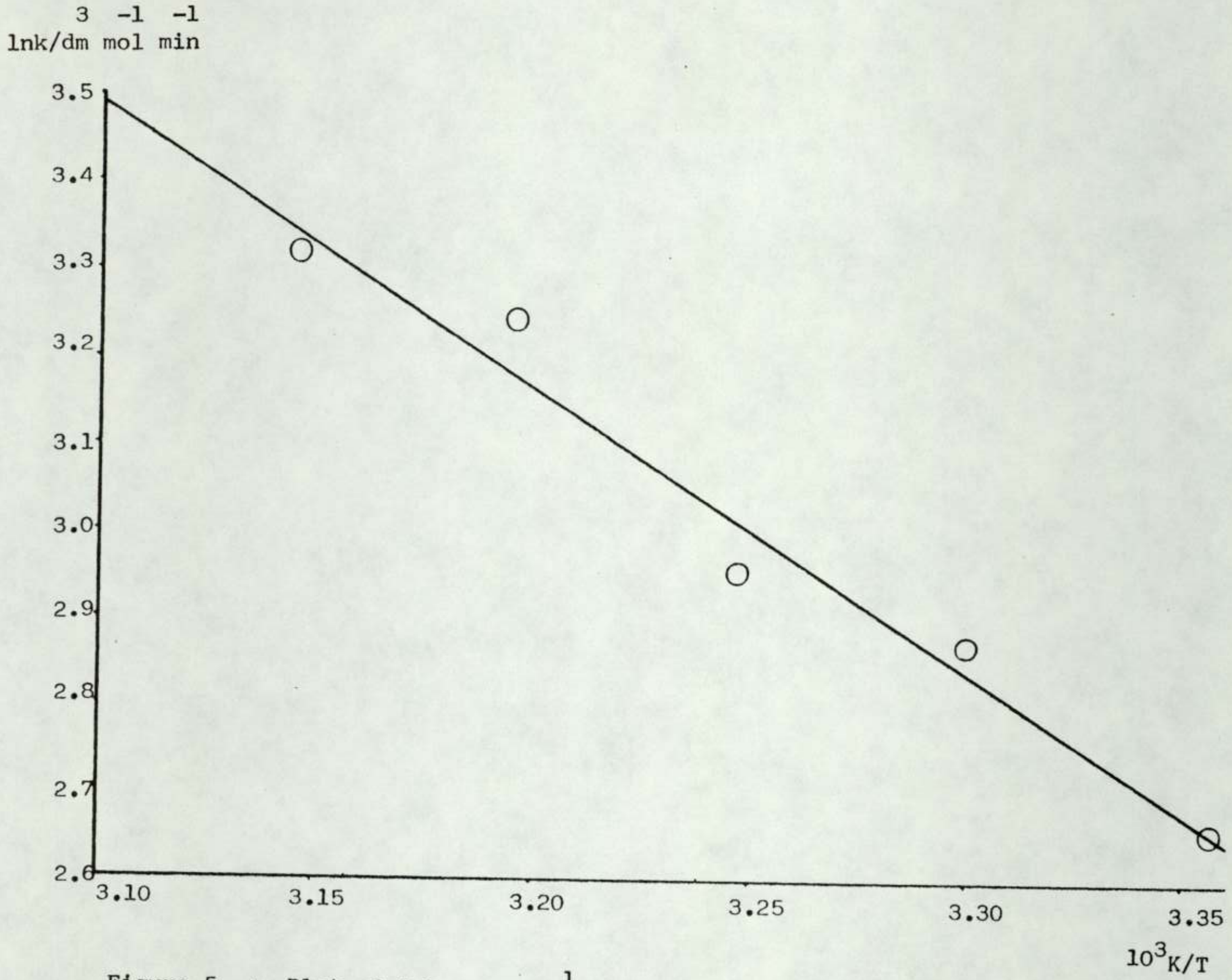


Figure 5 : Plot of Ink versus $\frac{1}{T}$ of the reaction of bis-p-chlorophenyl ditelluride with Vaska's compound.

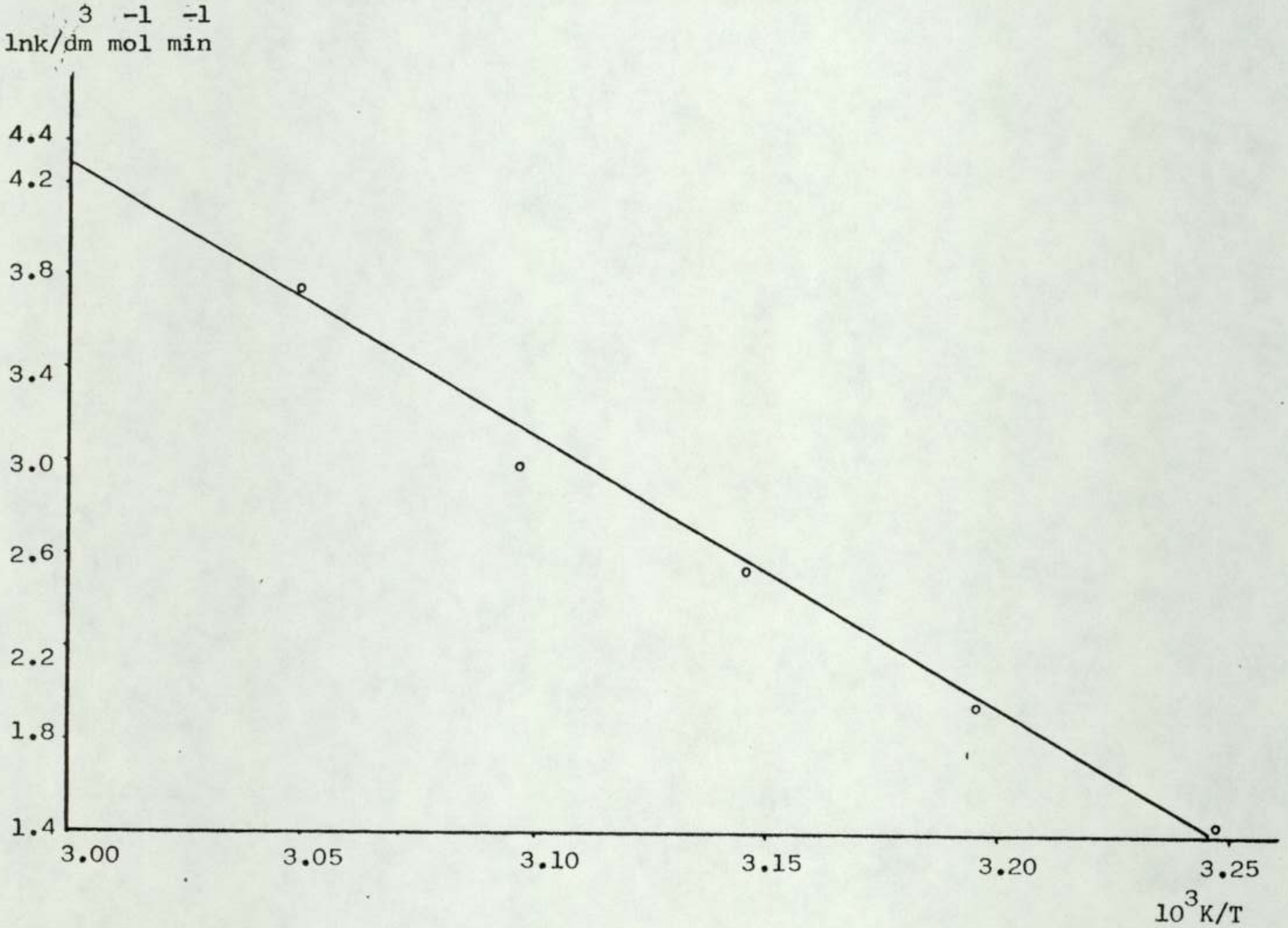


Figure 6 : Plot of Ink versus $\frac{1}{T}$ of the reaction of bis-p-methylphenyl ditelluride with Vaska's compound.

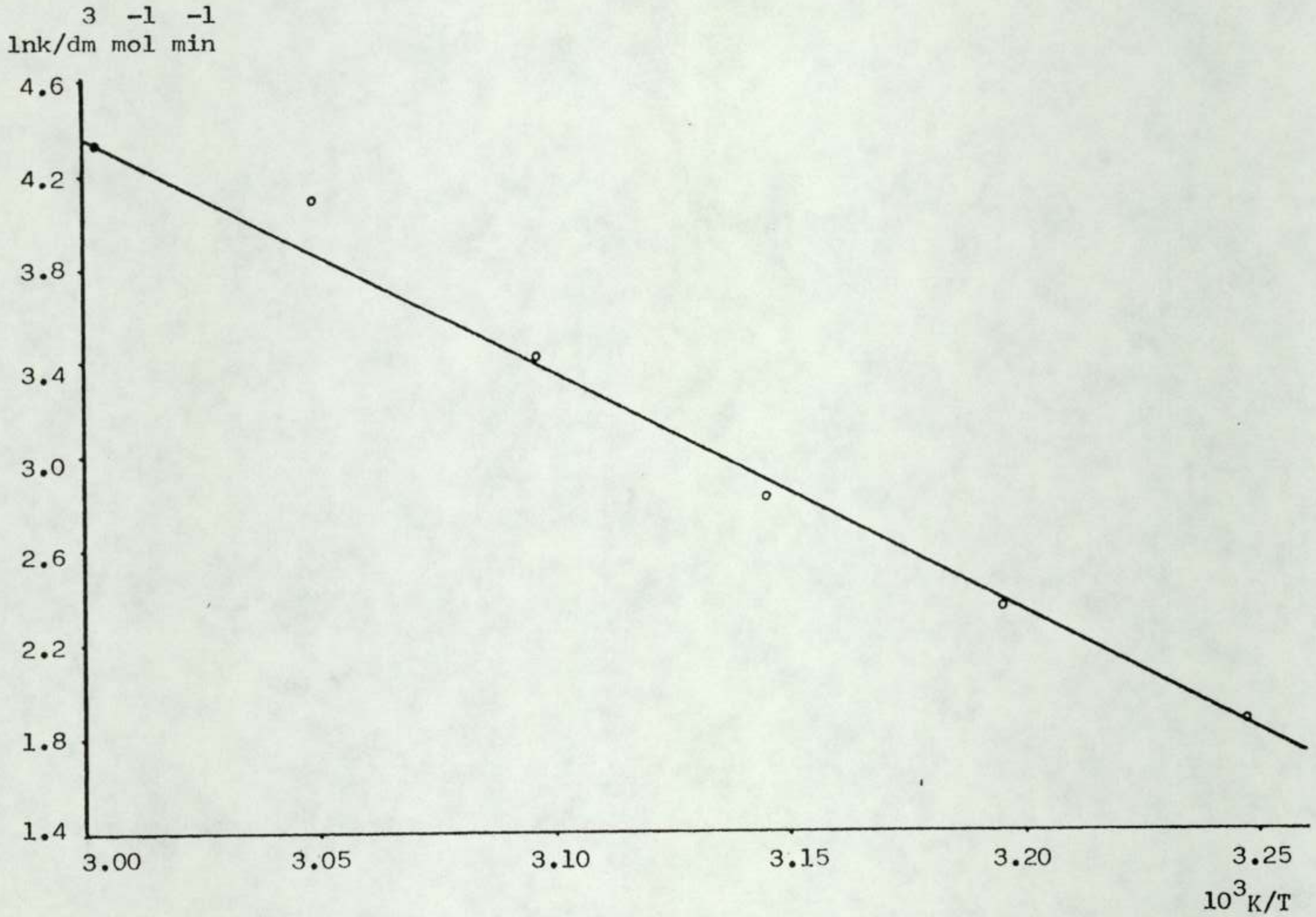
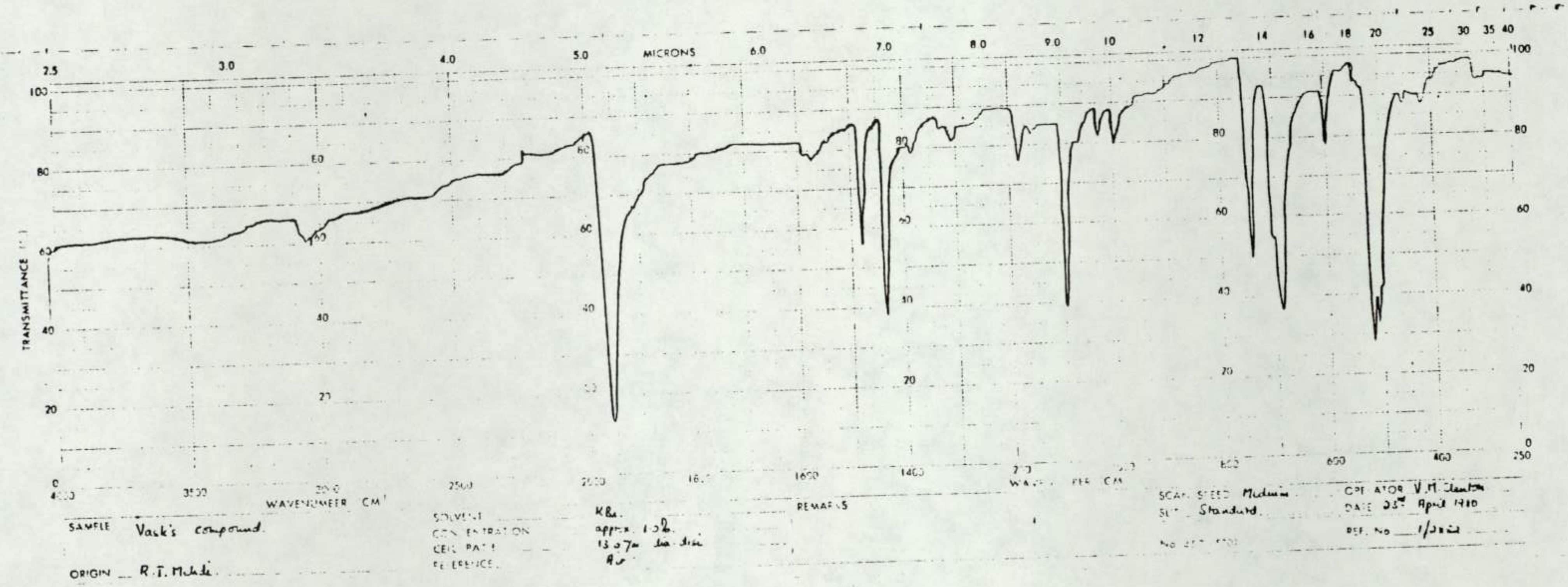


Figure 7 : Plot of Ink versus $\frac{1}{T}$ of the reaction of diphenyl ditelluride with Vaska's compound.



SAMPLE Vask's compound.

ORIGIN R.T. Mckde.

SOLVENT KBr.

CONCENTRATION approx. 1.0%.

CELL PATH 13 o 7m ka. disc

REFERENCE Air

REMARKS

SCAN SPEED Medium

SLIT Standard.

OPERATOR V.M. Clanton

DATE 23rd April 1980

REF. No 1/2

Figure 8 : Infrared spectrum of Vaska's compound.

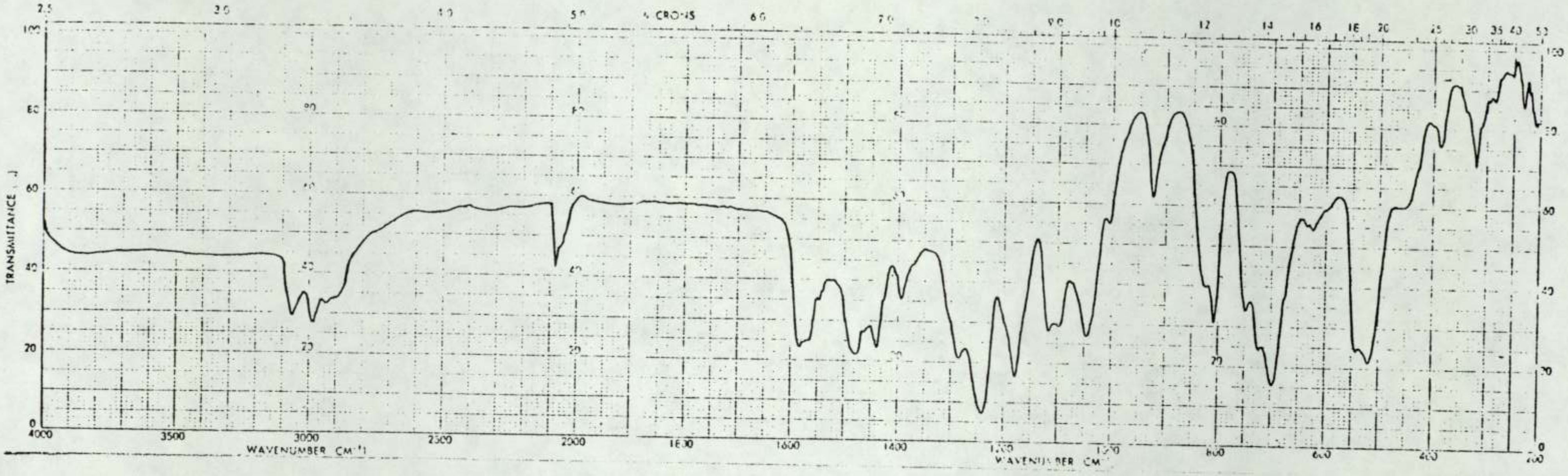


Figure 9 : Infrared spectrum of $IrCO(PPh_3)_2Cl\ (ArTe)_2$.

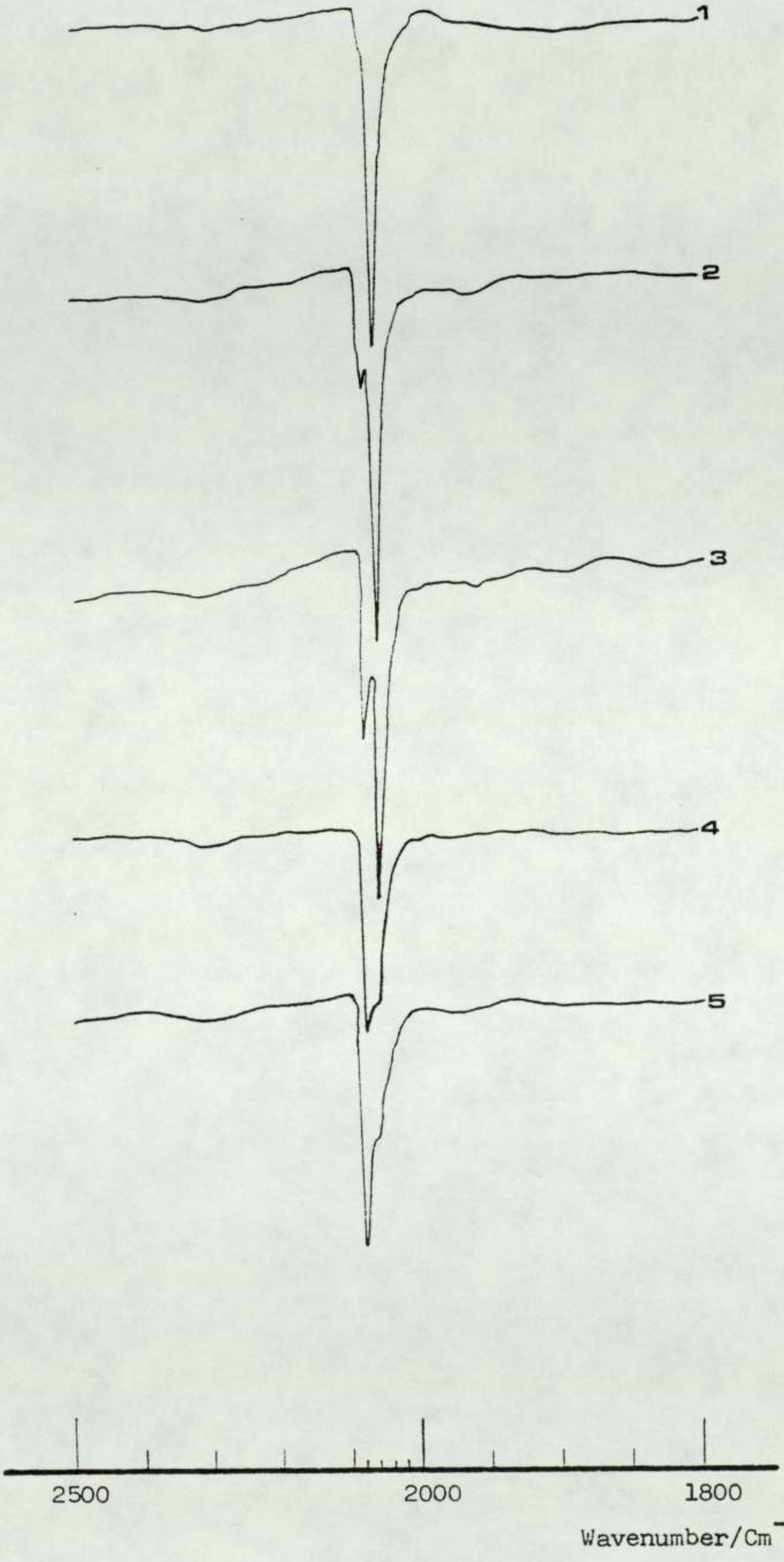


Figure 10 : The variation of carbonyl infrared absorption during the reaction of bis-p-ethoxyphenyl ditelluride and Vaska's compound, after the following periods : 1 - just after mixing; 2 - 20 minutes; 3 - an hour; 4 - 2 hours; and 5 - more than 4 hours.

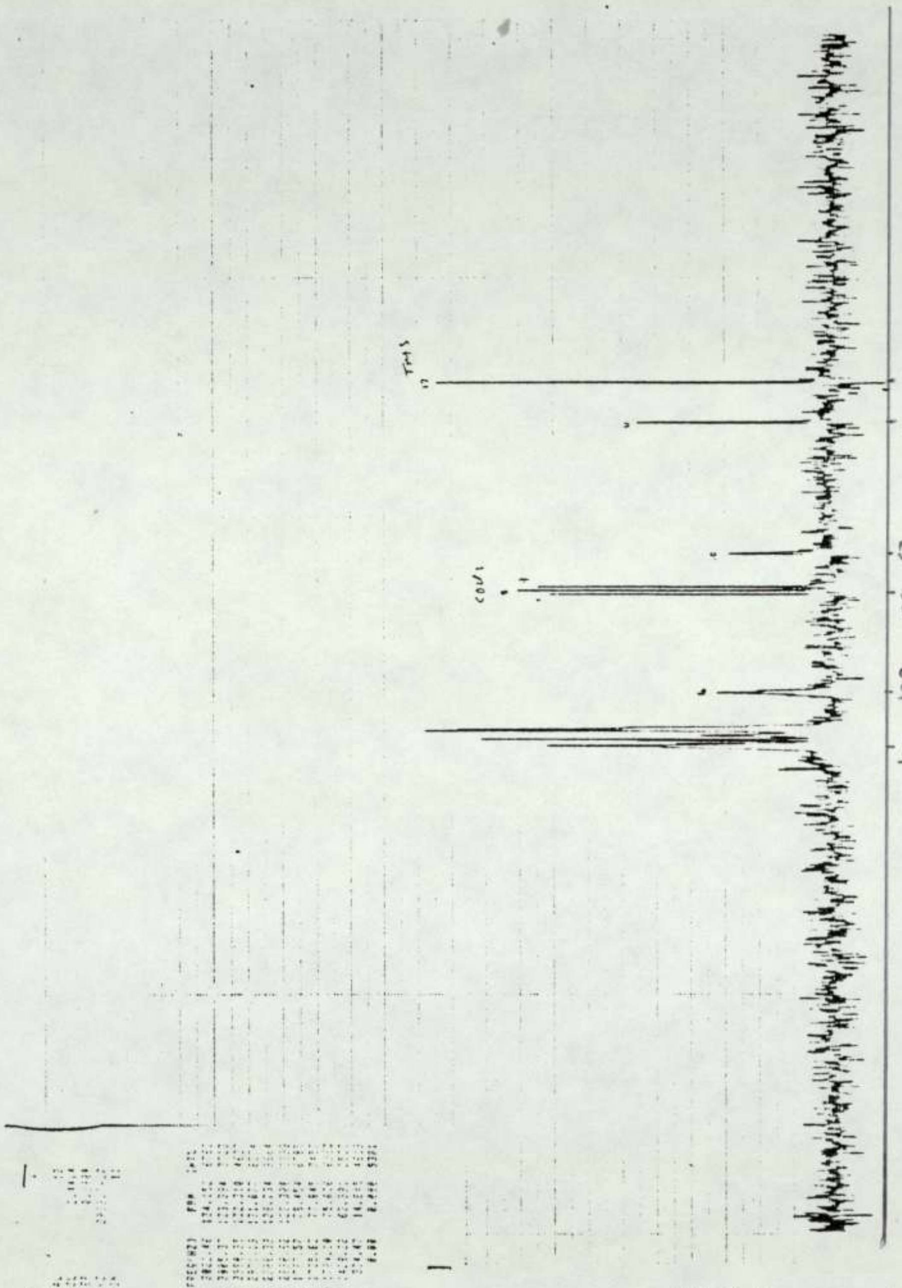


Figure 11 : ^{13}C NMR spectrum of the product IrCO(PPh$_3$)$_2$Cl (ArTe)$_2$.

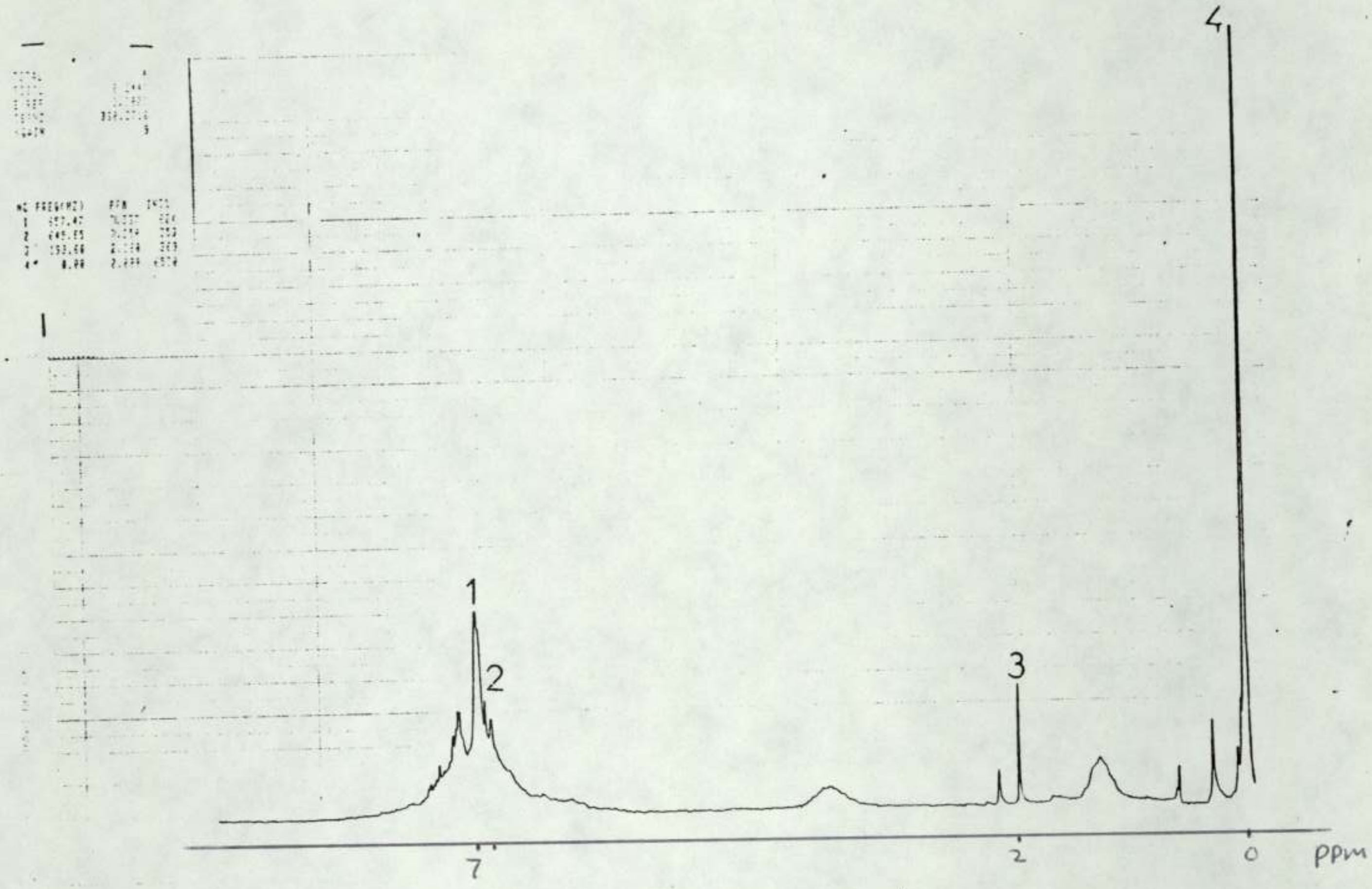


Figure 12 : ^{1}H NMR spectrum of the product IrCO$(PPh_3)_2$Cl $(ArTe)_2$.

DISCUSSION

The oxidative addition reaction of the transition metal complexes with the diaryl ditellurides has been carried out with three certain classes of complexes, notably those with nearly filled d shells, i.e. the oxidation additions of five co-ordinate d^7, four co-ordinate d^8 and four co-ordinate d^{10} complexes.

No definite conclusion can be drawn from the kinetic studies of the reactions of d^7 complexes; $Co\ (CN)_5^{3-}$, with the diaryl ditellurides in solution. This may be because of the difficulties of controlling the reaction which takes place very fast, as will be explained below.

In the case of using d^{10} complexes, i.e. $Pt^o\ (PPh_3)_4$ with the diaryl ditellurides in solution, it looks as though no reaction takes place between the reactants.

On the other hand, the reactions of d^8 complexes, i.e. $Ir\ Cl\ (PPh_3)_2\ CO$ with the diaryl ditellurides in solution seems very clearly to take place, as will be discussed later.

Attempts to study kinetically the reaction between a methanol solution of bis-p-ethoxyphenyl ditelluride and a solution of $K_3\ Co\ (CN)_5$ in water-methanol, from the disappearance of the peak at the wavelength of 967nm, have unexpectedly proved unsuccessful. Neither the flow system nor the stopped flow apparatus, Sections 2.7 and 2.8 respectively, could control this reaction.

The disappearance of the olive-green colour of the $Co(CN)_5^{3-}$ solution took place rapidly after adding a methanol solution of bis-p-ethoxyphenyl ditelluride. This was accompanied by the rapid disappearance of the peak at the wavelength of 967nm. This wavelength is recommended by King et al(108) that it can be used as an accurate measure of the $\left[Co^{11}(CN)_5\right]^{3-}$. The above reaction took place whether the ditelluride was added as a trace amount, or was added as an equimolar amount to the $K_3\ Co\ (CN)_5$ solution.

King et al(108) have observed few identifiable peaks in the UV-visible spectrum, i.e. 316nm peak which is particularly susceptible to the presence of impurities, a trace of O_2 for example being sufficient to obliterate the peak leaving an intermediate shoulder. Peak at 305nm has also been identified, the formation of the 305nm complex in solutions containing $Co(CN)_5^{3-}$ may be observed in certain circumstances, for example when C_sCl is added. It is then accompanied by a peak shift to 375 - 390nm, which is due to a complex whose absorption peak is at 380nm, and whose structure is $\left[Co^{111}(CN)_5OH\right]^{3-}$ or $\left[Co^{111}(CN)_5OH_2\right]^{2-}$. When trace amounts of the ditelluride were added, it may function as a catalyst in this reaction producing either $\left[Co^{111}(CN)_5OH\right]^{3-}$ or $\left[Co^{111}(CN)_5\ OH_2\right]^{2-}$. This is supported by the formation of the peak at the wavelength of 380nm.

The oxidative-addition reactions of the diaryl ditellurides to cobalt (II) complex have proved too fast for kinetic measurement, and the mechanisms of these reactions have not so far been elucidated.

Another set of experiments has been carried out with another kind of complex, a d^{10} complex. The best characterised reactions of d^{10} complexes are probably those of platinum(o) phosphines. When a mixture of toluene solution of tetrakis (triphenyl phosphine) platinum (o) and bis-p-ethoxyphenyl ditelluride was stirred for a long time, no reaction seemed to take place between the two compounds. The unreacted ditelluride can be obtained at the end, after evaporating the solvent; but not the $Pt(PPh_3)_4$ starting material, which may be decomposed during the stirring process. Malatesta et al(109) have observed the dissociation of $Pt(PPh_3)_4$ after dissolving it in benzene.

This is, in fact, not surprising according to what Halpern(99) has found. He found that the tendency of (triphenyl phosphine) platinum(o) complexes to undergo an oxidative addition reaction is limited to fairly reactive molecules such as acids, alkyl halides and certain metal halides. Unlike the d^7 complexes mentioned above and d^8 complexes discussed later, it does not extend for example to H_2 and to the diaryl ditellurides.

Clearly more work is needed in this area to delineate the range of metal complexes which can participate in radical reactions and to explain the complex behaviour observed.

The reaction of Vaska's compound with the diaryl ditelluride in solution takes place according to the facts discussed below. The following investigations have been carried out in order to ascertain the nature of the product:

^{1}H NMR studies of the adduct of Vaska's compound with the diaryl ditellurides, which may be formulated as:-
$Ir(PPh_3)_2CO(ArTe)_2Cl$, give a spectrum with different peaks in the aromatic proton range around δ = 7ppm, Figure 12. This indicates the involvement of different aromatic groups. This is also supported by the ^{13}C NMR investigations of the same adduct, which shows at least five recognisably different peaks in the aromatic carbon range (134.2 - 128.7 ppm) Figure 11. This again indicates the presence of different aromatic groups in the product.

^{125}Te NMR studies for the product of the above reaction gives a spectrum with a single line, which may indicate an equivalent symmetry for the tellurium atoms. It is known that both ^{191}Ir and ^{193}Ir have a nuclear spin quantum number, $I = \frac{3}{2}$, but the expected four lines are not seen. This may mean that the Te - Ir coupling constant is very small. Neither $^1J_{Te-Ir}$ nor $^2J_{P-Te}$ are yet known. Furthermore, the δ^{125}Te value obtained is 453.6 ± 1 ppm which is very close to that of the pure bis-p-ethoxyphenyl ditelluride, which is 456 ± 1 ppm. This may mean that the reaction of the diaryl ditellurides and Vaska's compound is reversible in solution, and that the product of the reaction has reverted to the starting materials, but that would seem to be unlikely at the high concentrations used for these NMR measurements. It is more reasonable to regard the evidence as showing very similar shielding in two different compounds.

^{31}P NMR studies on the above product show a spectrum with a single line, as does the reagent, Vaska's compound, · This indicates equivalent symmetry for the phosphorus atoms in the product. The chemical shift values obtained for phosphorus (31) for Vaska's compound and its adduct of, $Ir\,(PPh_3)_2\,CO\,(ArTe)_2Cl$, are: 16.45 ppm and 116.22 ppm respectively. This clearly indicates the variation in the structure of Vaska's compound and its adduct, which again means that a chemical reaction has taken place between the reactants.

Trans $[Ir\,Cl\,(CO)(PPh_3)_2]$ is known to undergo a bewildering number of oxidative addition reactions which may be followed by the shift in infrared band of the carbonyl group to a higher frequency as the degree of back-bonding is diminished through oxidation of iridium (I) to iridium (III).

The infrared spectra determined here for $Ir\ Cl\ (CO)\ (PPh_3)_2$ and its adducts show the general trend of increasing CO stretching frequencies, in agreement with that reported earlier.(110-112) This presumably reflects the decreasing extent of π-back donation from Ir to CO and hence the increasing effective oxidation state of the Ir.

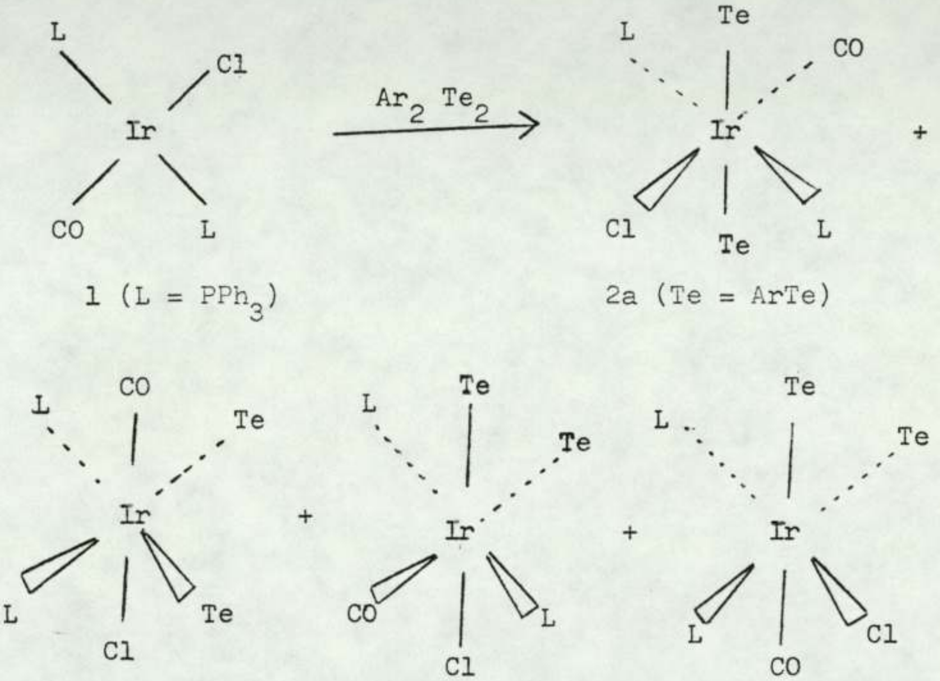
Infrared investigations of the reaction between Vaska's compound and bis-p-ethoxyphenyl ditelluride show that the strong absorption band at 1955 cm^{-1} associated with the carbonyl group in pure Vaska's compound is affected. This peak is quickly shifted to 2065 cm^{-1} after mixing solutions of the reactants in carbontetrachloride. This is followed by the slower appearance of a new peak at 2080 cm^{-1} Figure 10, which grows with the concomitancy of the disappearance of the 2065cm^{-1} band. This may indicate the formation of the final product, $Ir\ (PPh_3)_2\ (CO)\ Cl\ (ArTe)_2$. This can be supported by the following observations explained recently for some of the iridium (111) adducts: Nearly the same band position (2055 cm^{-1}) for the carbonyl absorption which is consistent with a iridium (111) carbonyl species, has been observed by Chia,(112) when 2 - Bromothiophen is added to Vaska's compound:

$$Ir(CO)(PPh_3)_2\ Cl\ +\ 2Br\ T \longrightarrow Ir(T)(CO)(PPh_3)_2\ BrCl$$

(where 2BrT = 2 - bromothiophen, T = 2 - thienyl).

Labinger et al(111) has found that the reaction of alkyl halides with the d^8 complex trans - $IrCO(PMe_3)_2Cl$ can be conveniently followed by infrared method. They proved that the strong sharp band at 1945 cm^{-1} (ν CO) of the Ir^1 complex gradually disappears with the concomitant growth of a band at 2030 cm^{-1} characteristic of the Ir^{111} adduct.

The reaction of the diaryl ditelluride molecule with trans-chlorcarbonyl bis(triphenyl phosphine) iridium (I) (1) might give rise to any of four isomers; 2a, 2b, 2c and 2d, which are possible as a result of cis or trans addition.



1 ($L = PPh_3$)

2a (Te = ArTe)

2b

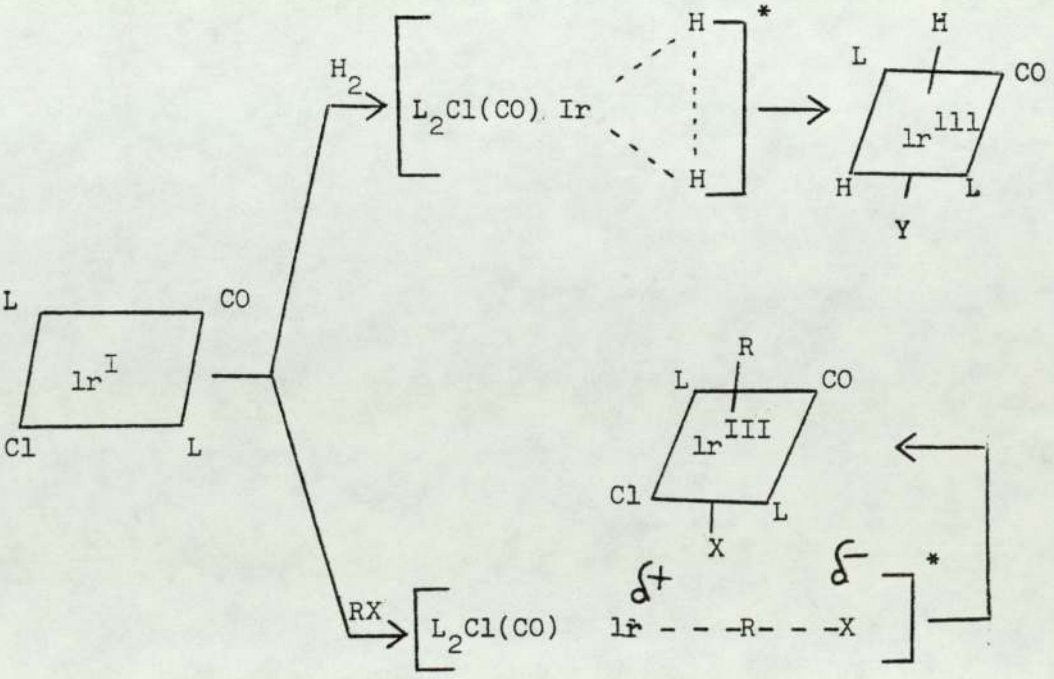
2c

2d

According to the nuclear magnetic resonance investigations explained above, the singlet peak obtained at ^{31}P NMR for the product means that the two phosphorus atoms are at equivalent symmetry, i.e. the two PPh_3 ligands are in similar environments. The same thing can be said of the tellurium atoms, due to the singlet peak observed at ^{125}Te NMR spectrum. This means that the structures cannot be (2c) or (2d), and it must therefore be (2a) or (2b).

Jenkins and Shaw(113) have measured the infrared spectra of a series of octahedral iridium (III) halide complexes and demonstrated that the iridium-chlorine stretching frequency depends primarily on the nature of the ligand trans to the chlorine and is insensitive to the cis ligands. ν(Ir-Cl) is observed at 320 cm^{-1} in the infrared spectrum of the product, Ir CO $(PPh_3)_2$ $(ArTe)_2Cl$, see Figure 9. On the basis of earlier studies(113,114) the absorption at 320 cm^{-1} is assigned to chlorine trans to carbonyl. This is additional evidence suggesting that the structure is either 2a or 2b.

Halpern(99) has described the variation in the kinetic data obtained for the oxidative addition reactions of Vaska's compound with H_2 and/or organic halides (RX = CH_3I, $C_6H_5CH_2Br$, _ _ _ etc.). It has been observed that the data obtained reveals marked differences between the two reactions.



The oxidative addition of alkyl or benzyl halides is believed to entail an S_N2 type attack. This mechanism is consistent with certain stereochemical features of the reactions, notably observations that at least under certain conditions the stereochemistry of oxidative addition of alkyl halides (unlike that of H_2) is trans.(99,114) The value of the activation parameters (ΔS^* and ΔH^*) obtained for the reaction of Vaska's compound and $Ar_2\ Te_2$ ($Ar = OC_2H_5C_6H_4$, ClC_6H_4), discussed below; are rather close to those obtained for the reactions of Vaska's compound with the alkyl or benzyl halides. Therefore, 2a is more likely to be the appropriate structure.

The reactions whose kinetics were examined are:

$$\text{trans} - IrCl(CO)(PPh_3)_2 + Ar_2\ Te_2 \longrightarrow IrCl(CO)(PPh_3)_2(ArTe)_2$$

($Ar = p - OC_2H_5C_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}CH_3C_6H_4$ and C_6H_5).

Under the conditions of the kinetic measurements all the reactions went essentially to completion.

The gradual change in the absorption spectra of the starting materials after mixing the toluene solutions of the diaryl ditellurides with Vaska's compound as shown in Figure 1, indicates that a chemical reaction takes place between the reactants.

Kinetic investigations on the above reaction were carried out by following the increase of the absorbance of the reaction mixture at the wavelength of 364nm. This is the best wavelength to follow this reaction as can be seen from Figure 1. It was found from the absorbance time curve that the above reaction obeys the second order rate law,

$$\text{rate} = k\left[\text{IrCO(PPh}_3)_2\text{Cl}\right]\left[\text{Ar}_2\text{Te}_2\right]$$

when Ar = p-ethoxyphenyl, p - chlorophenyl, p - methylphenyl and phenyl.

The parameters of activation, calculated at 40°C for the four reactions investigated in this work, are shown in Table 6. The Table also includes the available literature data for the purpose of comparison.

The kinetic patterns of the reactions with bis-p-ethoxyphenyl ditelluride and bis-p-chlorophenyl ditelluride are very similar. But, the reactions with bis-p-methyl ditelluride and diphenyl ditelluride, exhibit somewhat different reactivity patterns.

The variation in the values of the activation parameters of the above reactions may be due to the changes in the solvation of the reagent (R) and the product (T).

$$\text{R (solv)}_X \longrightarrow \text{T (solv)}_{X - Y}$$

As Y increases ΔS^* increases because of the increment of the disorder (the randomness) in the system, and ΔH^* also increases because of the breaking of more bonds in this case. The pronounced compensation between ΔH^* and ΔS^* obtained (see Table 7), supports the above assumption.

The shift in the infrared band at 1955 cm^{-1} (νCO) of the Ir^{1} complex to 2065 cm^{-1} explained above, is initially accompanied by some reduction in the band strength. The strength begins to increase with time, at least at the first half an hour. The shape of the band changes and a new band appears clearly at 2080 cm^{-1} after about 60 minutes. The band at 2065 cm^{-1} gradually disappearing with the concomitant growth of the band at 2080 cm^{-1}. These observations again prove that chemical reactions between the diaryl ditellurides and Vaska's compound took place to form the Ir^{111} adduct discussed above, and that at least two steps are involved.

A broad ESR signal has been obtained for the mixture of the ditellurides and Vaska's compound. This may indicate the involvement of free radical processes during the course of the reaction, which may take place by the cleavage of the Te - Te bond. Labinger$^{(115)}$ has observed that the reaction of iridium (I) with $C_6H_5CH_2CH_2Br$ is inhibited by radical scavengers. He proposed the following propagation mechanism for the oxidative addition of RX to iridium (I).

$$R^{\bullet} + Ir^{1} \longrightarrow Ir^{11} - R$$

$$Ir^{11} - R + RX \longrightarrow X - Ir^{111} - R$$

These observations can lead to the oxidative addition mechanism for the reaction of trans-chloro carbonyl bis(Triphenyl-phosphine) iridium(I), with the diaryl ditellurides in solution may be the same as that explained by Labinger$^{(115)}$ for the oxidative addition of RX to Ir^{1}, except that at the adduct of the first step of the reaction the Te – Te bond is still intact.

Therefore, the following reaction mechanism can be proposed:

$$\left[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}\right] + \mathrm{Ar_2\ Te_2} \xrightleftharpoons{K_1} \left[\mathrm{IrCl(CO)(PPh_3)_2}\right]\cdot\ \mathrm{Ar_2\ Te_2}$$

$$\left[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}\right]\cdot \mathrm{Ar_2\ Te_2} \xrightarrow{k_2} \left[\mathrm{Ir^{II}Cl(CO)(PPh_3)_2\ (Ar\ Te)}\right] + \mathrm{Ar\ Te}^{\bullet}$$

$$\left[\mathrm{Ir^{II}Cl(CO)(PPh_3)_2\ (Ar\ Te)}\right] + \mathrm{Ar\ Te}^{\bullet} \xrightarrow{k_3} \left[\mathrm{Ir^{III}Cl(CO)(PPh_3)_2\ (Ar\ Te)_2}\right]$$

applying the steady state hypothesis

$$k_2 \left[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}\right]\cdot \mathrm{Ar_2\ Te_2} = k_3 \left[\mathrm{lr^{II}\ Cl(CO)(PPh_3)_2\ \ (Ar\ Te)}\right]\left[\mathrm{Ar\ Te}^{\bullet}\right]$$

but

$$K_1 \left[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}\right]\left[\mathrm{Ar_2Te_2}\right] = \left[\mathrm{IrCl(CO)(PPh_3)_2}\right]\cdot\ \mathrm{Ar_2\ \ Te_2}$$

therefore

$$K_1\ k_2 \left[\mathrm{Ir^{I}Cl(CO)(PPh_3)_2}\right]\left[\mathrm{Ar_2Te_2}\right] = k_3\left[\mathrm{Ir^{II}Cl(CO)(PPh_3)_2\ (ArTe)}\right]\left[\mathrm{ArTe}^{\bullet}\right]$$

CHAPTER SIX

Appendix 1

```
TARTED :SST7072,HOPHA2, 9NOV78 09.52.40 TYPE: BACK  10 ; STREAM A ; PRIORITY 1 ; ENTERED WELL  9NOV78 09.35.
).52.40+ RJ HOPHA2,UAALGOL68,PARAM(PROG KINETIC,DATA RAHM,CHECK),JD(JT30,MZ3AK)
9NOV78 14.51 ;SSN0100        RESOURCES RESET:  PAGES  900  STORE     400  SHARES     81
).52.41 JOB IS NOW FULLY STARTED
).52.41+ UAALGOL68         PROG KINETIC,DATA RAHM,CHECK
).52.41+          TA AB,CM,JL

 UAALGOL68: STATUS REPORT NUMBER 4      DATE 23 NOVEMBER 77

).52.52 0.01 CORE GIVEN 2500
OMPILED BY THE ALGOL68-R COMPILING-SYSTEM   ON 09/11/78 AT 09/53/02          ASTON UNIVERSITY

).53.09 0.02 CORE GIVEN 37088
       OPTICAL
       'BEGIN'
       'C' RUN NO. REP.NO. 5A 'C'
       'C' TEMPERATURE = 30 DEGREE CENTIGRATE 'C'
       'C' ETHANOL = 25 % 'C'
       'CHAR' R ;READ((R,NEWLINE));
       'INT' N ;READ(N); 'C' N IS COUNTER VARIABLE 'C'
       'INT' T1 ; 'C' T1 IS THE INDUCTION PERIOD TIME 'C'
       [1:N] 'REAL' S;'C' S AN ARAY FOR CALCULATION PURPOSES 'C'
       'REAL' DF ; 'C' DF REPRESENT THE O.D. OF THE MIXTURE AT THE END OF REACTION 'C'
       [1:N] 'REAL' D ; 'C' D IS THE OPTICAL DENSITY AT ANY TIME 'C'
       [1:N]'INT' T ;  'C' T REPRESENT TIME 'C'
       'REAL' A := 0.0;
       'REAL' B := 0.0 ,C :=0.0,E:=0.0,K,Z,D0,Q;
       READ((DF,T1));
       'FOR' I 'TO' N 'DO'
               'BEGIN'
                READ(D[I]);                      T[I] := T1 + (I-1)*4;
                        B := B + T[I];
                        E := E + T[I] ↑2
               'END' ;
       'FOR' I 'TO' N 'DO'
               'BEGIN'
                         S[I] := SQRT (D[I]-DF);
                         A :=A+ S[I];
                         C:=C+S[I]*T[I]
               'END' ;
       K := (A*B-N*C)/(N*E-B↑2);
       Z:=(A+K*B)/N;
       D0 := Z↑2 + DF;
       PRINT((NEWLINE,"                OUTPUT DATA"));
       PRINT((NEWLINE,"                -----------"));
       PRINT((NEWLINE,"      RUN NO. =",R));




       PRINT((NEWLINE,"      TIME      D-OBS.      D-CALC."));
       PRINT((NEWLINE,"      ----      ------      -------"));
       'FOR' I 'TO' N 'DO'
               'BEGIN'
                         PRINT((NEWLINE,T[I],"    ",D[I],
                                "     ",(Z-K*T[I])↑2+DF));
                         Q :='ABS'((D[I]-((Z-K*T[I])↑2+DF))/D[I]);
                          'IF' Q < 0.05 'THEN' PRINT(("                   ",
                                                 "                   *"))
                                  'ELSE' Q < 0.1 'THEN'
                                                 PRINT(("              ",
                                                 "                    *"))
                                  'ELSE' Q < 0.2  'THEN'
                                                 PRINT(("              ",
                                                 "                     *"))
                      'FI'
               'END';
       PRINT((NEWLINE,NEWLINE,NEWLINE,NEWLINE));
       PRINT((NEWLINE,"      K =",K,"1/MIN.","       Z =",Z,"      DZERO=",D0))
       'END'
       'FINISH'
.03 :HALTED :      COMPILED OPTICAL
9.53.53 FREE *DA11,20 TRANSFERS
9.53.55 FREE *LP0 ,55 TRANSFERS
9.54.01 0.04 CORE GIVEN 6520,CLOCKED 0.01
ISPLAY : LD
.06 :DELETED ; OK
9.54.42 FREE *FR0 ,5 TRANSFERS
9.54.42 FREE *DA12,76 TRANSFERS
9.54.43 FREE *DA11,6 TRANSFERS
9.54.43 FREE *TR0 ,3 TRANSFERS
9.54.43 FREE *LP0 ,20 TRANSFERS
9.54.44 FREE *DA15,2 TRANSFERS
9.54.44 0.06 DELETED,CLOCKED 0.02
ARAMETER NUMBER 1,2 UNACCESSED
ISPLAY: UAALGOL68R: NORMAL EXIT
9.54.50 0.06 FINISHED : 2 LISTFILES
9.54.50 JOBTIME USED 7 ; MAXIMUM CORE USED 37088
9.54.50 JOB UNITS 20
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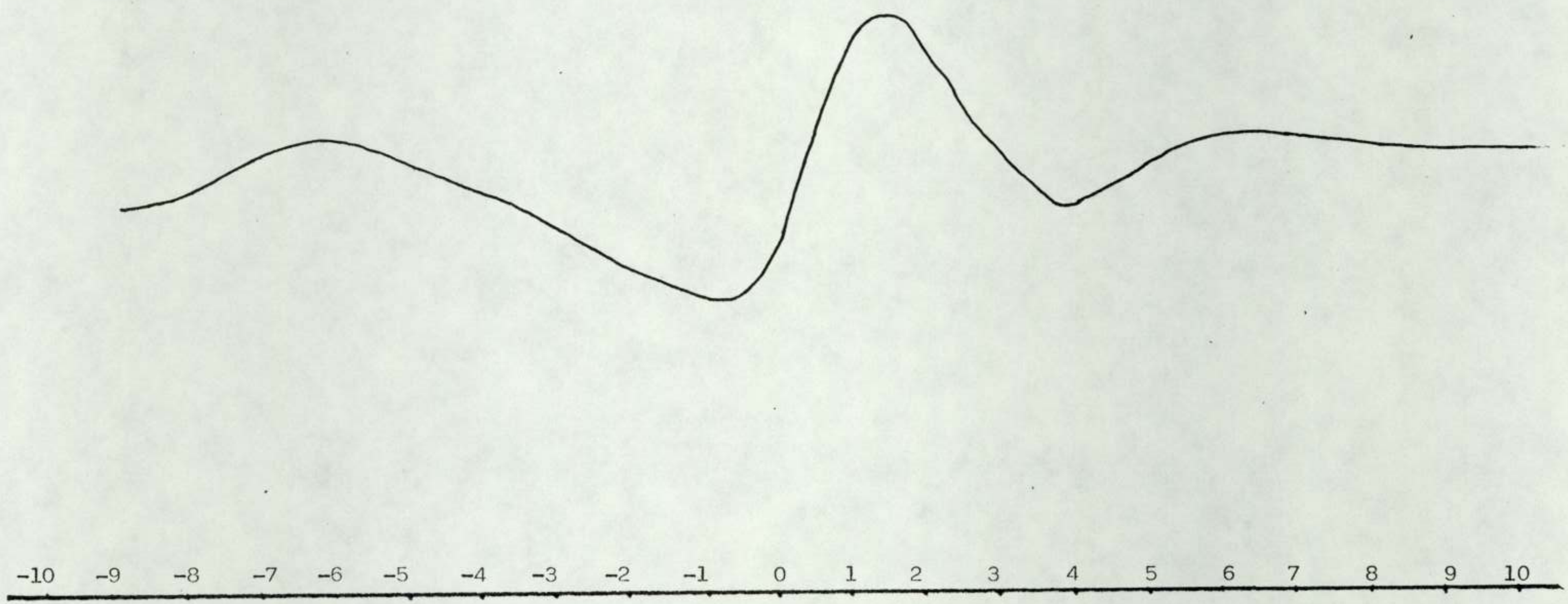

Figure 7 : E.S.R. spectrum of bis-p-ethoxyphenyl ditelluride with ethanol after 25 minutes irradiation outside the cavity. (arbitrary scale)

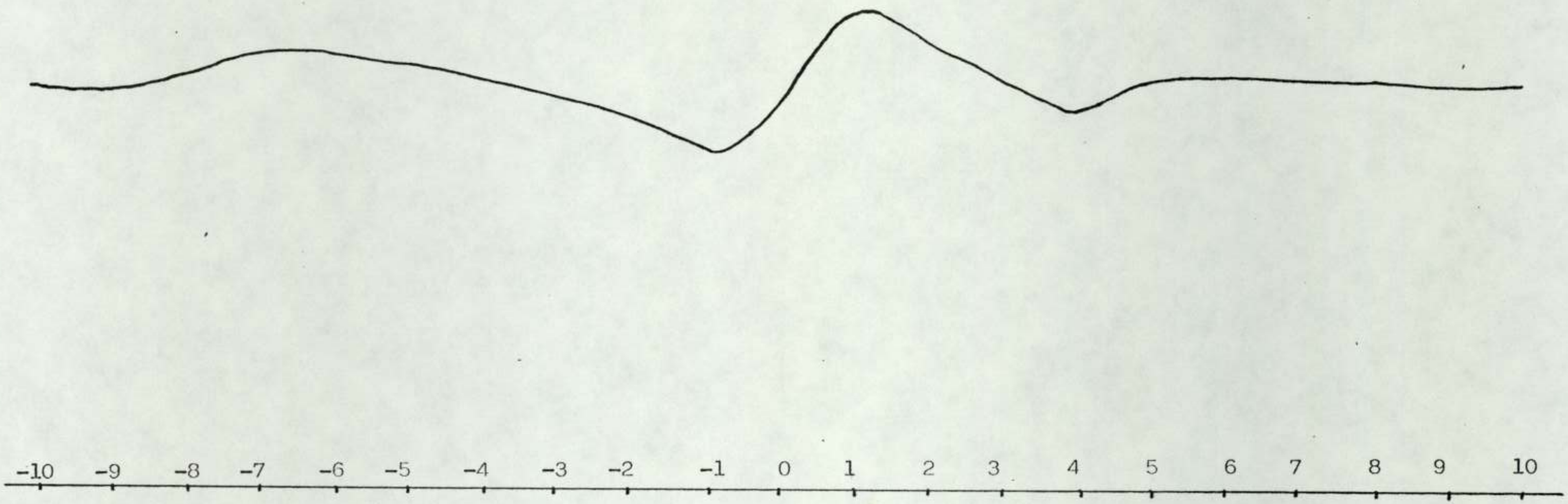

Figure 10 : E.S.R. spectrum of bis-p-ethoxyphenyl ditelluride without ethanol after irradiating the sample for about 10 minutes within the cavity of the instrument. (arbitrary scale)

Appendix Three

Basic

```
 10  DIM D(10,10)
 20  INPUT U,V                         No. of pts of (I2) (Te2)
 30  For J = 1 to V
 40  INPUT T(J)                        The various values of (Ar2Te2)
 50  NEXT J
 60  For J = 1 to U
 70  INPUT I(J)                        Value of [I2]
 80  For K = 1 to V
 90  INPUT D(J,K)                      Values of OD at this [I2]
100  NEXT K
110  NEXT J
120  INPUT I,T                         Extinction coefficient of
                                       I2 and Te2
130  LET Z = 1
140  LET Y = 1
150  INPUT A, B, C, D                  No. of guesses at E1:1  E2:1
                                       K1 and K2 (point 0,0,0,0 when
                                       best fit is found).
160  IF A = 0 then 720
170  For J = 1 to 8
180  INPUT A(J)                        Range of guesses at these quantities.
190  Next J
200  For J = 1 to A
210  Let E(1) = A(1) +(A(2) - A(1))  * J/A
220  For K = 1 to B
```

```
230  Let E(2) = A(3) + (A(4) - A(3))  * K/B
240  For L = 1 to C
250  Let E = A(5) + (A(6) - A(5))  * L/C
260  Let K(1) = 10 ↑E
270  For M = 1 to D
280  Let E = A(7) + (A(8) - A(7))  * M/D
290  Let K(2) = 10 ↑E
300  Let S = 0
310  For Ø = 1 to U
320  For P = 1 to V
330  If T(P) > I(Ø) then 440
340  If T(P) = I(Ø) then 400
350  Let F = I(Ø) + 1/K(2)
360  Let G = (F-SQR(F*F-4*T(P) * (I(Ø) - T(P))))/2
370  Let H = (T(P) - G)/(K(1)*(I(Ø) - T(P) - G))
380  Let Q = I*(I(Ø) - T(P) - G + H) + T*H + E(1) *(T(P)-G-H) + E(2)*G
390  Go to 480
400  Let F = I(Ø)/Cl + 2*(SQR(K(2)/K(1))))
410  Let G = 1/SQR(K(1)*K(2)))
415  Let H = F*(SQR(K(2)/K(1)))
420  Let Q = I*G + T*(G + H) + E(1)*F + E(2)*H
430  Go to 480
440  Let F = 1-4*K(2)/K(1)
450  Let G = (T(P)-SQR(T(P)*T(P)-I(Ø)*(2*T(P)-I(Ø))*F))/F
460  Let H = (I(Ø) - G)/(2*G*K(2))
470  Let Q = I*H + T*(T(P)-I(Ø)+G)/2)+E(1)*G + E(2)*(I(Ø)-G)/2
480  If Y = 0 then 520
490  Let S = S + (D(Ø,P)-Q) ↑2
500  If S > Z then 630
```

```
510  Go to 530

520  Print Q

530  Next P

540  If Y = 1 then 560

550  INPUT A                          Any number, this is a wait device

560  Next Ø

570  If Y = 0 then 780

580  Let Z = S

590  For P = 1 to 2

600  Let X(P) = E(P)

610  Let W(P) = K(P)

620  Next P

630  Next M

640  Next L

650  Next K

660  Next J

670  Print Z

675  If Z = 1 then 150

680  For P = 1 to 2

690  Print X(P), W(P)

700  Next P

710  Go to 150

720  For P = 1 to 2

730  Let E(P) = X(P)

740  Let K(P) = W(P)

750  Next P

760  Let Y = 0

770  Go to 310

780  End
```

During search prints out sum of square differences

$E_{1:1}$

K_1

$E_{2:1}$

K_2

after best fit is found prints out calculated optical densities.

Inputs as shown.

Appendix Four

Rapid Stage

Given suitable values of K_1 and K_2 we can treat as

$$A + B \xrightarrow{k_1} C$$

$$\frac{dc}{dt} = k_1(A_o - C)\ (B_o - C)$$

$$\therefore \quad \ln \frac{(Ao\ (Bo - C)\ )}{(Bo\ (Ao - C)\ )} = k_1\ (B_o - A_o)\ t. \quad \text{when } B_o \neq A_o$$

or $$\frac{1}{(A_o - C)} - \frac{1}{A_o} = k_1 t \qquad \text{when } B_o = A_o$$

consider optical densities (D)

$$D_o = E_A\ A_o + E_B\ B_o$$

$$D = E_A\ (A_o - C) + E_B\ (B_o - C) + E_C\ C$$

i.e. $$D = (A_o - C)\ (E_A + E_B - E_C) + E_B\ (B_o - A_o) + E_C\ A_o$$

$$D_{oo} \doteq E_B\ (B_o - A_o) + E_c\ A_o \qquad \text{when } B_o > A_o$$

$$\therefore\ D_o - D_{oo} = A_o\ (E_A + E_B - E_C)$$

and $$D - D_{oo} = (A_o - C)\ (E_A + E_B - E_C)$$

now

$$(B_o - C)\ (E_A + E_B - E_C) = \left[\ (A_o - C) + (B_o - A_o)\right]\ (E_A + E_B - E_C)$$

$$\therefore \qquad = (D - D_{oo}) + \left(\frac{Bo - Ao}{Ao}\right)\ (D_o - D_{oo})$$

$$\therefore \quad (B_o - C)\,(E_A + E_B - E_C) = D + \left(\frac{Bo - Ao}{Ao}\right) D_o - \left(\frac{Bo}{Ao}\right) D_{oo}$$

$$\therefore \quad \ln\left(\frac{Ao(Bo - C)}{Bo(Ao - C)}\right) = \ln\left(\frac{(D + (r - 1)Do - rDoo)}{r(D - Doo)}\right) \quad \text{where } r = \frac{Bo}{Ao}$$

$$\text{and } \frac{1}{(Ao - C)} - \frac{1}{Ao} = (E_A + E_B - E_C)\left(\frac{1}{D - Doo} - \frac{1}{Do - Doo}\right)$$

N.B. If $\Delta = D - Do$ then

$$\ln\left(\frac{Ao\ (Bo - C)}{Bo\ (Ao - C)}\right) = \ln \frac{(\Delta - r\,\Delta oo)}{(r(\Delta - \Delta oo)}$$

$$= \ln\left(\frac{(r\Delta oo - \Delta)}{r(\Delta oo - \Delta)}\right)$$

Appendix Five

Slow Stage

Assume that K_1 is large and complete .

Consider

$$B + C \overset{K_2}{\rightleftharpoons} D$$

$$D \xrightarrow{k_3} 2P + B$$

(i.e. assuming K_1 is very large)

where

$C \equiv Ar_2Te_2 . I_2$, $B \equiv I_2$

$D \equiv Ar_2Te_2.2I_2$, $P \equiv (ArTeI)$

$Te_o = C + D + 2P$

$I_o = B + C + 2P + 2D$

let $Z = Te_o - 2P$

and $Y = I_o - Te_o$

then $Z = C + D$

and $Y = B + D$

If concentrations are such that $B \simeq Y$ then

$$D = K_2Y(Z - D)$$

$$= \frac{K_2YZ}{(1+K_2Y)}$$

$$\frac{dp}{dt} = -2\frac{dz}{dt} = 2k_3D$$

$$= 2\left(\frac{K_2k_3Y}{1 + K_2Y}\right) Z$$

$$\therefore \quad \ln (Z/Zo) = - \frac{K_2k_3Y}{1 + K_2Y} \quad t$$

$$= - \text{kobs} \quad t$$

$$OD = E_B\,B + E_CC + E_DD + E_PP$$

but $B \simeq Y$, $C = Z - D$, $P = \frac{1}{2}\,(Te_o - Z)$

$$\therefore \quad OD = E_BY + \frac{1}{2}E_PTe_o + Z\;(E_C - \frac{1}{2}E_p) + D\;(E_D - E_C)$$

$$OD_{\infty} = E_BY + \frac{1}{2}E_PTe_o$$

$$\therefore \quad (OD_{\infty} - OD) = Z(\frac{1}{2}E_P - E_C) - D(E_D - E_C)$$

but $D = \frac{K_2\;Y\;Z}{(1 + K_2Y)}$

= (a constant) Z

$\therefore$ $(OD_{\infty} - OD)$ = (a constant) Z

$\therefore$ Plot of $\ln (OD_{\infty} - OD)$ VS t, will be linear, with

gradient = - kobs , where

$$\text{kobs} = \frac{K_2k_3Y}{1 + K_2Y}$$

$$\text{i.e.} \quad \left(\frac{1}{(\text{kobs})}\right) = \frac{1}{k_3} + \frac{1}{K_2k_3} \quad \left(\frac{1}{[I]_o - [Te]_o}\right)$$

If the slow step is

$$C \xrightarrow{k_3} 2P$$

$$Z = C + D$$

$$\therefore \quad C = \frac{Z}{1 + K_2Y}$$

$$\frac{dp}{dt} = - 2\frac{dz}{dt} = 2k_3C = \frac{2k_3Z}{1 + K_2Y}$$

$\therefore$ exactly as before

$\ln(OD_{\infty} - OD)$ VS t will be linear, but now

$$kobs = \frac{k_3}{1 + K_2Y}$$

$$\therefore \quad \frac{1}{(kobs)} = \frac{1}{k_3} + \frac{K_2}{k_3}\left([I]_o - [Te]_o\right)$$

$[I_2]$ \ $[Ar_2Te_2]$	5×10^{-4} M	4×10^{-4} M	3×10^{-4} M	2×10^{-4} M	1×10^{-4} M	5×10^{-5} M
5×10^{-4} M	0.081	0.281	0.447	0.536	0.550	0.531
4×10^{-4} M	0.073	0.066	0.248	0.379	0.427	0.421
3×10^{-4} M	0.095	0.063	0.051	0.208	0.297	0.308
2×10^{-4} M	0.117	0.085	0.053	0.036	0.160	0.192
1×10^{-4} M	0.140	0.107	0.075	0.043	0.022	0.069

Table 2A : Calculated absorbance of the mixture of bis(p-ethoxyphenyl) ditelluride with iodine at the wavelength of 500nm at 10°C.

$[Ar_2Te_2]$ $[I_2]$	5 X 10^{-4} M	4 X 10^{-4} M	3 X.10^{-4} M	2 X 10^{-4} M	1 X 10^{-4} M	5 X 10^{-5} M
5 X 10^{-4} M	0.053	0.124	0.227	0.324	0.414	0.457
4 X 10^{-4} M	0.045	0.049	0.118	0.218	0.311	0.356
3 X 10^{-4} M	0.074	0.042	0.045	0.112	0.209	0.254
2 X 10^{-4} M	0.103	0.071	0.039	0.041	0.106	0.153
1 X 10^{-4} M	0.133	0.100	0.068	0.035	0.036	0.052

Table 3A : Calculated absorbance of the mixture of bis(p-ethoxyphenyl) ditelluride with iodine at the wavelength of 500nm at 45°C.

CHAPTER SEVEN

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