TO MY PARENTS

CHEMISTRY OF TELLURIUM
APPLIED TO
RUBBER

BY

KALUACHCHI GAMAGE KARNIKA DE SILVA

A thesis submitted for the Degree of
Doctor of Philosophy
of the
University of Aston in Birmingham

July 1984

DECLARATION

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

K.G.K. de Silva

K G K de Silva

The University of Aston in Birmingham

The Chemistry of Tellurium Applied to Rubber

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Summary

A study of tellurium and its compounds in rubber has been carried out by using them as crosslinking agents and as ultra-accelerating agents when employed together with a tetraalkylthiuram disulphide. Reactions of tellurium tetrahalides with model alkenes, rubber solutions and solid rubber were employed in order to study the tellurium-carbon bond formation in the media.

The formation of black gels was observed with natural rubber solutions when reacted with tellurium tetrahalides (chlorides and bromides). A Mössbauer study was carried out for the black gel obtained with tellurium tetrachloride and natural rubber solutions and the results are discussed.

In order to explain the observations made with solid natural rubber, namely that tellurium tetrahalides and trihalides, and selenium tetrahalides enhance the crosslink density and acceleration rate of the natural rubber vulcanization reaction in the presence of thiurams; the tellurium compounds were reacted with a tetraalkyl(methyl or ethyl) thiuram disulphide in solution and the chemistry of the resulting complexes was studied.

Emphasis was placed on their reactions with sulphur donor ligands. Detailed or tentative assignments of the spectra for these complexes are suggested and in certain cases, structures proposed.

Using the tellurium (IV) complex prepared with tellurium tetrachloride and tetramethylthiuram disulphide, TMTD, as the starting material, reactions with some 1st row transition metals gave a new class of complexes.

Reactions of RTeNa (R=pEtOC$_6$H$_4$) with organic dihalides as model compounds were carried out with the idea that brominated natural rubber would react with RTe$^-$ affording tellurium-carbon bonds. However, the reaction of RTeNa with $X_2(CH_2)_n$ afforded charge-transfer complexes when n=1 and X=Br, I. The complexes showed a stoichiometry (RTe)$_2$CH$_2$.CH$_2$X$_2$. The nature of these materials is discussed. Some ^{125}Te Mössbauer data are also discussed and it is suggested that the unusually low value of Δ (7.58 mms^{-1}) for (pEtOC$_6$H$_4$Te)$_2$CH$_2$.CH$_2$Br$_2$ is related to removal of 5p-electrons from the spare pair orbital via the charge-transfer interaction.

For n=2 and X=Br, elimination of ditelluride occurred with the formation of an alkene whereas when n=3,4 and X=Cl,Br, telluronium salts were found.

KEY WORDS

TELLURIUM
RUBBER
TELLURIUM TETRAHALIDES
DISULPHIDE
MODEL ALKENES

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CHAPTER ONE

INTRODUCTION

1.1 Introduction

Intensive efforts have been made with some success to gain a greater understanding of the vulcanization reaction of natural rubber (NR). Vulcanization is the chemical reaction which, as is now known, brings about the formation of crosslinks between the long, linear, unsaturated polymeric chains of NR, leading to a high molecular weight three dimentional structure.

After well over a century of empirical vulcanization technology, the chemistry of vulcanization has now reached a stage where not only is it possible to explain the process used by the technologist, but to use the chemistry to advance the technology. As a result, the elucidation of the chemistry of vulcanization has had an important impact on technology over the last two decades(1,2).

Some views of the mechanism of vulcanization have appeared in the literature including suggestions for a free radical or for a polar process. The research work based on model compound studies by the British Rubber Producer's Research Association(3,4) has been interpreted to support the view that the vulcanization reaction proceeds through a polar mechanism. However, Turner(5) has measured the effect of radical traps on the radiation crosslinking of rubber and claims that the radiation crosslinking proceeds via a radical mechanism. Glazer and Schulman(6) have studied the gelation of natural rubber in benzene with sulphur monochloride at room temperature and also postulate a radical mechanism for the crosslinking reaction.

In view of the wide variety of material and methods used to effect cure in rubber, Schelton and McDonel(7) suggest that it is reasonable that the reaction can proceed by a variety of mechanisms, depending on the curing agents and the methods used and further, it is the author's responsibility to attempt to establish the free radical or polar nature of the reaction by determining the effect of free radical traps on the rate of crosslinking of rubber.

1.2 Vulcanizing Agents

Although sulphur still remains the basis of the most widely used crosslinking agents, new polymers have required other chemicals. Over the years many materials have been found to crosslink natural and synthetic rubbers. The most important materials are the compounds that liberate sulphur atoms, thiuram disulphides, metal oxides and peroxides. Selenium and tellurium can replace and supplement sulphur and have found some use in vulcanizing systems for particular purposes.

1.3 Vulcanization with Sulphur

1.3.1 Vulcanization with Sulphur Without Accelerator

The vulcanization with sulphur, without an accelerator is an extremely slow process and is therefore of no technical importance at all. The low crosslink yield which is obtained is mainly due to the fact that, as shown in Figure 1.1, cyclic, poly and vicinal sulphide links may be formed.

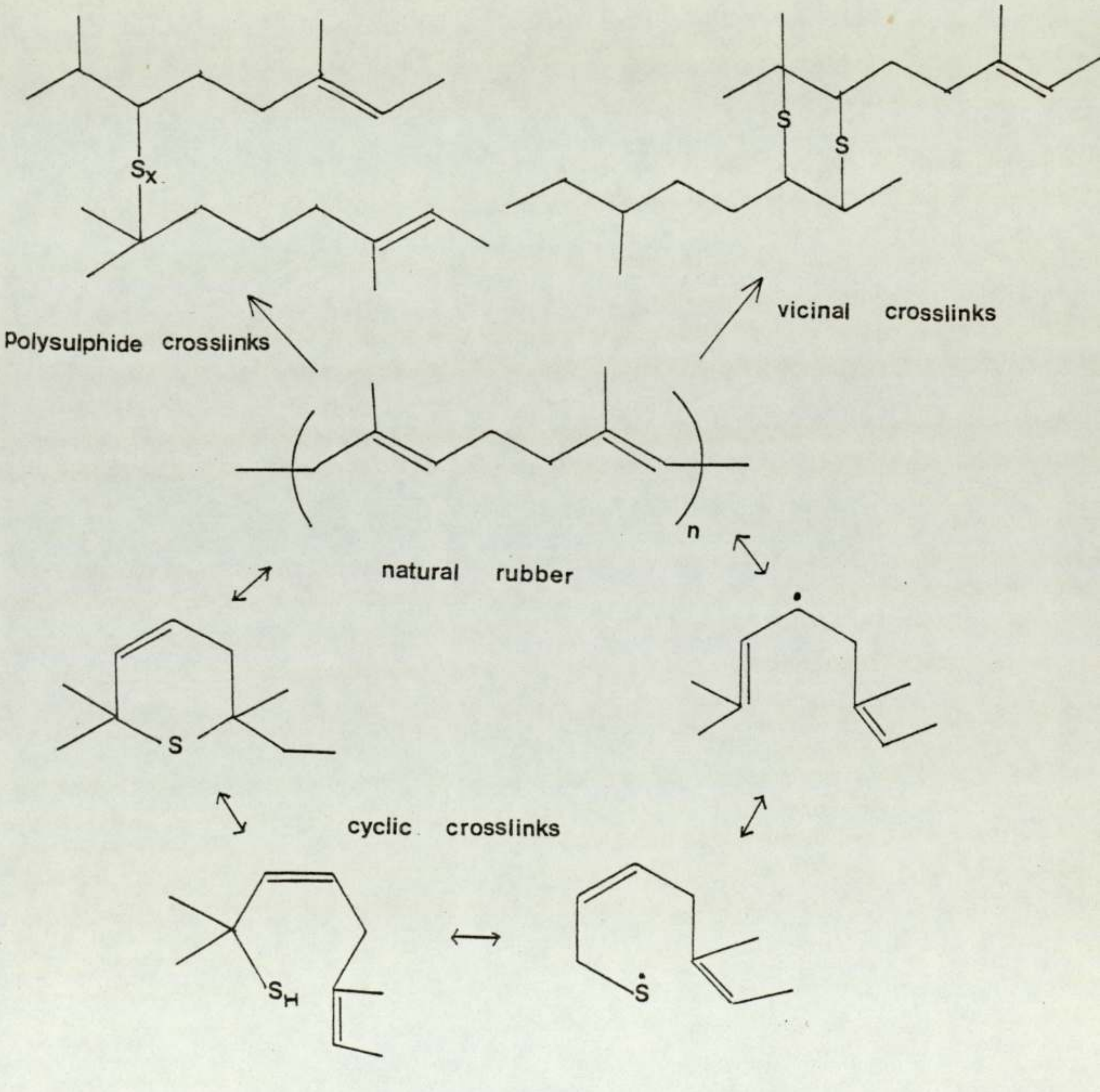


Figure 1·1

1.3.2 Structural Features of Sulphur Vulcanization

In the vulcanization network sulphur is combined in a number of ways (Figure 1,2), as enumerated by Porter(8). As crosslinks, it may be present as monosulphide, disulphide or polysulphide (Figure 1.2a), but it may also be present as pendent sulphides (Figure 1.2b) or cyclic monosulphides and disulphides (Figure 1.2c).

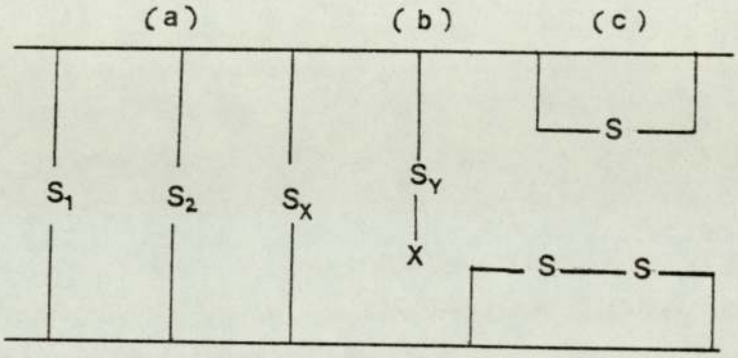


Figure 1.2

An estimate of the number of sulphur atoms consumed for each crosslink formed has been made; an unaccelerated rubber-sulphur vulcanizate may require 40-45, while in an accelerated vulcanizate this 'inefficiency' figure may drop to 10-15. Special 'efficient' vulcanizing systems can reduce it still further to 4-5.

1.3.3 Stability of the Sulphur Ring

The reluctance of sulphur to react with NR giving only monosulphidic crosslinks can be easily understood when one bears in mind the structure of the sulphur, existing as a stable S_8 ring. Such an eight membered ring should be stable in different steric forms, but only the crown shape (Figure 1.3a) is known.

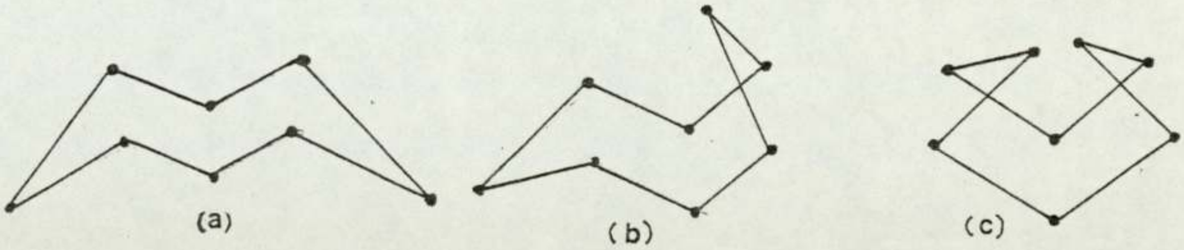


Figure 1.3

Warren and Burwell(9) proved the existence of sulphur as S_8 ring by means of infra-red spectra and this finding has been subsequently repeatedly confirmed by means of tests on the diffusion of radioactive sulphur, ^{35}S, in rubber. Bressler and coworkers(10) have confirmed that sulphur dissolved in rubber also has a molecular weight of about 225 i.e., that it is initially present as the S_8 ring.

The stability of the ring explains the lack of reactivity of sulphur with the double bonds or the reactive sites of the natural rubber. To make sulphur reactive, a considerable amount of activating energy (268 $kJ.mol^{-1}$) must be expended and the sulphur ring must be split. This process of activation occurs at high temperatures and can be promoted by the use of activators, such as zinc oxide and stearic acid and accelerators such as dithiocarbamates and disulphides.

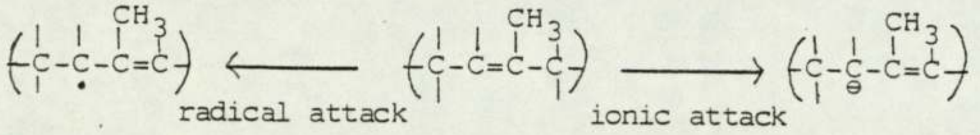
Peachy and Skipsey(11) showed that the reaction of hydrogen sulphide with sulphur dioxide in which active sulphur is formed insitu (Eq. 1.1), could be used to vulcanize NR even at room temperature.

$$2H_2S + SO_2 \longrightarrow 2H_2O + 3S \text{ atomic} \qquad \text{Eq. 1.1}$$

After being activated by any of the above methods, the sulphur is able to react with the reactive sites on the rubber molecules - where there are α methylene groups, or double bonds - in such a way that no intermolecular cross-links are formed initially.

1.3.4 Possible Reaction Pathways for Sulphur Only Vulcanization

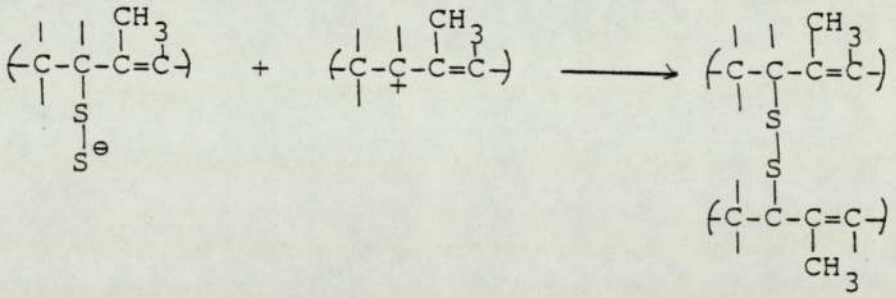
The fact that the number of double bonds remains unchanged in the vulcanizates shows that the addition of radicals or ionic reagents to the NR with unsymmetric double bonds is not governed according to the well known polar addition rule of Markownikoff. Therefore the primary reaction should not always be viewed as involving addition to the double bonds. Because of the electron donor action of the methyl group, which is overcompensated by the electron affinity of the double bond, the α-methylene group has an extensive electron agglomeration which makes it partially reactive (Eq. 1.2).



Eq. 1.2

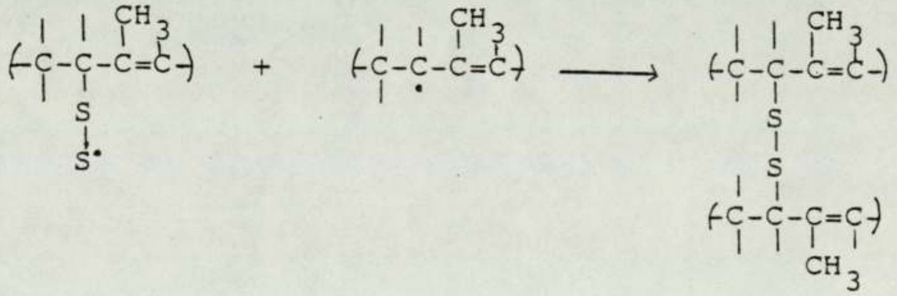
According to Krebs(12) the sulphur ring can generally be split up in two ways. In the first case the splitting is ionic, in the second it is radical. Depending on whether the sulphur attacks the NR ionically or radically (from S_8 fission products) the process of vulcanization could proceed by an ionic or radical method as shown in Equation's 1.3 and 1.4 respectively.

Ionic crosslinking



Eq. 1.3

Radical crosslinking



Eq. 1.4

1.4 Accelerated Sulphur Vulcanization

1.4.1 Nature and the Formation of the Active Sulphurating Agent

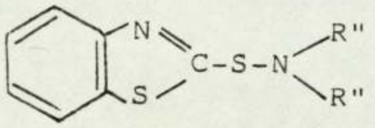
The use of activating agents zinc oxide and stearic acid together with an accelerator shows that the active sulphurating agent is itself produced by a multistep reaction. The first step involves the reaction of zinc oxide and the accelerator with sulphur to give a zinc perthio-salt XS_xZnS_xX, where X is a group derived from the accelerator insitu with rubber. The most common of the so-called accelerators are the thiuram disulphides, sulphenamides and thiozoles.

In an attempt to solve the precise mode of 'sulphur activation', one of the yet unsolved mysteries of the vulcanization, McCleverty(13) found that S_8 activation is greatly facilitated by the presence of anionic species in the 'sulphurating' system. This observation was made by reacting $[Zn(S_2CNMe_2)_3]^-$, as its tetraalkylammonium salt $(NR_4)Zn(S_2CNMe_2)_3$, with S_8 in an organic solvent.

It is known(14) that the zinc dimethyldithiocarbamates formed in the rubber vulcanization system do not show significant reactivity towards attack on S_8 or have appreciable solubility in hydrocarbons but many accelerator systems containing stearic acid form a 1:2 adduct with zinc dithiocarbamate which may enhance the nucleophilicity of the coordinated dithiocarbamate towards attack on S_8.

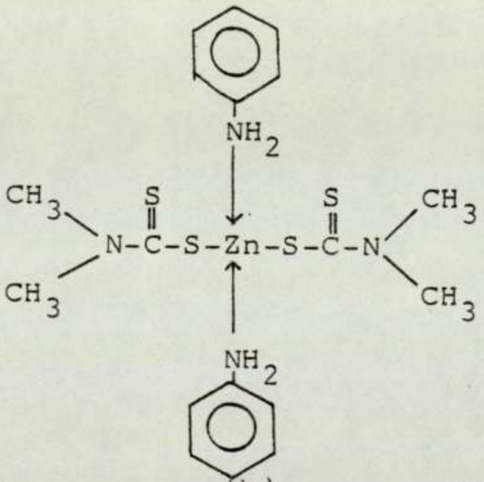
McCleverty's studies$^{(15)}$ with carboxylate anions showed that acetate forms only a 1:1 adduct with $[Zn(S_2CNMe_2)]_2$ via $[NR_4][Zn(S_2CNMe_2)_2(OCOMe)]$. The reaction of tetra-alkylammonium stearate with zinc dimethyldithiocarbamate showed the formation of $Zn(S_2CNMe_2)_3^-$. The inability of $[Zn(S_2CNMe_2)]_2$ to react with HOCOR' or M(OCOR') (M=alkali metal) to form an adduct or anionic species clearly demonstrated that the carboxylic acid must be in the form of an ammonium salt. Thus, the production of $[Zn(S_2CNMe_2)_3]^-$ in 'sulphurating systems' containing zinc oxide, tetramethylthiuramdisulphide, S_8 and stearic acid is distinctly possible and this species may be an important precursor in the activation of sulphur in zinc assisted vulcanization. The analogue $C_7H_4NS_2$ (2-mercaptobenzothiozole) accelerator was also found to behave in a similar way to tetramethylthiuramdisulphide.

In the 'sulphurating systems' an ammonium stearate could be formed by neutralization of the added acid by amines which either occur naturally in rubber latex or which are formed by acid decomposition of tetramethylthiuramdisulphide or zinc dimethyldithiocarbamate. In the benzothiozole activated system, 2-mercaptobenzothiozole is frequently used as a sulphenamide derivative $C_7H_4NS_2NR''_2$ (R"=alkyl-) (a) and treatment of these with acids readily affords $[NH_2R''_2]^+$.



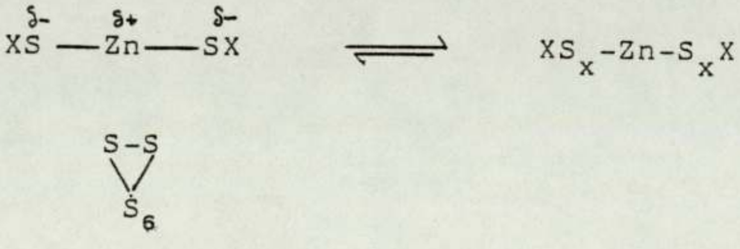
(a)

Typical coordination products with nitrogen bases, amines (either naturally occurring in rubber or deliberately added) as shown in (b), or with carboxylates formed, will help to dissolve the zinc dimethyldithiocarbamate.



(b)

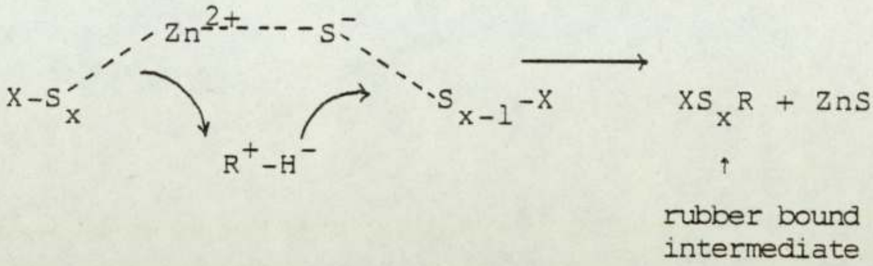
The zinc perthio salt XSZnSX or its complex such as (b) is then believed to react with sulphur to form a perthio-salt with a polysulphidic anion (Eq. 1.5)



$$\overset{\delta-}{XS}-\overset{\delta+}{Zn}-\overset{\delta-}{SX} \quad \rightleftharpoons \quad XS_x-Zn-S_xX \qquad \text{Eq. 1.5}$$

1.4.2 Formation of the Rubber Bound Intermediate

The active sulphurating agent so formed then reacts with the rubber hydrocarbon, RH, to give a rubber bound intermediate, as in Equation 1.6.

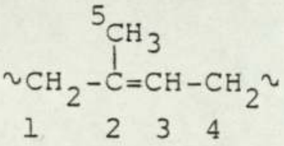


Eq.1.6

Evidence for the rubber bound intermediate has been obtained from the use of a ^{14}C labelled accelerator, by Parks(16).

The perthio-accelerator group $HS_{x-1}X$ formed as in Equation 1.6, further reacts with zinc oxide to give a perthio-salt of lower sulphur content; nevertheless, this again is an active sulphurating agent, forming intermediates of the form $XS_{x-1}R$. In this way each molecule of accelerator gives rise to a series of intermediates of varying 'degrees of polysulphidity'.

The hydrogen atom which is removed from the rubber molecule is likely to be attached to a methylene group in the α-position to the double bond i.e., in natural rubber, figure 1.4 the hydrogen atoms at positions 4 and 5 are the most labile in this type of reaction.



$$\underset{1}{\sim CH_2}-\underset{2}{\overset{{}^{5}CH_3}{\overset{|}{C}}}=\underset{3}{CH}-\underset{4}{CH_2}\sim$$

Figure 1.4

1.4.3 Conversion of Rubber Bound Intermediate Into Crosslinks

The rubber bound intermediate XS_xR, reacts with a molecule of rubber hydrocarbon RH to give a crosslink, and the accelerator is regenerated as shown in Equation 1.7.

$$XS_xR + RH \longrightarrow RS_{x-1}R + XSH \qquad \text{Eq. 1.7}$$

Hence, the formation of crosslinks of the natural rubber.

The probable course of sulphur vulcanization of natural rubber in the presence of accelerator and activator is shown in Figure 1.5.

1.5 Crosslinking Without Elemental Sulphur

1.5.1 Crosslinking With Sulphur Monochloride

Almost as soon as the original discovery of vulcanization had been made public, Parkes in 1840(17) issued a patent in which he described the vulcanization of thin sheets of rubber by exposure to the vapour of sulphur chloride at room temperature. Monosulphidic crosslinks were formed,

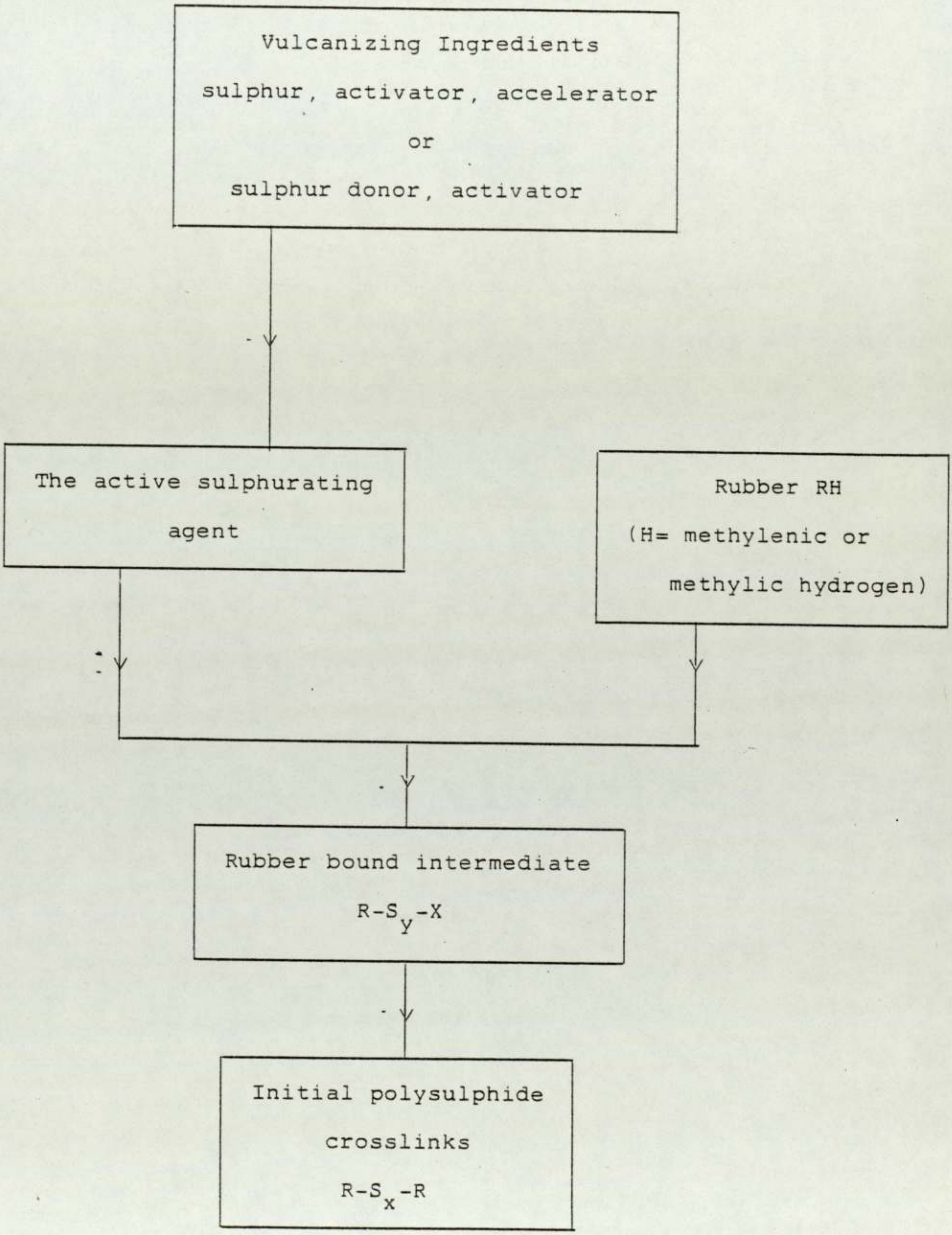
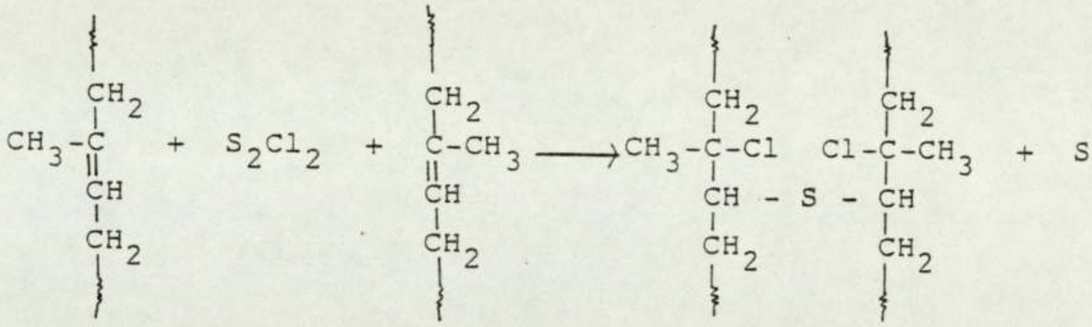

Vulcanizing Ingredients
sulphur, activator, accelerator
or
sulphur donor, activator
The active sulphurating agent
Rubber RH
(H= methylenic or methylic hydrogen)
Rubber bound intermediate
$R-S_y-X$
Initial polysulphide crosslinks
$R-S_x-R$

Figure 1.5

together with chlorine addition to the molecule, as shown in Equation 1.8.



Eq.1.8

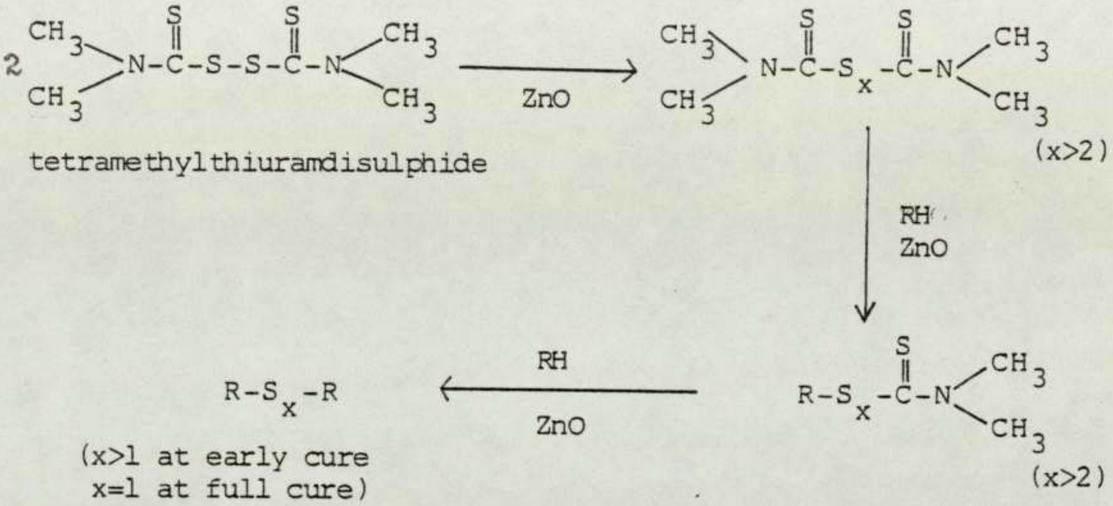
Presumably the method, so called 'cold cure', is applicable to all alkene rubbers, but there is little evidence of it being used for any polymer other than natural rubber.

1.5.2 Crosslinking With Disulphides

1.5.2.1 The Course of Disulphide Crosslinking

Since the early 1920's tetraalkylthiuram disulphides, besides being accelerators for sulphur vulcanization, have been used in conjunction with zinc oxide as non-sulphur vulcanizing agents. It is thus possible to vulcanize a rubber by a mechanism broadly similar to that of an accelerated sulphur system without the use of elemental sulphur.

Since one of the sulphur atoms is readily removable to give the monosulphide, itself an accelerator, this was assumed to be the method of action, but prolonged investigation by Scheele and coworkers(18) and Moore(19) has shown that the mechanism is highly complex, giving mainly monosulphide crosslinks. The disulphide in fact reacts with the zinc oxide to yield a tetraalkylthiuram polysulphide. This then reacts with the rubber molecule and further zinc oxide to produce a rubber bound intermediate polysulphide which then crosslinks to eventually yield monosulphidic crosslinks as in Equation 1.9.

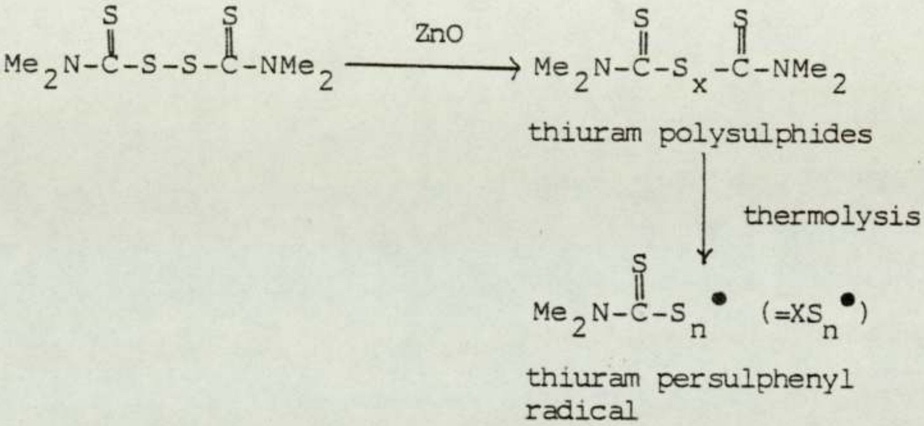


Eq.1.9

Tetraalkylthiuram disulphides give vulcanizates with natural rubber which are lower in tensile strength than sulphur vulcanizates but have very good ageing properties.

1.5.2.2 Proposed Mechanism for the Vulcanization With Disulphides

A free radical mechanism for the formation of the rubber bound intermediate was proposed in the literature for disulphide crosslinking. The polysulphides found at a certain stage in the vulcanizing system rapidly disappeared suggesting a free radical mechanism. This rapid disappearance of the polysulphides has not been observed in the absence of cis-1,4 poly(butadiene). It is attributed to a rapid free radical reaction of the polysulphides with the active hydrogen of the rubber, which results in the formation of the rubber bound intermediate. The formation of polysulphides and their rapid disappearance is consistent with the mechanism proposed in Equation 1.10;



$$Me_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S\text{-}S\text{-}\overset{S}{\overset{\|}{C}}\text{-}NMe_2 \xrightarrow{ZnO} Me_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S_x\text{-}\overset{S}{\overset{\|}{C}}\text{-}NMe_2$$

$$\xrightarrow{\text{thermolysis}} Me_2N\text{-}\overset{S}{\overset{\|}{C}}\text{-}S_n^{\bullet} \quad (=XS_n^{\bullet})$$

$$XS_n^{\bullet} + R\text{-}H \longrightarrow R^{\bullet} + xS_nH$$

$$R^{\bullet} + XS_nX \longrightarrow RS_mX + XS^{\bullet}_{x-m}$$

$$R^{\bullet} + XS_n \longrightarrow R\text{-}S_n\text{-}X \qquad \text{Eq. 1.10}$$

free radical mechanism.

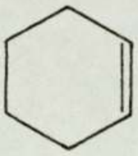
The use of bis-morpholinedisulphide as a vulcanizing agent was reported by Sibley$^{(20)}$ in an investigation which covered a number of organic sulphides. This reagent gives mainly mono and disulphide crosslinks and may be used as a curing agent for any of the alkene polymers. Dipentamethylenethiuramtetrasulphide acts in a similar manner.

1.6 Role of Model Compound Studies in Natural Rubber Vulcanization

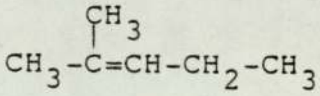
Beyond providing information on elemental proportions, attempts to gain a greater understanding of structures and the kinetics involved in NR reactions by analysis, proved very difficult due to the insolubility and high molecular weight of the crosslinked end products.

It is therefore not surprising that much of the present knowledge has come from the use of model compounds; that is to say, the reaction of sulphur and other vulcanizing ingredients with alkenes structurally related to the rubbers but of low molecular weights.

The structures of some of the alkenes which have been commonly used and the rubbers for which they are models are shown in Figure 1.6 and Figure 1.7 respectively.

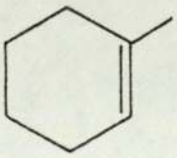


Cyclohexene



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{C}=CH-CH_2-CH_3$

2-methyl 2-pentene

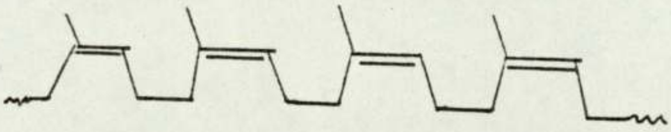


$CH_2{=}CHCH_2CH_2CH_2CH_2CH_2CH_3$

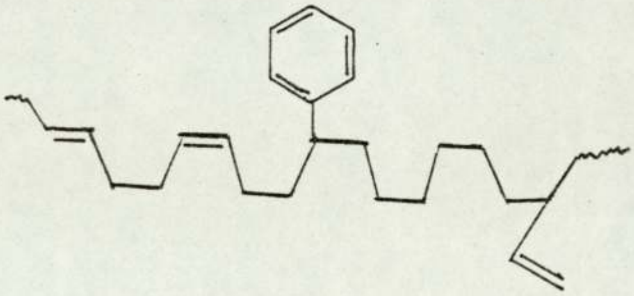
1-methylcyclohexene

1 octene

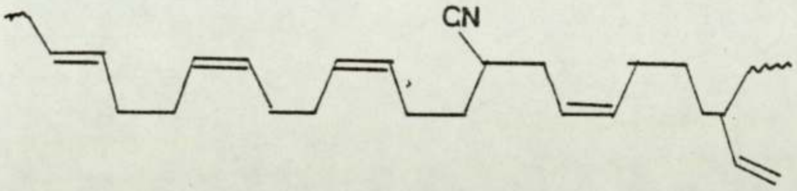
Figure 1.6



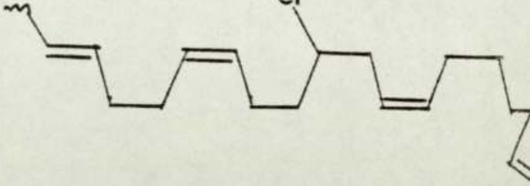
natural rubber
cis-(polyisoprene)



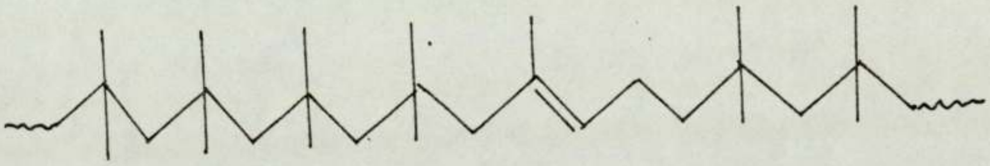
styrene-butadiene rubber
(SBR)



acrylonitrile-butadiene rubber
(NBR)



chloroprene rubber
(CR)



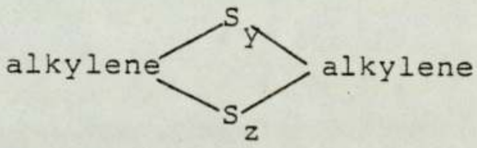
butyl rubber

Figure 1.7

The low molecular weight products were more readily and easily analysed using mass, infra-red, nuclear magnetic resonance and electron spin resonance spectroscopy and the predictions based on the results obtained with the systems enable improvements to be made in the performance of real rubber networks. However, it should be pointed out that the disadvantage of the model compound studies is that they cannot provide any information on intramolecular reactions involving more than one double bond.

Early research work by Farmer and Shipley(21) and by Armstrong, Little and Doak(22) on the reactions of alkenes such as cyclohexene and isobutylene with sulphur at 100°C to 140°C in the absence of other reactants established that the predominant products are alkyl-(R) alkenyl-(R') polysulphides, where R is saturated and R' contains one double bond. In addition, the following products in Figure 1.8 may occur with isobutene but are less likely with cyclohexene and 1-methylcyclohexene. x ranges from 1-6 with relatively little x=1.

alkenyl-S_x-alkyl
(major product)



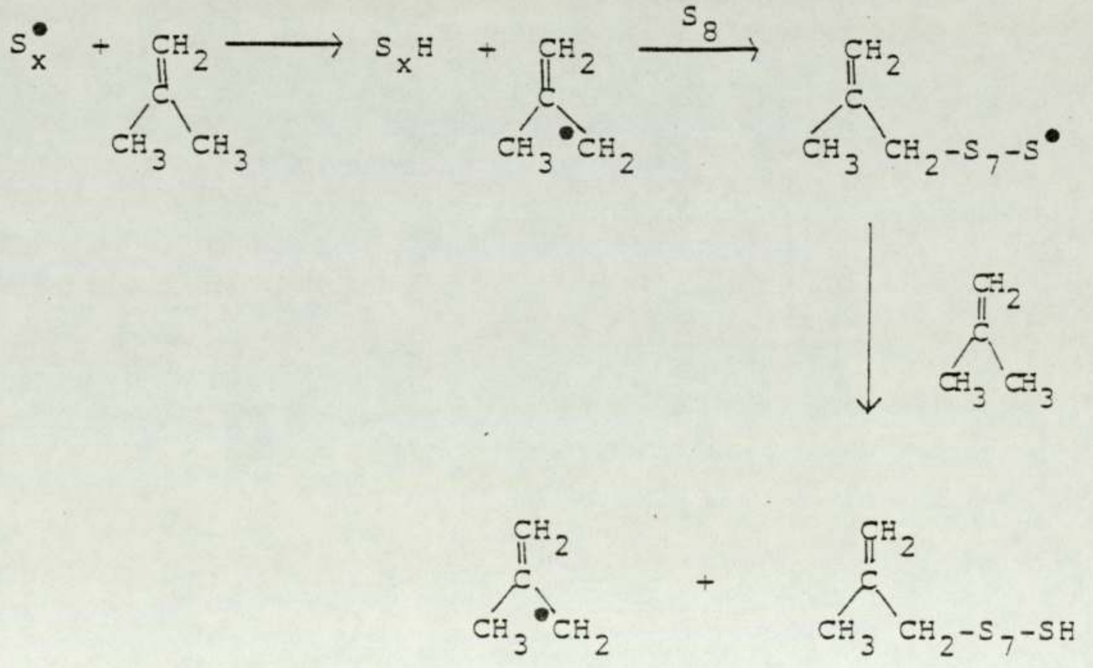
alkenyl-S_y-alkylene-S_z-alkyl

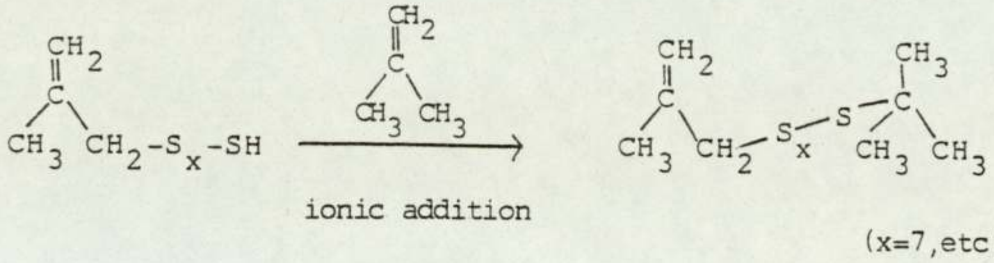
Figure 1.8

Another series of studies designed to elucidate the mechanism of the reactions of sulphur with alkenes examined the reactions of alkenes with hydrogen sulphide. It was shown that hydrogen sulphide adds to alkenes in the presence of sulphur to give Markownikoff addition in an ionic reaction(23,24). In the absence of sulphur and with ultra-violet light, hydrogen sulphide adds to produce non-Markownikoff products in a free-radical reaction that is fast even at 0°C(25).

On the basis of the information on the reaction of alkenes with sulphur, hydrogen sulphide and other sulphur containing compounds, Farmer and Shipley(21) and Bloomfield and Nayer(26) proposed the mechanism given below (Eq. 1.11) for the overall reaction of sulphur with alkenes. Sulphur forms a sulphenyl-radical by an unspecified pathway; this sulphenyl-radical abstracts an allylic hydrogen from the alkene, forming a carbon radical. The carbon radical so formed attacks sulphur to produce a polysulphenyl-radical which abstracts hydrogen from a second alkene molecule and then adds to a third alkene molecule in an ionic addition which obeys the Markownikoff rule.

Initiation by unknown mechanism $\longrightarrow S_x^{\bullet}$



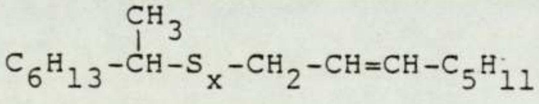


Eq.1.11

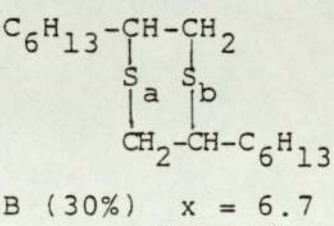
The salient feature of this mechanism is that it separates the radical hydrogen abstraction steps from the ionic addition reaction. One difficulty with this mechanism is that the hydrogen-alkyl-polysulphides RS_xH, which are postulated as intermediates, have not been isolated$^{(27)}$.

In 1959, the reactions of sulphur with alkenes were re-examined by the workers at the British Rubber Producer's Association and the previously published mechanism was modified$^{(28)}$. The reaction of sulphur with 1-octene, cyclehexene, 2-heptene, 2-methyl-2-pentene, 1-methylcyclohexene and 2,6-dimethyl-2-octene has been studied and the products examined by elemental analysis, chemical and spectroscopic methods. The main product is a mixture of polysulphides as previously reported.

The polysulphide products from 1-octene were shown by careful analysis to be a mixture of the compounds shown below in Figure 1.9.


$C_6H_{13}-\overset{CH_3}{\overset{|}{C}H}-S_x-CH_2-CH=CH-C_5H_{11}$

A (25%) $x = 6.7$ (av)



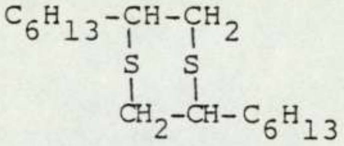
B (30%) $x = 6.7$ (av a+b)

$C_8H_{17}\text{-}S\text{-}C_8H_{17}$ and/or A(x=1)

C (15%)

$C_8H_{17}\text{-}S_a\text{-}C_8H_{16}\text{-}S_b\text{-}C_8H_{17}$

D (15%) x = 4.7 (av a+b)



+ $C_8H_{17}\text{-}S\text{-}C_8H_{16}\text{-}S\text{-}C_8H_{17}$

E (15%)

Figure 1.9

This gives an anomalously low amount of alkyl-alkenyl polysulphide, A, and more cyclic products B and E, relative to the other alkenes studied (Table 1.1).

Kinetic studies by Ross$^{(29)}$ on the reaction of cyclohexene with sulphur between 110° and 140°C followed by dilatometry shows that the reaction goes through three steps (Figure 1.10);

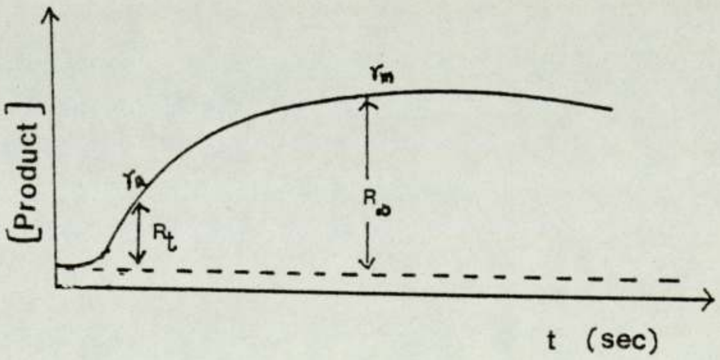


Figure 1.10

1. An accelerating rate until about 20% of the sulphur is consumed (γa).

Alkene	alkyl-S_x-alkenyl (A)	cyclic sulphides (B)	polymer (C)	unreacted alkene and others	alkyl-S-alkenyl (A,x=1)
1 octene	25	30	15	15	15
2,6-dimethyl-2-octene	45	35	20	0	0
1-methylcyclohexene	60	20	10	10	0
2 methyl-2-pentene	80	15	0	5	0

Table 1.1 Approximate distribution of the products from the reaction of various alkenes with sulphur (29)

2. A constant, maximum rate, γm.
3. A decreasing rate.

An induction period occurs and has increasing length at smaller initial concentrations.

The increasing rate γa, is proportional to the square root of the product concentration and the square root of the initial sulphur and alkene concentrations (Eq. 1.12).

$$\gamma a = \frac{dP}{dt} = k(P)^{\frac{1}{2}}(S_8)^{\frac{1}{2}}_{o}(RH)^{\frac{1}{2}}_{o} \qquad \text{Eq. 1.12}$$

where P = product

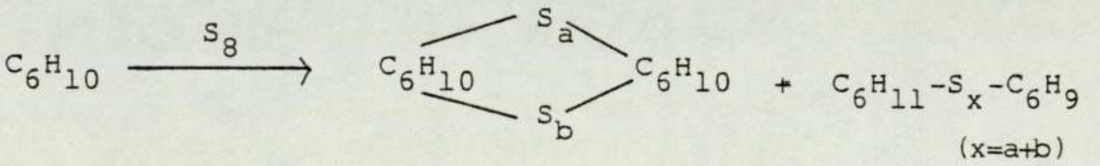
RH= cyclohexene

and the subzero indicates initial concentrations.

The constant rate γm, as measured by the time required for the reaction of one-half of the sulphur was found to be,

$$\gamma m = k'[(S_8)_o[(RH)^{\frac{1}{2}}_{0} - [S]_0\, x^{-1})^{1/2} \qquad \text{Eq. 1.13}$$

The products formed in this reaction appear to be both cyclic sulphides and alkyl- alkenyl- polysulphides, and to be constant during a kinetic run (Eq. 1.14)(26).



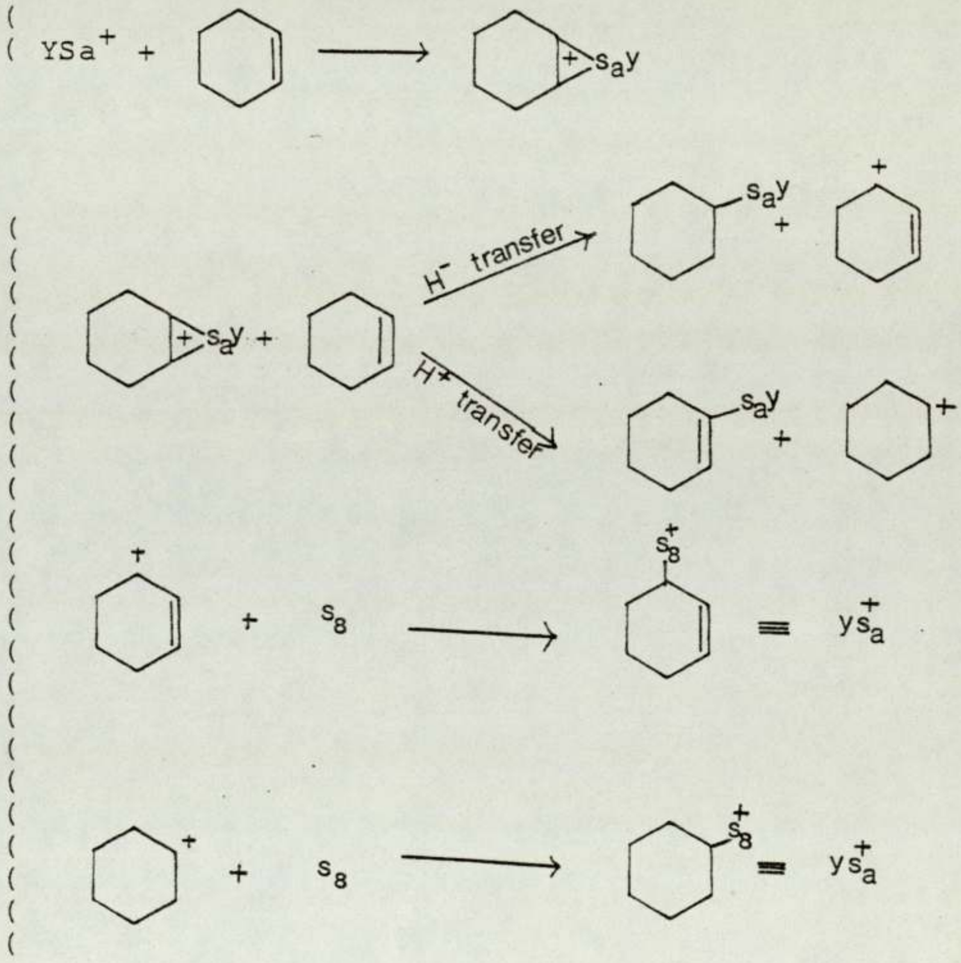
Eq. 1.14

During the kinetic runs x remains constant over the period described by γa and then decreases slightly.

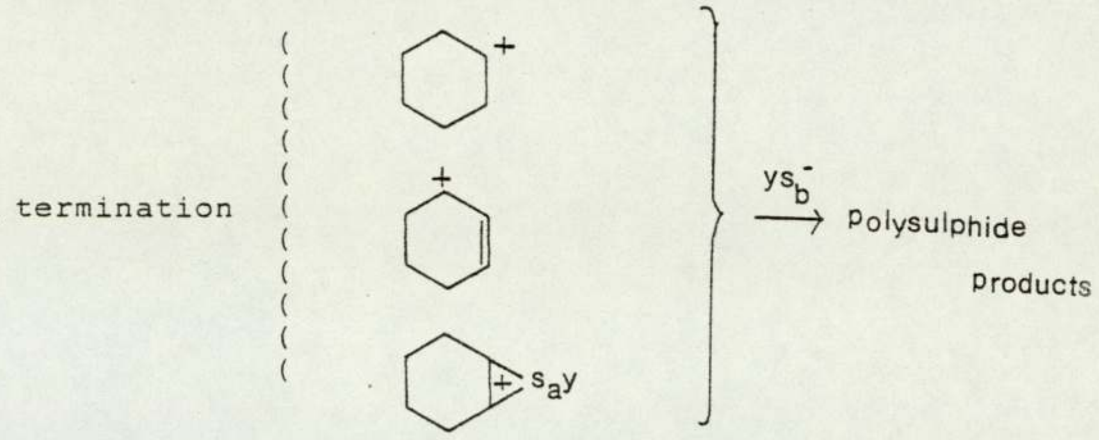
This evidence has led to the replacement of the older mechanism for sulphur-unsaturation reactions, Equation 1.11. It is proposed that the initiation reaction involves heterolytic scission of an S-S bond to give polysulphide and polysulphenium ions. The polysulphenium ions add to an alkene to produce a carbonium ion which either accepts a hydride ion or loses a proton as shown in the set of Equations 1.15.

initiation

Dissociation by unknown mechanism → $YSa^+ + YSb^-$



propagation



Eq. 1.15

The authors$^{(27)}$ proposed the presence of bridged ions as support for an ionic mechanism. The effects of polar solvents on the rate of the reaction of sulphur with cyclohexene also has been proposed as support for the ionic mechanism$^{(29)}$.

The overall reaction of sulphur with cyclohexene increases 50% in rate when the solvent is changed from cyclohexane to nitromethane (dielectric constants increase from 2 to 39). If the two neutral molecules, sulphur and cyclohexene, were to react to produce a transition state with a considerable charge separation, then a solvent effect much larger than this would be expected$^{(30)}$.

However the solvent effect does not lend strong support to an ionic mechanism for sulphur-alkene reactions. The 50% increase in overall rate with a twenty-fold increase in dielectric constant is more consistent with a radical mechanism.

Although a number of studies with indicative evidence may be cited, no conclusive proof for this assumption has been published.

A reference to the similarity of the chemical behaviour of the group VIA elements is appropriate. This similarity became evident since not only oxygen, sulphur and selenium atoms react with the unsaturation, but also tellurium atoms. The reaction of tellurium and of some tellurium compounds with model alkenes and the factors that govern the reactions are discussed in the third chapter in this thesis.

1.7 Role of Tellurium and Selenium in Rubber

The use of sulphur, disulphides and peroxides as vulcanizing agents and similarities in chemistry of selenium and tellurium with sulphur have prompted the examination of selenium and tellurium as substitutes for sulphur. Both these elements have found applications in rubber technology. Thus, selenium and tellurium compounds significantly improve the resistance of rubber compositions to ageing. Tellurium is employed mainly as the element or as tetrakis (diethyldithiocarbamato) tellurium (IV), $Te(d_Etc)_4$. 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 ageing and mechanical properties of the elastomer.

Styrene Butadiene Rubber (SBR), is generally cured either with sulphur or with sulphur liberating compounds. Unless high temperature resistance is necessary, it is common to use sulphur as the curing agent and a sulphur containing compound as an accelerator.

The effect of tellurium and selenium on the ageing of SBR has been studied by the Battelle Memorial Institute(31). They found that a combination of elemental tellurium with tetrakis(diethyldithiocarbamato) selenium(IV) $Se(d_Etc)_4$, as the curing system, gave vulcanizates having superior ageing properties at temperatures in the range 100-150°C. Cures based on $Se(d_Etc)_4$ alone and $Te(d_Etc)_4$ with elemental selenium also gave vulcanizates with promising ageing properties. The effects of selenium and tellurium on the ageing of SBR are given in Table 1.2(31).

The superior high temperature ageing properties afforded by tellurium are indicated by the results on SBR system aged for two days at 150°C and cured with a combination of one part tellurium and two parts $Se(d_Etc)_4$. This vulcanizate had a tensile strength of 119 kg cm^{-2} and elongation of 280%. The sulphur containing control formula had much lower tensile strength and elongation under these ageing conditions.

Ageing studies on nitrile rubbers using a variety of selenium and tellurium compounds in the curing systems have

Curing-accelerator system (g per 100 NR)	Days of ageing at 100°C	100% modulus kgcm^{-2}	300% modulus kgcm^{-2}	tensile strength kgcm^{-2}	elongation at break %	hardness Shore
2S+3benzothiozyl disulphide	0	11.24	86.46	294.55	650	65
	7	-	-	108.96	90	81
0.5S+2TMTD	0	19.68	154.66	196.84	350	67
	7	36.55	-	156.06	220	73
0.5S+Se$(d_Etc)_4$	0	33.74	-	157.47	250	71
	7	62.56	-	178.56	180	76
0.5Se+2Se$(d_Etc)_4$	0	8.43	74.51	293.85	660	63
	7	31.63	201.05	224.25	330	73
2Se$(d_Etc)_4$	0	8.43	68.89	267.14	670	63
	7	20.38	160.28	245.34	400	70
1Se+2Se$(d_Etc)_4$	0	14.06	104.74	253.08	530	65
	7	45.64	-	197.54	240	75
1Se+2Te$(d_Etc)_4$	0	6.32	31.63	207.38	820	62
	7	20.38	137.08	241.12	430	70
1Te+2Te$(d_Etc)_4$	0	6.32	41.47	242.52	730	61
	7	16.16	123.72	292.44	520	67
1Te+2Se$(d_Etc)_4$	0	3.51	15.46	127.94	950	61
	7	11.24	46.39	172.93	720	66

Table 1.2

Basic recipe(%)

SBR	100
EPC black	40
Zinc Oxide	5.0
Stearic acid	1.5

Curing-accelerator system as shown
Cure 30 min. at 150°C

been carried out by the same group. A vulcanizate with one part tellurium and two parts $Se(d_Etc)_4$ gave slightly better properties than the low sulphur formula after ageing at 150°C. The effects of selenium and tellurium on nitrile rubber vulcanizates are shown in Table 1.3

Waggner(32) in his studies showed that $Te(d_Etc)_4$ gives more stable linkages than the disulphide and similar accelerators in the vulcanization of butyl rubber. Further, he emphasised that the discolouration and staining problems in the vulcanizates could be overcome by the use of this tellurium salt. It has also been shown that in combination with thiuram, $Te(d_Etc)_4$ provides superior heat resistant vulcanizates compared with other types of accelerators(33).

The patent filed by Murrill(34) claims that tellurium itself is a vulcanizing agent and somewhat analogous to sulphur in its properties. Furthermore, he showed that nickel and zinc salts of the dithio-acids which act as accelerators are not vulcanizing agents as opposed to the tellurium salts which are accelerators as well as valuable vulcanizing agents.

Recent work on the decomposition of the tetrakis and bis-(diethyldithiocarbamato) tellurium(IV) and (II) in solution(35) under U.V. light showed the formation of tellurium oxide and tetraethylthiuram disulphide. The formation of the disulphide could be the reason for the ability of $Te(d_Etc)_4$ and

Curing-accelerator system (g per 100)	Days of ageing at 100°C	100% modulus kgcm^{-2}	300% modulus kgcm^{-2}	tensile strength kgcm^{-2}	elongation at break %	hardness Shore
0.5S+2TMTD	0	30.22	151.14	151.14	300	69
	4	-	-	89.98	70	80
$2Se(d_Etc)_4$	0	14.76	80.14	177.85	630	66
	4	75.22	-	87.17	110	79
$1Te+2Se(d_Etc)_4$	0	13.35	65.37	185.59	710	66
	4	9.84	-	99.82	110	78

Table 1.3

Basic recipe	Nitrile rubber (Hycar 1001)	100 parts
	SRF black	40
	Zinc oxide	5.0
	Stearic acid	1.0
	Curing-accelerator system	as shown
	Cure 40 min. at 150°C	

$Te(d_Etc)_2$ to act as vulcanizing agents. Interestingly, however, it has been shown$^{(34)}$ that the natural rubbers vulcanized with tellurium salts contain tellurium as well as sulphur in their end products.

Direct vulcanization of rubber to metal surfaces particularly to steel, using tellurium, its alloys or its compounds as couplers, were reported to give vulcanizates with better adhesion$^{(36)}$. Thus 3% sulphur and 0.0425% tellurium compounded rubber is directly bound to steel tyre cords in saturated steam at 90°C, resulting in an improvement of desirable properties.

The effect of tellurium in rubber has been principally in providing improved ageing and mechanical and heat resistance. Of increasing importance in many applications are the physical properties of elastomers at high temperatures. It is possible that, as new polymers are developed, tellurium curing may play a more important role in improving the high temperature mechanical properties of these materials.

1.8 Use of Tellurium in Polymers Other Than Rubber

Tellurium and certain of its compounds have found applications in certain other polymers. In the curing of polysulphide elastomers, a system involving tellurium oxide has been shown to provide improved heat stability at 150°C and improved aromatic fuel resistance$^{(37)}$.

The research work carried out in U.S.A. in 1965(38) showed tellurium tetrachloride and bromide could be used as crosslinking agents for polyvinylchloride (P.V.C.) at 150°C and the crosslinked polymer is used as an electric insulator material.

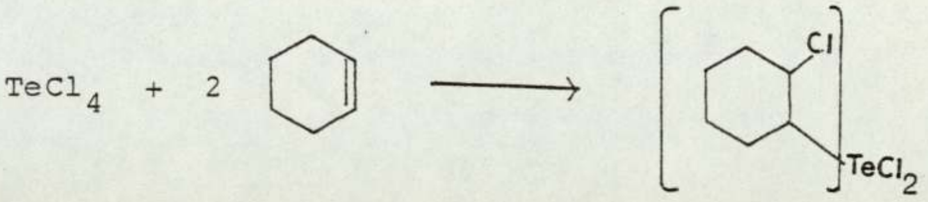
Although there has been a limited amount of work carried out on the technological applications of tellurium in polymers, the information is mostly empirical and very little is known about the chemistry of these applications. Only recently, Abdullaev(39) illustrated some spectroscopic evidence for the effect of tellurium and selenium in nitrile rubber using electron spin resonance and infra-red techniques.

1.9 Use of Model Alkenes with Tellurium Compounds

The literature shows that some tellurium compounds could react with the unsaturation, suggesting the possibility of tellurium compounds acting as crosslinking agents in NR.

The first attempts to add tellurium compounds to double bonds were found to be unsuccessful. Fischer and Eisner(40) observed the formation of elemental tellurium and tarry products when tellurium tetrachloride was treated with cyclohexene and styrene, while Farrar and Gulland(41) reported the lack of reactivity of tellurium tetrachloride with cyclohexene.

Funk and Weiss(42) reported that tellurium tetrachloride would react with the unsaturation under different conditions thus giving bis(2-chlorocyclohexyl)tellurium dichloride and bis(2-chloroethyl)tellurium dichloride with cyclohexene and ethylene, as shown in Equations 1.16 and 1.17 respectively.



Eq. 1.16

$$TeCl_4 + 2CH_2{=}CH_2 \longrightarrow (ClCH_2CH_2)_2TeCl_2$$ Eq. 1.17

Wittig(43) observed different results, finding that even with great excess of cyclohexene only (2-chlorocyclohexyl)-tellurium trichloride was obtained. This observation was also made by Petragnani(44,45), Arpe(46) and Ogawa(47). Thus it appears that several authors reported contradictory results on the same reaction carried out with tellurium tetrachloride with cyclohexene.

However the crystal structure of bis(2-chlorocyclohexyl) tellurium dichloride has been studied(48).

In the molecule itself the tellurium atom has the expected environment with two apical tellurium-chlorine bonds as suggested by McCullough(49). The molecule consists of two equatorial tellurium-carbon bonds with the third equatorial site of a trigonal bipyramid being occupied by the lone pair electrons. In both C_6 rings the tellurium-carbon and adjacent carbon-chlorine bonds are equatorial.

There are two possible configurations for this arrangement; one has the two cyclohexyl groups related (with appropriate rotation about a tellurium-carbon bond) by a mirror plane bisecting the carbon-tellurium-carbon angle, and the other has a two-fold axis bisecting the carbon-tellurium-carbon bond. Only crystals of the first arrangement have been prepared, whose X-ray structure is given in Figure 1.11.

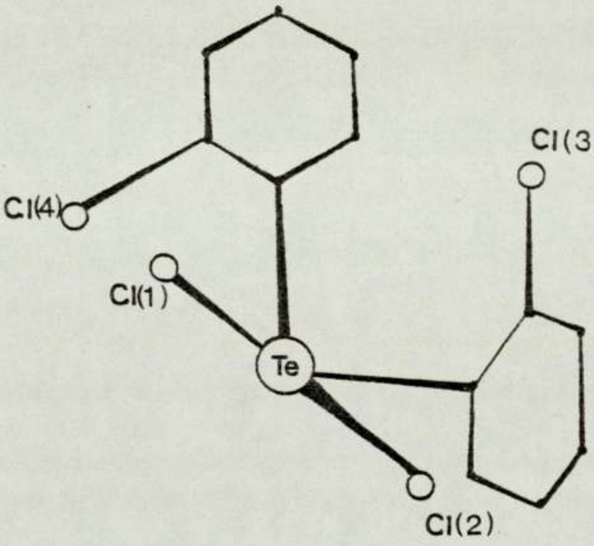


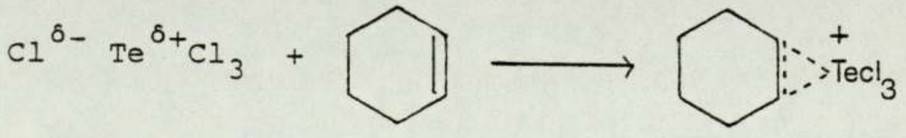
Figure 1.11

A different suggestion was put forward for the reaction of tellurium tetrachloride and the unsaturated hydrocarbons by Michael and Tamary(50). They suggest that tellurium tetrachloride brings about aromatization of various unsaturated cyclohydrocarbons and halocyclohydrocarbons by dehydrogenation and dehydrohalogenation respectively. End products from the particular reactions studied were isolated and identified.

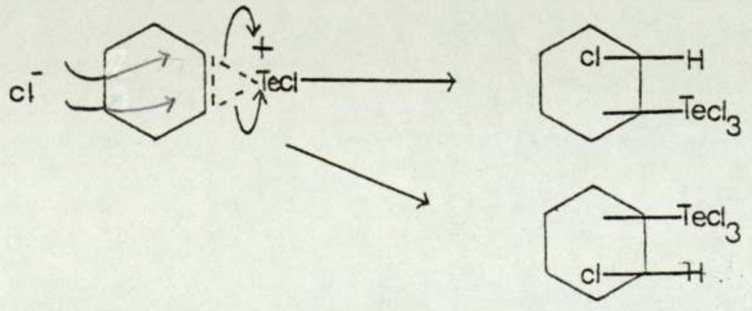
For the reaction of tellurium tetrachloride with cyclohexene in 1:1 molar proportions the formation of 2-chlorocyclohexyltellurium trichloride was observed which was converted to benzene with an additional one molar proportion of tellurium tetrachloride. In other cases such as with 9,10-dihydroanthracene, 3-chlorocyclohexene, 1-methylcyclohexene, decalin, tetralin and limonene, no addition adducts were detected, only the aromatic products being obtained directly.

The end products obtained with different alkenes are tabulated below (Table 1.4).

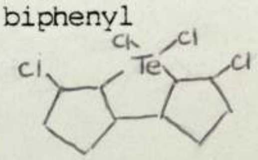
Very little work has been aimed at elucidating the mechanism of these reactions. It was suggested(45) that a cyclic telluronium ion intermediate could probably be involved which suffers a nucleophilic attack by the chloride ions giving rise to a racemic trans-compound as shown in Equations 1.18 and 1.19.



Eq. 1.18



Eq. 1.19

Reagent	Solvent	T°C	Products(a)
9,10-dihydro anthracene	$CHCl_3$,CCl_4 $CHCl_3$,CCl_4	25 76	9,10-dichloro anthracene 9,10-dichloro anthracene
decalin	neat	200	1,2-dichloro napthalene, napthalene and 1 chloro-napthalene
tetralin	neat	200	products as above
2,2' bicyclo hexene	toluene CCl_4 $CHCl_3$	reflux 76 63	biphenyl biphenyl biphenyl
2,2' bicyclo pentene	CCl_4	76	 (b)
cyclohexene(c)	CCl_4,$CHCl_3$, CH_3CN	76	C_6H_6
4-methylcyclo hexene	CCl_4,CH_3CN	76	toluene
cyclohexyl chloride	CCl_4	76	C_6H_6
3 chlorocyclo hexene	CH_3CN CCl_4	25 76	C_6H_6 C_6H_6
cyclohexyl bromide	CCl_4	76	C_6H_6

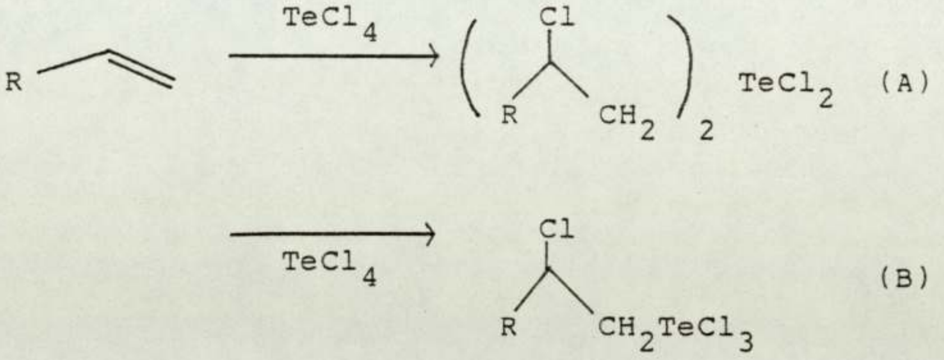
(a) reaction time was 6 hrs

(b) identified by elemental analysis, ^{13}C NMR

(c) a reaction with tellurium tetrabromide gave the same results (much slower)

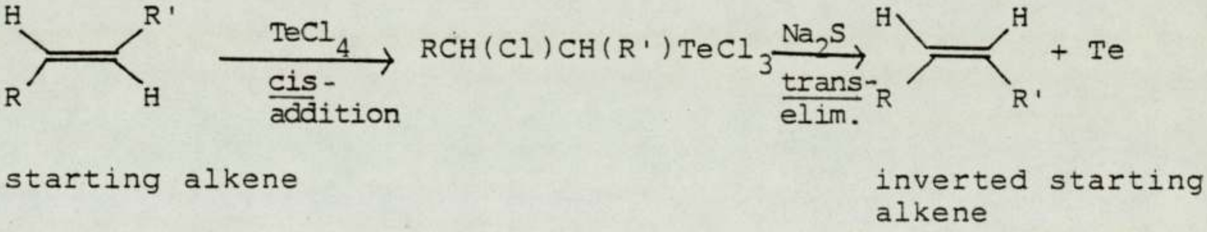
Table 1.4(50) Aromatization of cyclic hydrocarbons and halo-cyclohydrocarbons by tellurium tetrachloride

Recently the steric course of these reactions was studied by Engman(51). In this study the formation of bis(2-chloroalkyl)tellurium dichloride (A) and (2-chloroalkyl) tellurium trichloride (B), with 1:2 and 1:1 ratios of tellurium tetrachloride and alkene, were supposed to go through a <u>cis</u>-addition mechanism (Eq. 1.20).



Eq. 1.20

The trichloride (B) so formed was easily reduced by sodium sulphide to yield the inverted starting alkene and elemental tellurium as shown in Equation 1.21.

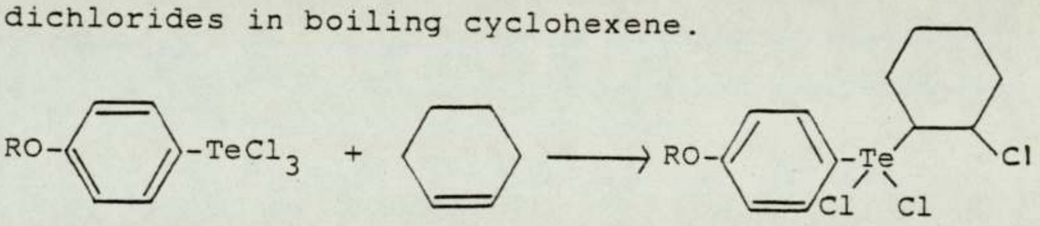


Eq. 1.21

Among the numerous procedures reported for inversion of alkenes, the above is a simple, mild one-pot procedure involving a <u>cis</u>-addition of tellurium tetrachloride followed by a sodium sulphide-induced <u>trans</u>-elimination.

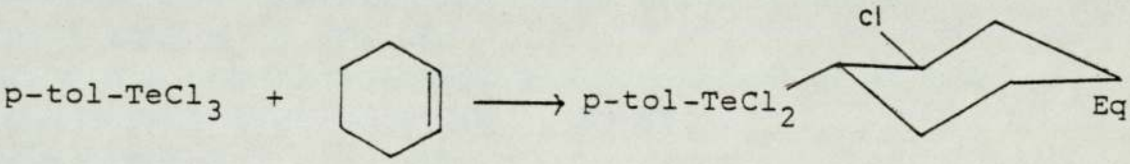
A radical mechanism was also suggested for some of the tellurium tetrachloride, alkene reactions by the same workers(52). The results obtained here ruled out the mechanism previously suggested(45) involving a telluronium ion intermediate as the major pathway. A more or less concerned, stereospecific <u>cis</u>-addition and a competing radical chain reaction have been proposed as the major pathways for the addition of tellurium tetrachloride to alkenes.

The addition of aryltellurium trichlorides to alkenes have also been studied(44). These are less reactive than the tetrachloride, giving (aryl-2-chlorocyclohexyl) tellurium dichlorides in boiling cyclohexene.



Eq.1:22

The crystal structure of (p-tolyl-2-chlorocyclohexyl) dichlorotellurium (IV) has been studied(53). This compound results from the addition of a tellurium-chlorine group across the double bond of a cyclohexene molecule.

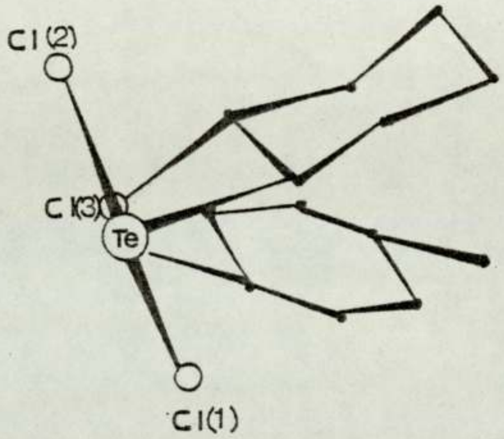


Eq.1.23

This structure has been determined to see if the stereospecificity previously observed for the addition is maintained.

The tellurium atom has the expected configuration for a four coordinated species with an additional lone pair of electrons. It is a trigonal bipyramid with the lone pair at one of the equatorial sites and with Cl(1) and Cl(2) at the apical sites.

Addition across the double bond of cyclohexene appears to be stereo-specific and yields, as previously observed, only the <u>cis</u>-product.



<u>Figure 1.12</u>

The reaction of tellurium dibromide, $TeBr_2$, with cycloheptene in ethanol, however, produced <u>cis</u>-2-ethoxycycloheptyltribromotellurium (IV) and the crystal structure of this compound has been determined by X-ray crystallography and is illustrated in Figure 1.13(54).

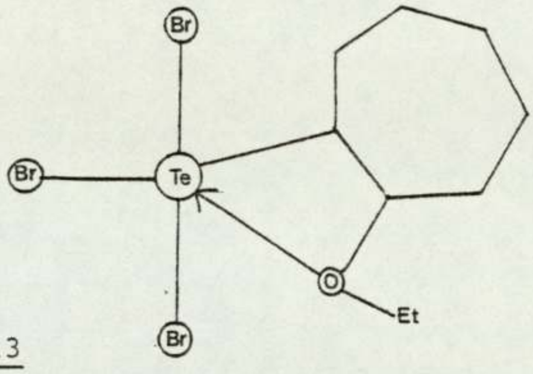
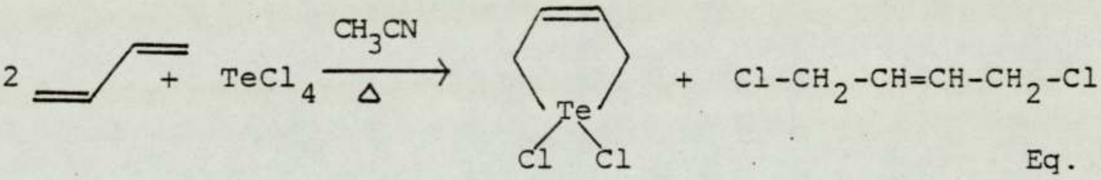


Figure 1.13

The oxygen atom of the ethoxy group acts as an internal Lewis base donating a pair of electrons to the tellurium atom.

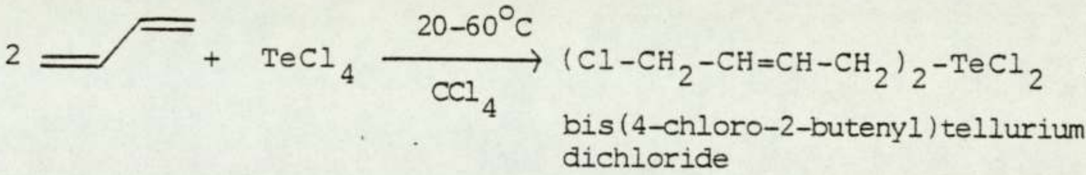
Addition of tellurium tetrachloride to dienes has also been reported(55). In refluxing acetonitrile, tellurium tetrachloride adds reproducibly to butadiene forming 2,5-dihydrotellurophene 1,1-dichloride and 1,4-dichloro-2-butene, according to the Equation 1.24.



Eq. 1.24

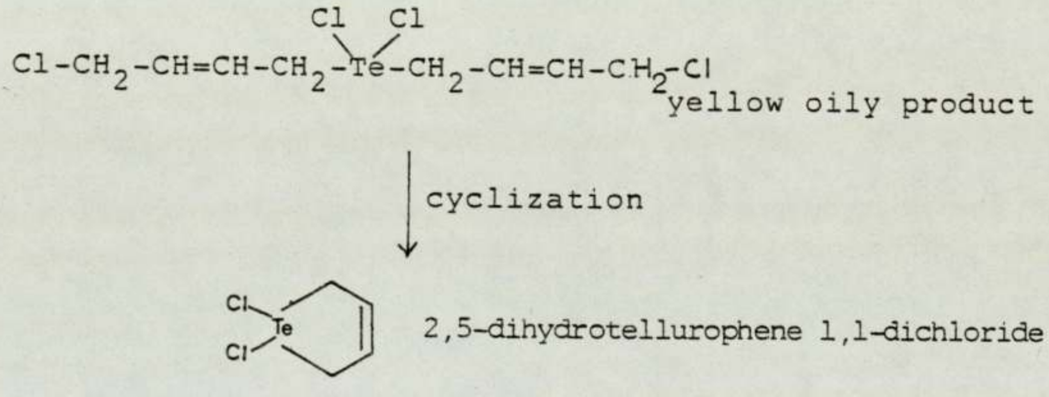
2,5-dihydrotellurophene 1,1-dichloride

The same reaction has earlier been studied by Arpe and Kuckertz(56) under somewhat different reaction conditions. They reported the formation of bis(4-chloro-2-butenyl)tellurium dichloride, when butadiene was introduced into a 30% suspension of tellurium tetrachloride in carbon tetrachloride at 20-60°C. A yellow oily product was separated out (Eq.1.25) crystallised from carbon tetrachloride and characterised by elemental analysis, ^1H NMR and infra-red spectroscopy.



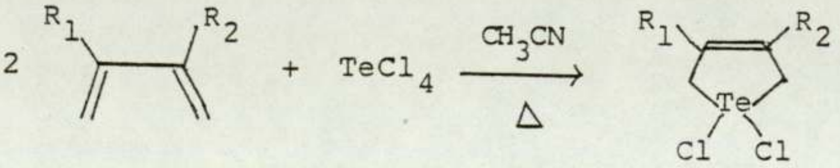
Eq.1.25

Further, it has been found that the product formed is converted into 2,5-dihydrotellurophene when refluxed in toluene for 1 hour. The yellow oily product is therefore likely to be an intermediate on the reaction pathway from butadiene to the heterocyclic tellurium dichloride (Eq. 1.26). The intermediate is probably a hexacoordinated tellurium species (not isolatable), that should be expected to readily undergo a reductive elimination as shown below;



Eq.1.26

Isoprene and 2,3-dimethylbutadiene were also found$^{(55)}$ to react similarly affording the 3-methyl- and the 3,4 dimethyl-substituted 2,5-dihydrotellurophene 1,1-dichloride (Eq. 1.27).



Eq.1.27

where R_1 = H; R_2 = CH_3 for isoprene
and R_1 = CH_3; R_2 = CH_3 for 2,3-dimethyl-butadiene
when R_1 = C_6H_5; R_2 = C_6H_5 no reaction.

The corresponding bromides and iodides were obtained by treatment with bromine and iodine. The fact that the double bond of 2,5-dihydro-tellurophene-1,1-dichloride was inert to treatment with bromine and iodine, was supposed to be due to an interaction, either steric or electronic; with the $TeCl_2$ group i.e., the interaction through space of the tellurium atom, with the double bond pulling the electrons from the π bond and thus rendering it less susceptible to electrophilic attack.

However in all the reactions of tellurium tetrachloride with the unsaturation, the precipitation of small amounts of elemental tellurium is observed.

1.10 Coordination Chemistry of Some Tellurium Compounds

The coordination chemistry of tellurium II and IV compounds is also of interest in this thesis as they could be formed in the NR vulcanization reaction of TMTD and TETD with tellurium tetra-and trihalides.

McCleverty et al(13) showed that the formation of coordinated compounds with zinc in the vulcanization systems containing zinc oxide, TMTD, stearic acid and sulphur are the important precursors in the activation of sulphur in zinc assisted vulcanization.

Tellurium can exhibit oxidation states -II, I, II, IV and VI. Of these IV is the most stable and coordination number six is common.

Tellurium shows the -II state in tellurides, +I in ditellurides and +II in many inorganic and organometallic tellurium compounds with two or four coordinated structures (Figure 1.14).

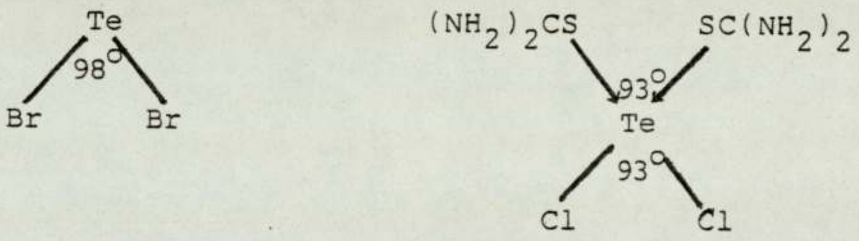
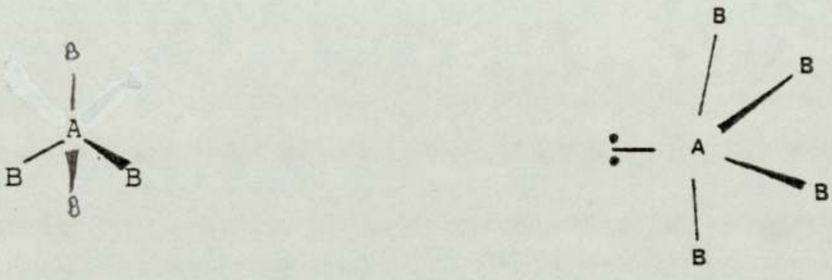


Figure 1.14

The bond angles at the tellurium in all these cases are of the order of 90°. In the four coordinated structure the angles are found to deviate from 90° by only about 3°, resulting in distorted square planar structures. It has also been found that one of these bonds is often much longer than the other three bonds(57). This is presumably due to the use of a single p orbital for bonding at 180° so that if one ligand is strongly bound, the other is less strongly held.

Tellurium in oxidation state (IV), with electronic configuration $[kr]4d^{10}\ 5s^{2}$ can show coordination number of 3, 4, 5 or 6. The presence of the non-bonding electron pair in the compounds of tellurium (IV) will create a distorted tetrahedral shape for compounds with four bonds such as halides, MX_4. The molecules become a ψ-trigonal bipyramid shape with one equatorial position occupied by an unshared pair of electrons.

This is explained by the Valence Shell Electron Pair Repulsion Theory (VSEPR)(58) or Electron Pair Repulsion Theory(59). For a molecule of four atoms AB_4 the shape of the molecule which is most stable is that having the minimum electrostatic repulsion between the electron-dense regions in the bonds in a tetrahedron (Figure 1.15).



a. T_d

b. C_{2v}

Figure 1.15

The angles between B-A-B are $109^{\circ}28'$. The configuration of the molecule is also that of the highest symmetry. A good example is the methane (CH_4) molecule.(Fig 1.15a)

When the central atom is replaced by tellurium IV which has an unshared pair of electrons, the geometry of four and six coordinated tellurium (IV) molecules and ions could be subjected to possible distortion effects arising from the presence of the unshared electron pair. Since the lone pair electron density is concentrated close to the central tellurium atom, it could exert a greater repulsion effect than the bonding pairs, thus causing a distorted molecular shape. (Fig 1.15b)

For four coordinated species whose structures have been investigated, a configuration consistent with a stereochemically active role for the lone pair has been found. Thus, crystalline α-dimethyltellurium dichloride $(CH_3)_2TeCl_2$, and tellurium tetrachloride either in the gas phase$^{(60)}$ or in benzene solution$^{(61)}$ have been described as ψ-trigonal-bipyramidal molecules with the electron pair occupying one of the equatorial positions.

Gillespie and Nyholm$^{(62)}$ have predicted that hexacoordinated complexes of tellurium (IV) should have a distorted structure based on seven coordination with a lone pair of electrons occupying the seventh position. Thus, the structure of trans-tetrachlorobis(tetramethylthiourea)tellurium (IV) was believed to have a distorted octahedral structure as shown in Figure 1.16 with the central tellurium atom being bonded to the two sulphur atoms of the tetramethylthiourea groups and to the four chlorine atoms.

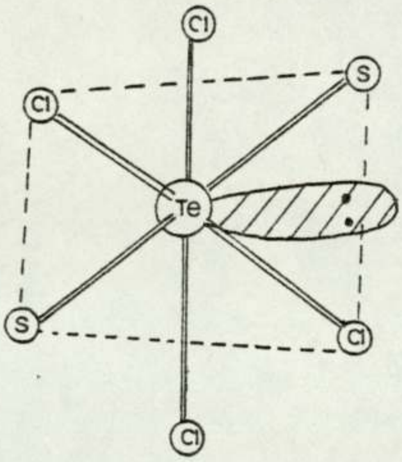


Figure 1.16

The electron pair appears to play no detectable role in determining the disposition of ligand atoms or groups about the central atom and a regular octahedral configuration results. X-ray crystallographic examination provides such evidence for hexachlorotellurates(63,64,65) and hexabromotellurates(64,66) and conformation is afforded by the results of vibrational and Mössbauer spectroscopic investigations.

However, McWhinnie et al(67) studied the ^{125}Te Mössbauer data of the complexes derived from $[TeCl_6]^{2-}$ i.e., $[TeCl_6]^{2-}$ and suggested that the anion $[TeCl_6]^{2-}$ may be distorted towards C_{3v} symmetry from a regular octahedron with O_h symmetry following the results obtained with a much larger cation $[Ph_4As]^+$.

Husebye(64) studied the crystal structure of trans-(tetrabromo) and trans-(tetrachloro)bis(tetramethylthiourea)tellurium (IV) complexes which involves the addition of tetramethylthiourea in methanol to a mixture of tellurium dioxide dissolved in concentrated hydrochloric at room temperature.

The crystal structure of trans-(tetrachloro)bis(tetramethylthiourea)tellurium (IV) as shown in Figure 1.17 is a regular octahedron which is in agreement with the suggestion that the lone pair plays no detectable role in the structure of six coordinated tellurium (IV) compounds.

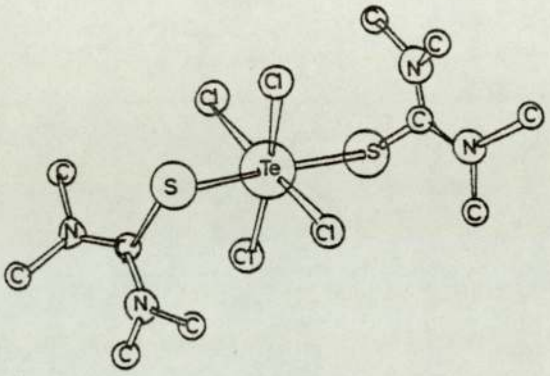


Figure 1.17

The preparative method of trans-(tetrachloro)bis(tetramethylthiourea)tellurium (IV) involves addition of tetramethylthiourea in methanol to a mixture of tellurium oxide dissolved in concentrated hydrochloric acid at room temperature(68). The tetravalent tellurium complex described above, $Te(tMtU)_2Cl_4$, when dissolved in a warm 4N hydrochloric acid-methanol 2:1 mixture, forms a divalent tellurium complex at boiling temperature which in the course of a few hours separates out as dark-red crystals.

Presumably tetramethylthiourea acts as the reducing agent being itself oxidised to the disulphide cation, $(tMtU)^{2+}$, as in Equation 1.28, of which salts are known.

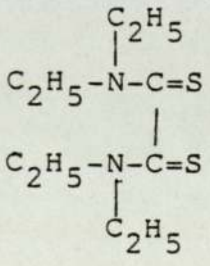
$$\mathrm{Te(IV)} + 6\mathrm{HCl} \longrightarrow (\mathrm{TeCl_6})^{2-} + 2\mathrm{H^+} + 2\mathrm{H_2O}$$

$$[\mathrm{TeCl_6}]^{2-} + (n+2)\mathrm{S{=}C(NR)_2} + 2\mathrm{X^-} \longrightarrow \mathrm{Te^{II}[S{=}C{-}(NR_2)_2]X_2} + [\mathrm{(R_2N)_2C{-}S{-}S{-}C(NR_2)_2}]^{2+} + 4\mathrm{Cl^-} \qquad \text{Eq.1.28}$$

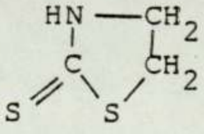
where X=Cl, Br or F

The corresponding iodides, thiocyanates, nitrates and perchlorates can be produced by ionic exchange reactions.

Clark$^{(69,70)}$ studied the reaction of some tellurium (IV) compounds with NNN'N' tetraethyldithio-oxamide(A) and thiazolidine-2-thione (ttz)(B) and suggested that the compounds formed may have a structure based on a coordination number of six for the tellurium (IV).

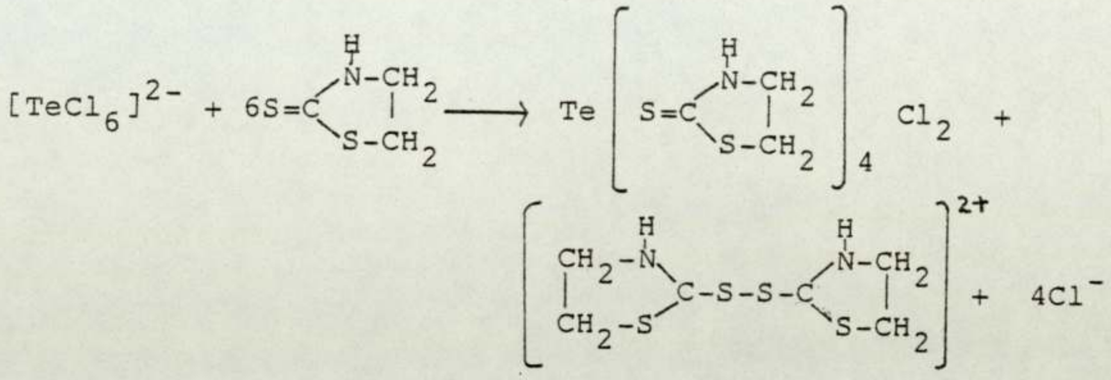


tetraethyldithio-oxamide(A)



thiazolidine-2-thione(B)

The tellurium (IV) complexes were prepared by reacting tellurium tetrahalides with A and B in dry methanol media and it is possible to effect the change in oxidation state of tellurium (IV) to tellurium (II) and oxidation of ligand 0 to +II by using aqueous acid media and varying the ratio of tellurium:ligand (Eq. 1.29).



Eq.1.29

Al-Turaihi$^{(71)}$ listed a number of tellurium (IV) compounds as shown in Figures 1.18 and 1.19 using NNN'N' tetramethyldithio-oxamide and thiazolidine-2-thione as ligands respectively.

In the complex $CH_3TeSC(NMe_2)_2Cl_3$, the tellurium (IV) atom is five coordinated$^{(72)}$ and this compound is said to have a square pyramidal structure, as shown in Figure 1.20.

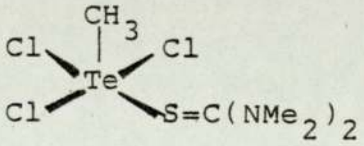


Figure 1.20 where $S{=}C(NMe_2)_2$ is tetramethylthiourea

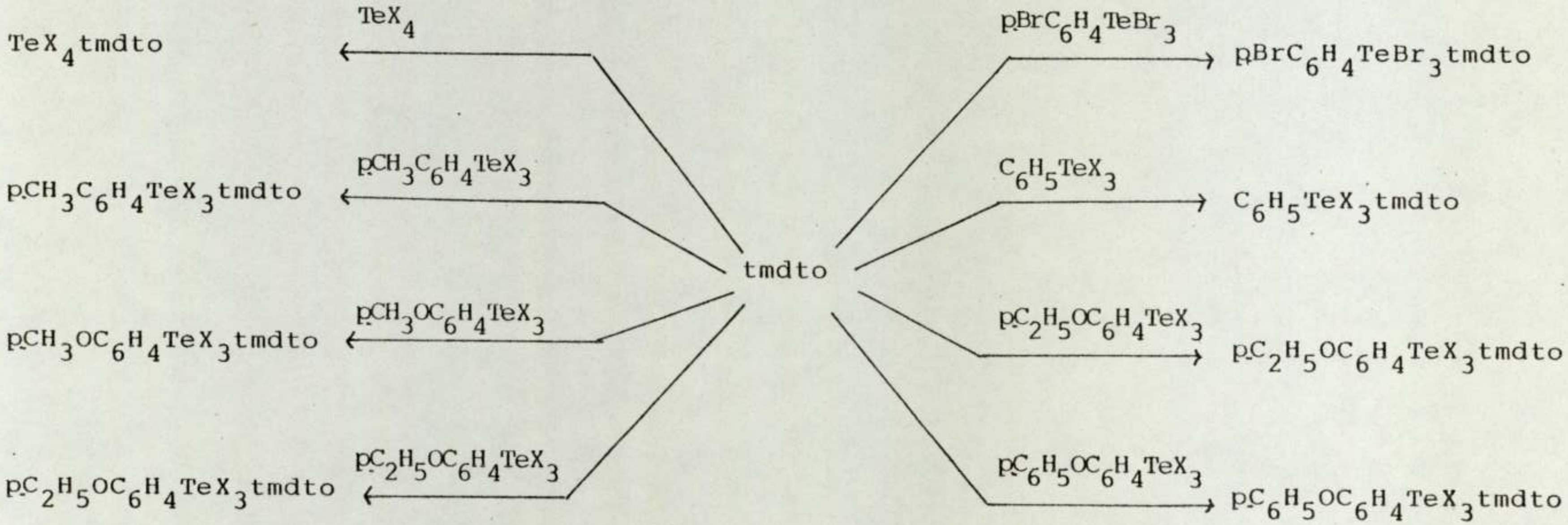
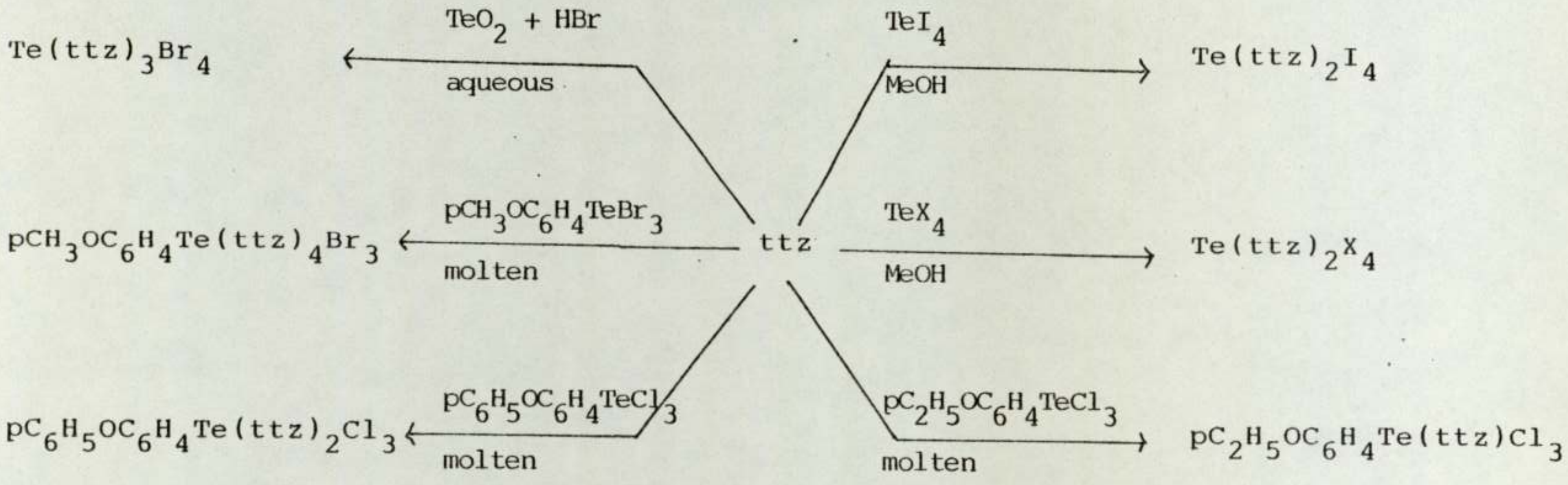


Figure 1.18

where tmdto is NNN'N'tetramethyldithio-oxamide
and X=Cl, Br



where ttz is thiazolidine-2-thione
and X=Cl, Br

Figure 1.19

Tellurium (IV) complexes with higher coordination number have also been reported(73,74,75).

Tetrakis(diethyldithiocarbamato)tellurium(IV) forms flat prismatic orange crystals where the crowding around tellurium is large and steric factors may also play a role. The configuration around the central tellurium atom is slightly distorted from dodecahedral D_{2d} symmetry. This corresponds to the energetically most favourable distribution of the eight bonding electron pairs in the valence shell of tellurium(76,77). Thus the lone pair is stereochemically inert in the sense that it does not occupy a position in the coordination dodecahedron. This can be visualized as two interleaving planar trapezoids at right angles to each other. The average coordination within a trapezoid for tetrakis(diethyldithiocarbamato)tellurium(IV) is shown in Figure 1.21.

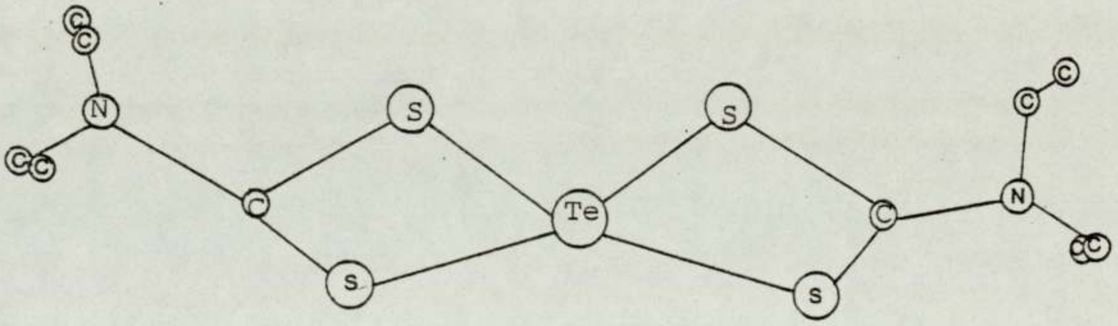


Figure 1.21

Several explanations have been given for the distorted structure, one delocalizing the lone pair mainly on the ligands (78,79), another using three-centre four electron description (80) and a third explaining it in terms of steric repulsion (81).

CHAPTER TWO

EXPERIMENTAL

2.1 Experimental (Generally Used Techniques)

All the general physical methods involved in characterizing the complexes, together with the methods used in rubber technology are gathered in this chapter.

2.2 Chemicals

All the chemicals used in complex synthesis and rubber technology were obtained from commercial sources and "Analar R" grades were used wherever possible.

2.3 Solvents

In general, all the solvents obtained from commercial sources were distilled prior to use and kept over molecular sieves (Linde 3n) and if necessary were purified by literature methods e.g., nitromethane$^{(82)}$, acetonitrile$^{(83)}$ and N,N-dimethylformamide$^{(84)}$. Pyridine was dried and distilled from barium oxide.

2.4 Techniques Used in Complex Characterization

2.4.1 Infra-red Spectra

The infra-red spectra in the range 4000-250 cm^{-1} were recorded on a Perkin Elmer 457 spectrophotometer. Solid state samples were examined as KBr discs or Nujol mulls supported between KBr plates. Far infra-red spectra were recorded for Nujol mulls in caesium iodide or polyethene plate supports in the region of 400-200 cm^{-1}.

2.4.2 Electronic Spectra

Electronic absorption spectra in the ultra-violet and visible region were obtained on Unicam and SP800B instruments using matched silica cells.

2.4.3 Mass Spectra

The mass spectra were recorded on an AEI MS9 mass spectrometer at an ionizing voltage of 70 eV.

2.4.4 Elemental Analysis

Micro-analysis for carbon, hydrogen, nitrogen, halogen, sulphur and phosphorus were carried out by micro-analytical laboratories of the Chemistry Department of Aston University.

First row transition metal analysis was carried out by atomic absorption spectroscopy and the tellurium analysis by a volumetric titration(85).

2.4.5 Electron Spin Resonance (ESR) Spectra

ESR spectra were determined with a Jeol PE-1X electron spin resonance spectrometer operating in the X-band and calibrated with a standard manganese (II) (line 4g=1.981; separation of lines 3 and 4=86.9 G) sample diluted with magnesium oxide. Spectra were run at room temperature.

2.4.6 Magnetic Susceptibility Measurements

Paramagnetic susceptibilities were measured by the Gouy method at room temperature. A semi-micro balance (Stanton Instruments Ltd) was used in conjunction with an electromagnet. The tube constants α and β were determined using $HgCo(CNS)_4$ as calibrant and taking its specific susceptibility $\chi g=16.44 \times 10^{-6}$ c.g.s.units at 20°C.

Magnetic susceptibilities were calculated using the standard equation;

$$10^6\chi = \frac{\alpha + \beta f'}{w}$$

where α = 0.016 mg

β = 0.209 mg

f'= effective force on the sample in mg

w = weight of the sample in g

Diamagnetic corrections were made from Pascals constants as listed in Figgis and Lewis(86).

Effective magnetic moments (μ_{eff}) were calculated using the following formula;

$$\mu_{eff} = 2.83(\chi'_M T)^{\frac{1}{2}}$$

where χ'_M is the molar susceptibility corrected for diamagnetism and T is the absolute temperature.

2.4.7 Conductivity

Molar conductivities of freshly prepared solutions were determined with Mullard conductivity bridges, using standard conductivity cell of the type E7591B with a cell constant of 1.46 with bright platinum plates.

2.4.8 Nuclear Magnetic Resonance Spectra

^1H nuclear magnetic resonance spectra, at 100 MHz were measured in $(CD_3)_2SO$ using either a Perkin Elmer R14 or Jeol FX 90Q instrument. The spectra were referenced to the internal standard-tetramethylsilane.

^{13}C NMR spectra were obtained using a Jeol FX90Q instrument at the University of Aston.

2.4.9 Gas Liquid Chromatography

The GLC analyses were carried out with Pye-Unicam equipment.

2.4.10 Melting Points

The melting points of all the complexes synthesised were determined using a Gallenkamp electrically heated melting point apparatus.

2.4.11 Mössbauer Spectroscopy

Mössbauer data in Chapters 3 and 4 were obtained at 77K using ^{125}Sb/Rh source, at the University of Birmingham and the Mössbauer data in Chapter 5 were obtained at 4K using the equipment as described in reference (87). These data were obtained at Simon Fraser University, Burnaby, B.C., Canada.

The conversion of ^{125}Sb/Rh to ^{125}I/Cu was made by adding +0.15 mm s^{-1}.

2.5 Techniques Used in Characterization of Rubber

2.5.1 Monsanto Rheographs

A curve obtained from a Monsanto Rheometer provides information regarding the curing behaviour and therefore it is necessary to mention briefly the theoretical aspects.

The Monsanto oscillating disc rheometer consists of a biconical disc surrounded by the compound specimen contained in a cavity. The temperature of the cavity, specimen and the disc is maintained at a desired level with an accuracy of ± 0.5°C by means of electrical heating.

The cavity is made up of two halves which open and close pneumatically. A motor-driven eccentric oscillates the shaft of the biconical disc sinusoidally. A torque transducer is recorded on a chart. In a typical Monsanto rheograph for a natural rubber stock, there is an initial drop in torque due to the decrease in the viscosity of the rubber as its temperature rises. This is followed by an induction period after which the torque increases steadily showing that curing is taking place. After a certain period of time, the torque reaches a maximum. In certain cases this maximum can further increase or decrease after some time, indicating a secondary vulcanization or a reversion respectively. Reversion can be caused by the breaking down of crosslinks.

A typical Rheometer trace obtained with a Monsanto oscillating disc Rheometer is shown below in Figure 2.1;

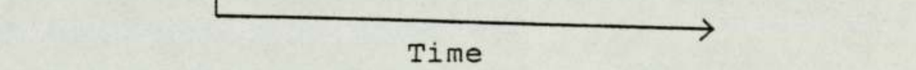


Figure 2.1

2.5.2 Crosslink Density

The physical crosslink density was assessed with the help of the swelling properties of the vulcanizates.

The samples cut from the vulcanizates were weighed and immersed in toluene at 25°C for 24 hours. The samples were removed after 24 hours and wiped with a filter paper and reweighed. Samples were deswollen at 50°C to a constant weight to calculate the weight of the toluene absorbed.

The physical crosslink density of the vulcanizates cured was determined using the Flory Rehner equation(88);

$$\frac{1}{M} = \frac{-V + V^2\mu + 2.303\log(1-V_r)}{\rho_r V_o (V_r^{\frac{1}{3}} - V_{r/2})}$$

where V = effective number of physical crosslinked units (mol g^{-1} of rubber)

V_r = volume fraction of rubber in swollen vulcanizate

μ = solvent polymer interaction parameter (Huggins interaction constant)

ρ_r = density of rubber

V_o = molar volume of solvent

2.5.3 Measurement of Tensile Properties

The tensile strength, elongation at break, modulus at 100 and 300 percentages were determined using a K301 type tensometer.

CHAPTER THREE

THE CHEMISTRY OF TELLURIUM APPLIED TO RUBBER

3.1 Introduction

The general introduction in Chapter One indicates that the model alkenes which were used successfully with sulphur and its compounds in the investigation of crosslinking mechanisms may react with tellurium and tellurium compounds. Being a member of the sulphur family, this ability to react with the unsaturation should be taken into consideration in the study of tellurium and its compounds with NR. According to the literature, tellurium is known to play a useful role in rubber technology even though the mode of action is still a mystery.

This chapter is concerned with the attempted reactions of elemental tellurium with model alkenes and the reactions of tellurium compounds with model alkenes, NR solutions and solid NR.

3.2 Experimental

3.2.1 Attempts to React Elemental Tellurium with Unsaturated Hydrocarbons

Preliminary investigations were carried out as follows using elemental tellurium with cyclohexene and 2-methyl-2-pentene.

a. A mixture of cyclohexene (10.4 cm^3, 10 mmol) and tellurium powder (1.2 g) were added to a 2-neck flask and heated with stirring under dry nitrogen for 24 hours at 100°C. The filtrate was examined by g.l.c. and contained only unreacted alkene.

b. 2-methyl-2-pentene (10.6 cm^3, 10 mmol) and tellurium powder (1.2 g) were added to a thin pyrex tube, which was then sealed and immersed in a metal cylinder for protection. This was then heated for 8 hours at 140°C using an oil bath. The product was cooled in liquid nitrogen for 1 hour, tellurium which had separated was filtered off and the filtrate was examined by g.l.c. and showed unchanged 2-methyl-2-pentene.

The following Table 3.1 summarises the experiments carried out with tellurium powder and cyclohexene/2-methyl-2-pentene in different conditions together with the observations made.

3.2.2 Reaction of Tellurium Tetrachloride with Unsaturated Hydrocarbons

All the reactions with tellurium tetrachloride were carried out in dry solvents under dry nitrogen.

The first few attempts to react tellurium tetrachloride with cyclohexene and 2-methyl-2-pentene were unsuccessful. Black tarry products were observed when the reactions were carried out at room temperature, in different solvents. The only

alkene*	temp (^{o}C)	solvent	reaction time (hr)	observation
cyclohexene ($10.4\ cm^3$)	r.t.	acetonitrile	24	no change in alkene
	140	acetonitrile	8	
	r.t.	chloroform	24	no change in alkene
	140	chloroform	8	
2-methyl-2-pentene $10.6\ cm^3$)	r.t.	acetonitrile	24	no change in alkene
	140	acetonitrile	8	
	r.t.	chloroform	24	no change in alkene
	140	chloroform	8	

* reacted with 1.2 g of tellurium powder

Table 3.1

product that could be isolated was obtained in the following experiment.

Cyclohexene (41.6 cm^3, 40 m mol) was added to a round bottom flask containing acetonitrile (50 cm^3). The flask was covered with ice and the mixture was stirred for about 10 minutes. Tellurium tetrachloride (5.38 g, 20 m mol) was then added immediately to the cold cyclohexene/acetonitrile mixture. Stirring was continued for another 30 minutes. The pale yellow precipitate obtained was filtered off, vacuum dried, recrystallised from acetonitrile and analysed.

Found	C, 20.8; H, 2.90; Cl, 39.8; Te, 35.9%
$C_6H_{10}Cl_4Te$ requires	C, 20.5; H, 2.80; Cl, 40.4; Te, 36.4%
$C_{12}H_{20}Cl_4Te$ requires	C, 33.2; H, 4.60; Cl, 32.7; Te, 29.4%

Tables 3.2 and 3.3 indicate the attempts to react tellurium tetrachloride with cyclohexene and 2-methyl-2-pentene respectively in differing conditions, together with the observations made.

The tellurium precipitated in most of the reactions was filtered off and the filtrates were centrifuged to separate any fine powder left after initial filtration. The filtrates were then subjected to g.l.c. analysis.

alkene*	temp^{o}C	solvent	observations
cyclohexene (20.8 cm^{3},0 mmol)	r.t.	chloroform,ethanol, carbontetrachloride, neat	Tarry products immediately after the mixing of the two reactants.
	0	chloroform	A yellow precipitate formed which turned black after few minutes.
	-50	chloroform	No reaction below -10^{o}C. A pale yellow precipitate formed with the temperature increase to room temperature.
	r.t.	acetonitrile	A yellow precipitate formed initially which turned black after few minutes.
	0	acetonitrile**	A yellow precipitate formed which was filtered after about 45 minutes and analysed.
	0	tetrahydrofuran	No precipitation of tellurium or formation of tarry products was observed. The yellow oily material formed was difficult to isolate.

* alkene was reacted with tellurium tetrachloride (5.38 g, 20 m mol)
** the reaction was also carried out with cyclohexene (41.6 g, 40 m mol)

Table 3.2

alkene*	temp°C	solvent	observations
2-methyl-2-pentene (10.6 cm^3,10 mmol)	r.t.	chloroform, ethanol, acetonitrile	Black tarry products immediately after mixing the two components.
	0	chloroform	The reaction mixture turned black after few minutes.
	-50	chloroform, acetonitrile	No reaction below -15°C but when the temperature increased the mixture turned black.
	0	acetonitrile, tetrahydrofuran	No precipitation of tellurium was seen immediately but after about ½ hr the solution gradually turned black.

* alkene was reacted with tellurium tetrachloride (5.38 g, 20 m mol)

Table 3.3

The reaction of 2-methyl-2-pentene with tellurium tetrachloride at 0°C was repeated in the presence of anhydrous aluminium chloride in order to increase the polarity of the tellurium tetrachloride. A yellow precipitate was observed initially but the solution turned black after some time as in the other reactions. A suggestion that the filtrates obtained in these reactions contained chlorinated alkenes was confirmed by comparing the peaks obtained from chlorinated cyclohexene and 2-methyl-2-pentene by g.l.c. with peaks obtained from the filtrates.

3.2.3 Reaction of Tellurium Tetrachloride and Tetrabromide with Natural Rubber Solutions

SMR 10 (Standard Malaysian Rubber) 10 g was masticated in a two-roll mill and was dissolved in 100 cm^3 of dry chloroform to make a 10% natural rubber solution. Tellurium tetrachloride (5.38 g, 20 m mol) was dissolved in 50 cm^3 of dry chloroform under dry nitrogen and was added to the natural rubber solution. The mixture was stirred vigorously at 30°C for 3 hours. A black gel formed which was washed several times with dry chloroform and vacuum dried. The same reaction was repeated with tellurium tetrabromide, but was found to be slower.

The black brittle material obtained upon drying was cooled in dry ice in a sample bottle and was used in a KBr disc for infra-red analysis. The sample cooled in this was easily ground to make KBr discs.

A tellurium analysis was done for this black gel using the titrimetric method(85) described in the literature.

The black gel was treated with concentrated nitric acid in order to remove any elemental tellurium that has not reacted with NR. This resulted in a yellow precipitate, whose infra-red spectrum was recorded as before. The percentage tellurium and the other elements present in the black gel obtained with tetrachloride are shown below.

Elemental analyses for the black gel with tellurium tetrachloride.

C, 30.8; H, 3.2; Cl, 27.2; Te, 37.3%

The elemental analyses for the yellow material obtained after treating the black gel with concentrated nitric are as follows:

C, 38.7; H, 3.8; Cl, 8.9; Te, 23.8%

3.2.4 Reaction with Styrene Butadiene Rubber (SBR)

The method described above was used in the reaction of tellurium tetrachloride with SBR. The unsaturation was reduced due to the phenyl substituent and gelation was found to be somewhat slower than in NR.

3.2.5 Reaction with Acrylonitrile-butadiene Rubber (Nitrile Rubber)

10% nitrile rubber solution in chloroform was added to a 10% tellurium tetrachloride solution in chloroform as before while stirring at 30°C. There was no sign of tellurium precipitation or a black gel formation even after 24 hours stirring. A portion of the yellow emulsion formed was poured into a beaker and the solvent was evaporated by passing dry nitrogen. The thin film formed was examined by infrared spectroscopy.

3.2.6 Reaction with Solid Natural Rubber

3.2.6.1 Crosslinking with Tellurium and its Compounds Only

These tests were carried out in a Shawbury curometer using the vulcanizates shown in Table 3.4. The amount of vulcanizate used in this curometer is very little compared with the quantity required in the Monsanto rheometer. Hence failure of the rubber to crosslink does not leave a sticky unvulcanized product, so it can easily be removed from the curometer.

Sample	tellurium/tellurium compound
Al	tellurium powder
Bl	tellurium tetrachloride
Cl	tellurium tetrabromide
Dl	(p-ethoxyphenyl)tellurium trichloride
El	bis(N-Ndiethyldithiocarbamato)tellurium(II)
Fl	bis(N-Ndimethyldithiocarbamato)tellurium(II)
Gl	tetrakis(N-Ndiethyldithiobarbamato)tellurrium(IV)
Hl	tellurium oxide
Il	fresh tellurium powder
Jl	sulphur (control)

Table 3.4

The rubber used in these experiments was purified using the following method.

The rubber was masticated in a two-roll mill and rolled in aluminium foil after which it was extracted with acetone in a soxhlet extractor for 24 hours. The purified natural rubber so obtained was dried in a vacuum oven for 30 minutes before use.

All the compounds (3 g each) in Table 3.4 were milled with 100 g of purified natural rubber and used in the preheated Shawbury curometer at 160°C.

The bis(diethyldithiocarbamato)tellurium(II) and bis(dimethyldithiocarbamato)tellurium(II) used in these experiments were prepared by refluxing tellurium powder (3.81 g) with the corresponding thiuram disulphide (30 m mol) in xylene for 2 hours under nitrogen.

M.P. of bis(diethyldithiocarbamato)tellurium(II) - (red crystals) 165°C

M.P. of bis(dimethyldithiocarbamato)tellurium(II) - (orange precipitate) 248°C

3.2.6.2 Crosslinking with Sulphur Containing Compounds, Tetramethylthiuram Disulphide (TMTD) and Tetraethylthiuram Disulphide (TETD)

A second set of experiments with solid natural rubber and

parts per 100 NR	A2	B2	C2	D2	E2	F2	G2	H2	I2	J2	K2	L2
NR	100	100	100	100	100	100	100	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5
TMTD	3.0	-	3.0	3.0	3.0	3.0	3.0	3.0	3.0	-	-	-
TETD	-	3.0	-	-	-	-	-	-	-	3.0	3.0	3.0
Te	-	-	1.5	-	-	-	-	-	-	1.5	-	-
$TeCl_4$	-	-	-	1.5	-	-	-	-	-	-	1.5	-
$TeBr_4$	-	-	-	-	1.5	-	-	-	-	-	-	-
$Te(d_Etc)_4$	-	-	-	-	-	1.5	-	-	-	-	-	-
$Te(d_Etc)_2$	-	-	-	-	-	-	1.5	-	-	-	-	1.5
$Te(d_Mtc)_2$	-	-	-	-	-	-	-	1.5	-	-	-	-
TeO_2	-	-	-	-	-	-	-	-	1.5	-	-	-

Table 3.5

TMTD 3g .01 mol

$TeCl_4$ 1.5 .005 mol

and tellurium compounds was carried out using tetramethylthiuram disulphide (TMTD) and tetraethylthiuram disulphide (TETD) together with other essential ingredients for effective vulcanization as shown in Table 3.5.

Another set of Monsanto rheographs was obtained with different percentages of tellurium tetrachloride as shown in Table 3.6, in order to obtain the percentage of tellurium tetrachloride to give the highest crosslink density and better enhanced acceleration.

	A3	B3	C3	D3	E3
NR	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.5	2.5	2.5	2.5	2.5
TMTD	3.0	3.0	3.0	3.0	3.0
$TeCl_4$	1.0	2.0	2.5	3.0	4.0

Table 3.6

In the fourth set of experiments, different proportions of the complex derived from tellurium tetrachloride and TMTD, prepared as described in Chapter Four, were used as tabulated in Table 3.7.

The formulations A2, C2, D2, E2, F2, G2 and H2 in Table 3.5 were also milled with 20% carbon black to observe the effect of fillers on the vulcanizates containing tellurium compounds.

Parts per 100 NR	A4	B4	C4	D4	E4
NR	100	100	100	100	100
ZnO	5.0	5.0	5.0	5.0	5.0
Stearic acid	2.5	2.5	2.5	2.5	2.5
$TeCl_4$/TMTD complex	4.0	5.0	6.0	7.0	4.0
TMTD	-	-	-	-	3.0

Table 3.7

3.3 Results

The Mössbauer spectrum of the black gel obtained with tellurium tetrachloride and natural rubber is shown in Figure 3.1.

The infra-red spectra of typical NR and the black gel obtained with tellurium tetrabromide are shown in Figure 3.2a and 3.2b respectively.

The Monsanto rheographs obtained with TMTD and tellurium and its compounds are illustrated in Figures 3.3a - 3.3e.

Figure 3.4 and Figure 3.5 show the infra-red spectra of the precipitates obtained on extracting the vulcanizates containing tellurium and TMTD, and TMTD respectively.

Log(R_{max} - R_t) vs. t graphs, where R_{max} and R_t are the maximum torque and the torque at time t, for the samples A2, C2, D2 and E2 are illustrated in Figure 3.6a and for samples H2, G2 and A2 are illustrated in Figure 3.6b. From these plots, two parameters of the kinetics of crosslink formation were obtained. They are the 'delay time' for the induction period t and the first order rate constant k_2, which is the negative slope of the straight line obtained after time t. R_{max} gives a measure of the ultimate crosslink density.

The rate constants and the induction periods for the vulcanizates are tabulated in Table 3.8.

Sample	R_{max}	Rate constant k* (min^{-1})	t(induction period) (min)
A2	41.0	0.2741	6.0
C2	73.4	0.2132	5.2
D2	52.5	0.3198	4.0
E2	48.2	0.1515	4.2
G2	58.5	0.0690	6.4
H2	59.1	0.0511	7.3

* $k=2.303 \times \log_{10}(R_{max} - R_t)/t$

Table 3.8

The heat stability of TMTD, TETD, tellurium and tellurium compound containing samples (together with TMTD) at 180°C are shown in Monsanto rheographs illustrated in Figures 3.7a and 3.7b.

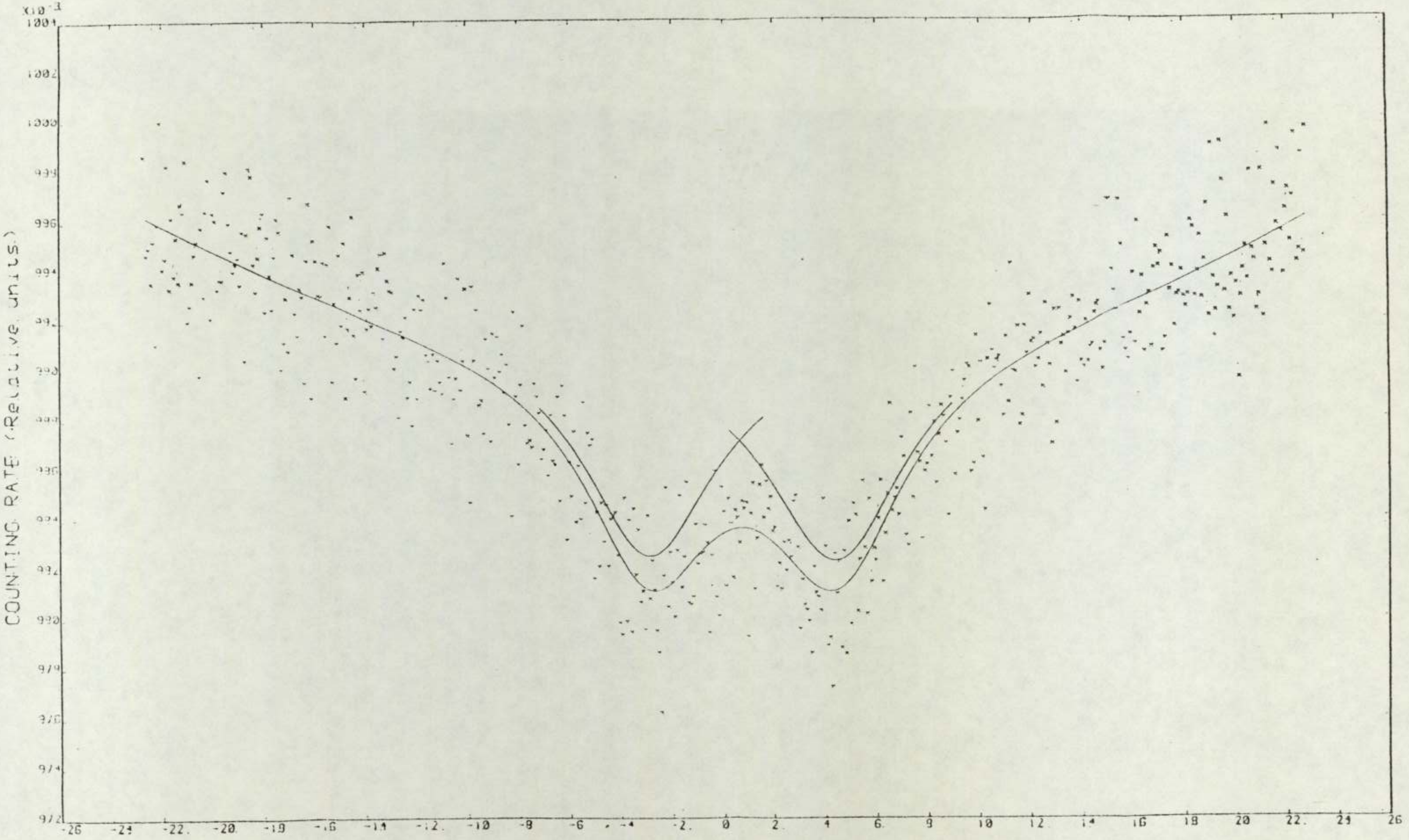


Figure 3.1 Mössbauer spectrum of $TeCl_4$ and natural rubber with respect to $^{125}Sb/Rh$ source at 77K.

Typical Rubber Spectra

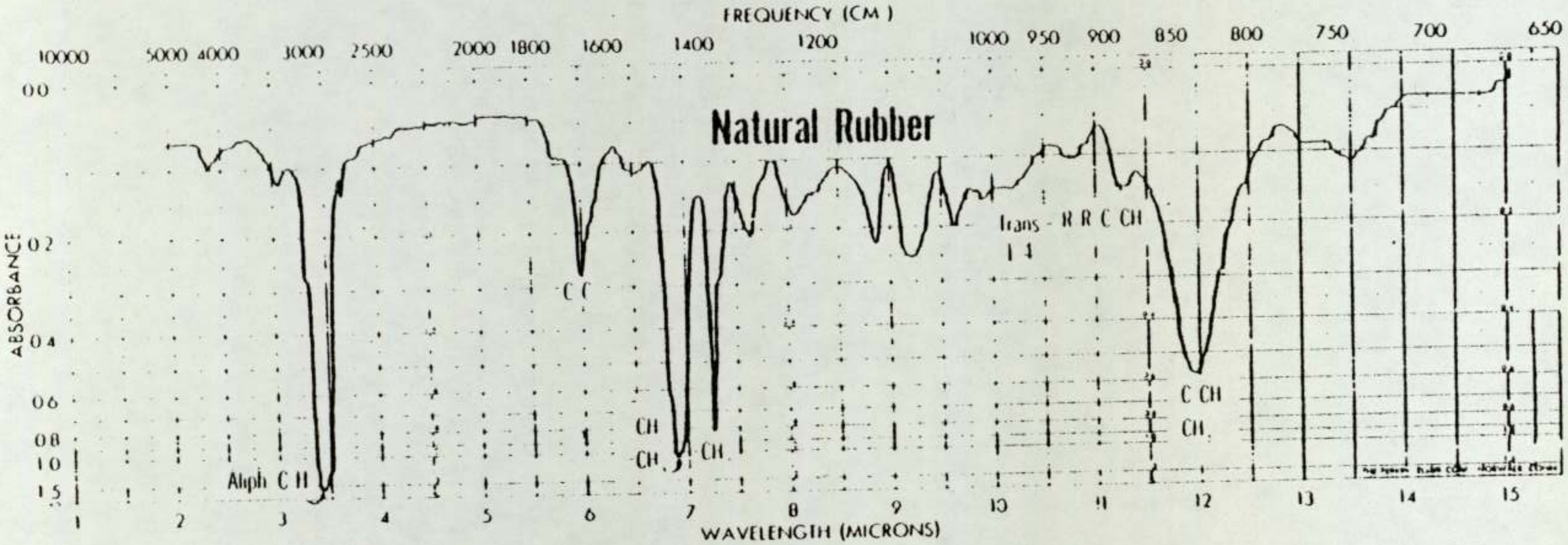


Fig. 3·2a

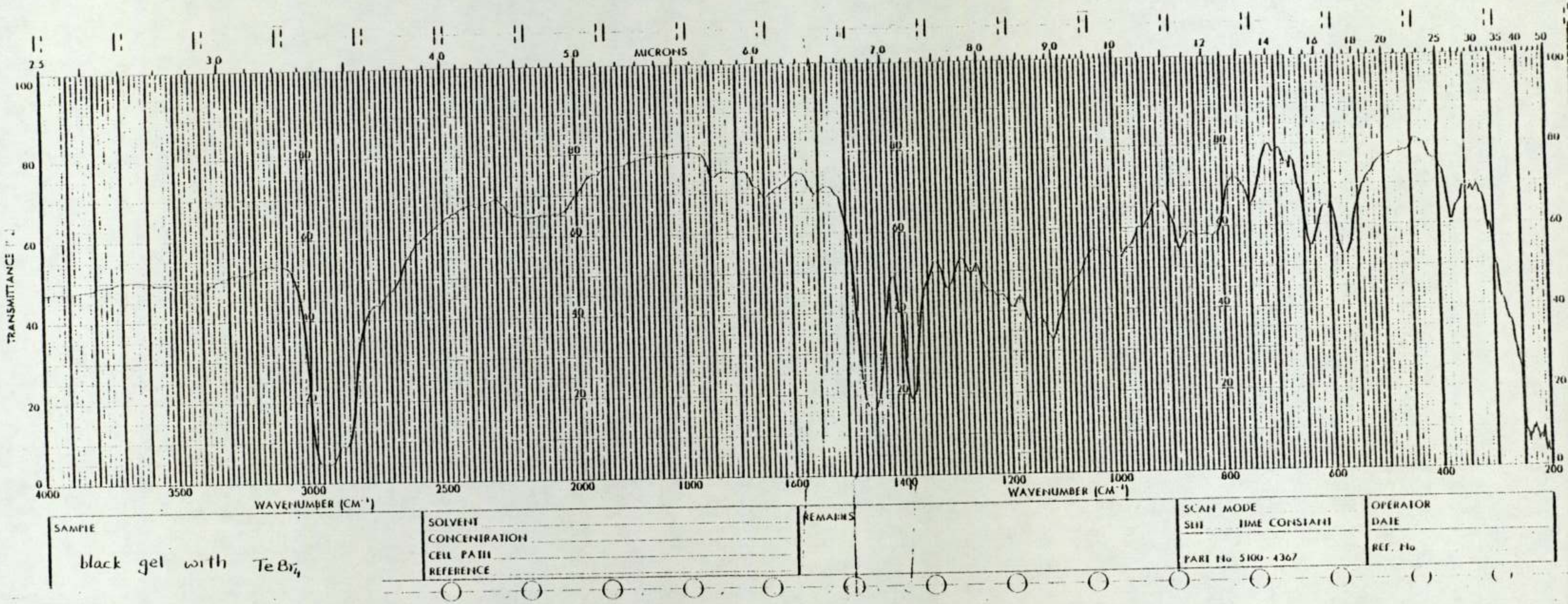

MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
TRANSMITTANCE [%]
0
20
40
60
80
100
WAVENUMBER (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
SAMPLE
black gel with TeBr4
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN MODE
SLIT
TIME CONSTANT
PART No 5100-4367
OPERATOR
DATE
REF. No

Figure 3.2b

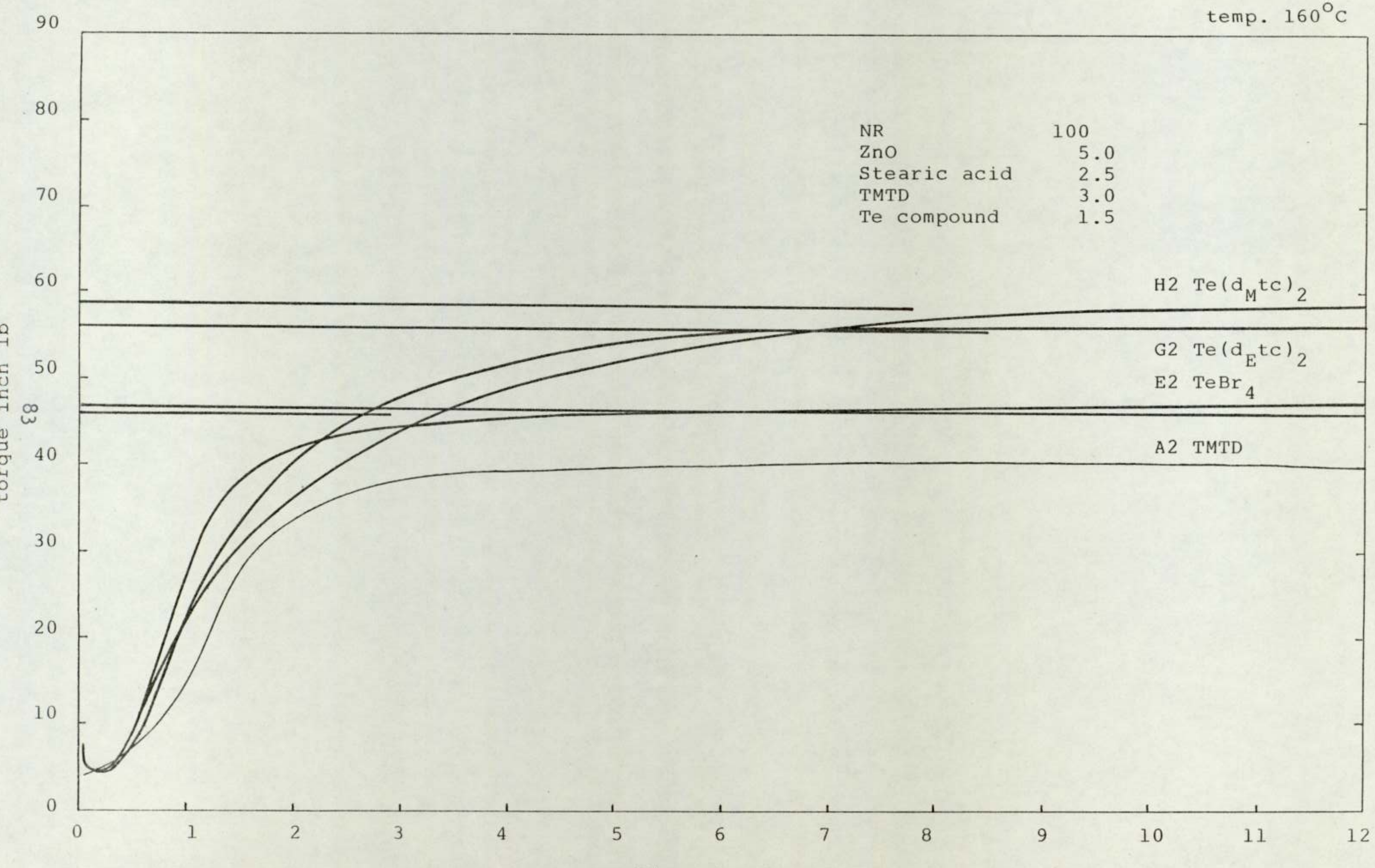

temp. 160°C
NR 100
ZnO 5.0
Stearic acid 2.5
TMTD 3.0
Te compound 1.5
H2 Te(d$_M$tc)$_2$
G2 Te(d$_E$tc)$_2$
E2 TeBr$_4$
A2 TMTD
0
10
20
30
40
50
60
70
80
90
0
1
2
3
4
5
6
7
8
9
10
11
12
Time minutes

Figure 3.3a

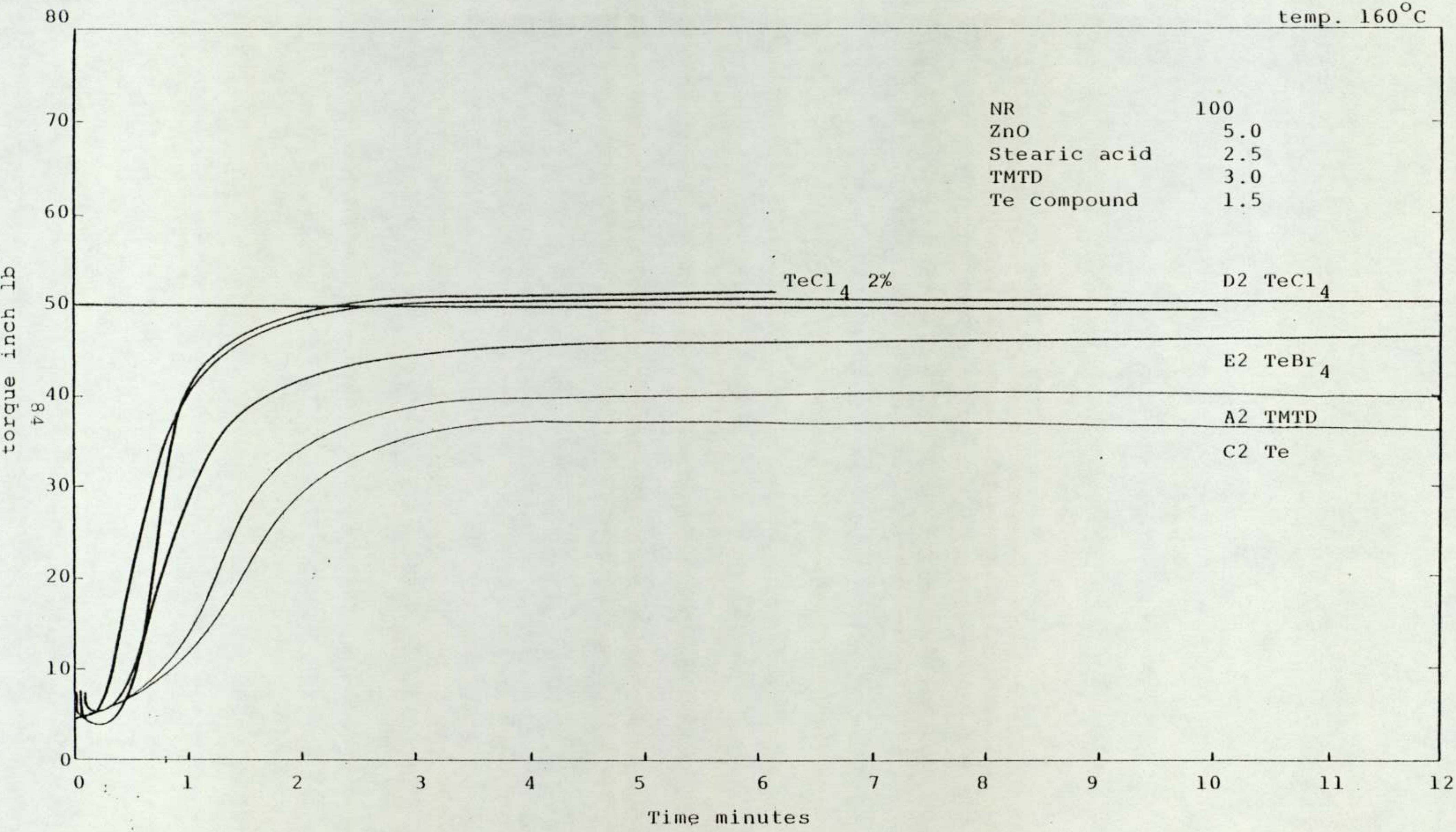

temp. 160°C
NR 100
ZnO 5.0
Stearic acid 2.5
TMTD 3.0
Te compound 1.5
TeCl4 2%
D2 TeCl4
E2 TeBr4
A2 TMTD
C2 Te
torque inch lb
Time minutes
0
10
20
30
40
50
60
70
80
0
1
2
3
4
5
6
7
8
9
10
11
12

Figure 3.3b

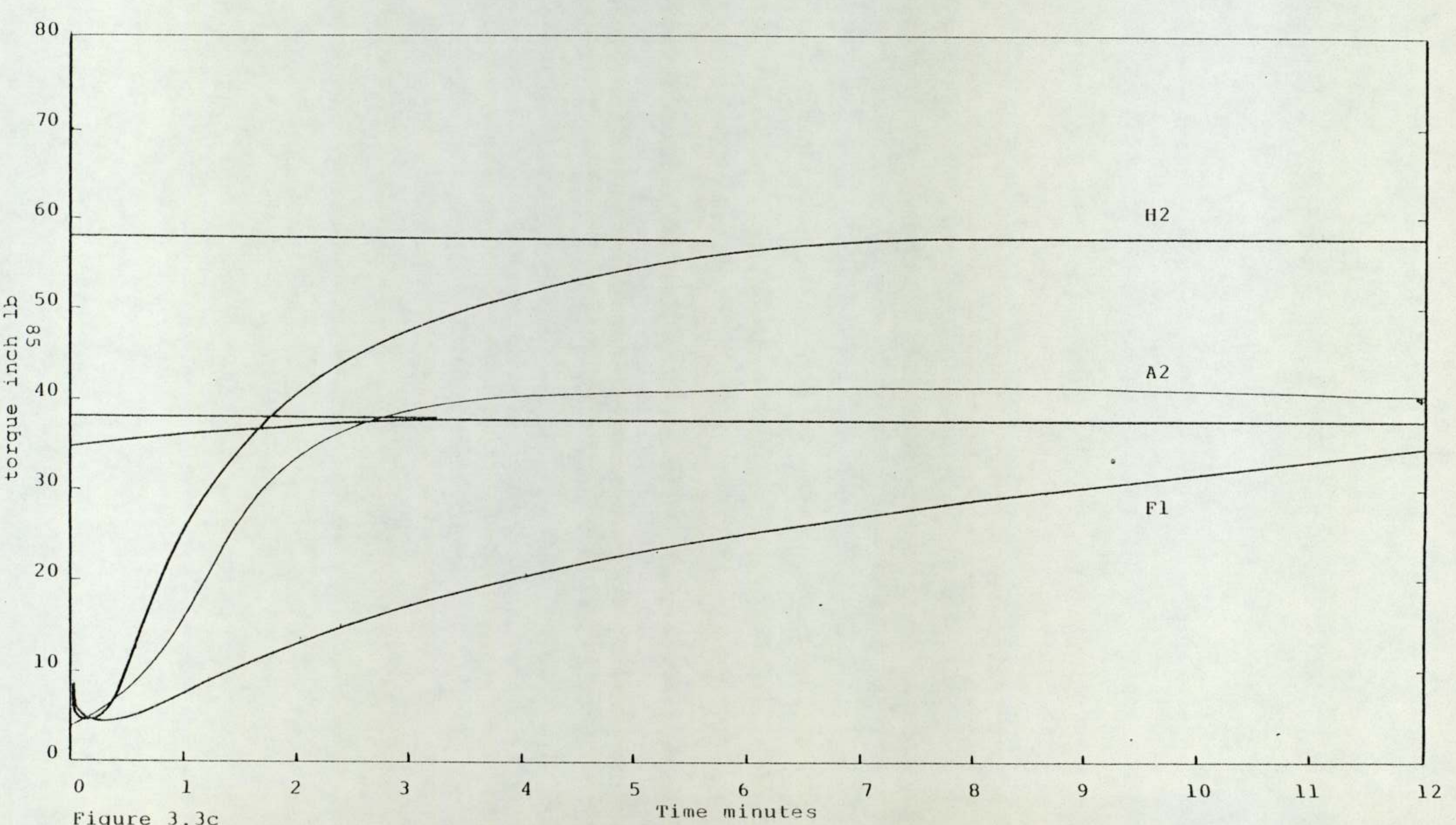

torque inch lb
80
70
60
50
40
30
20
10
0
0
1
2
3
4
5
6
7
8
9
10
11
12
Time minutes
H2
A2
F1

Figure 3.3c

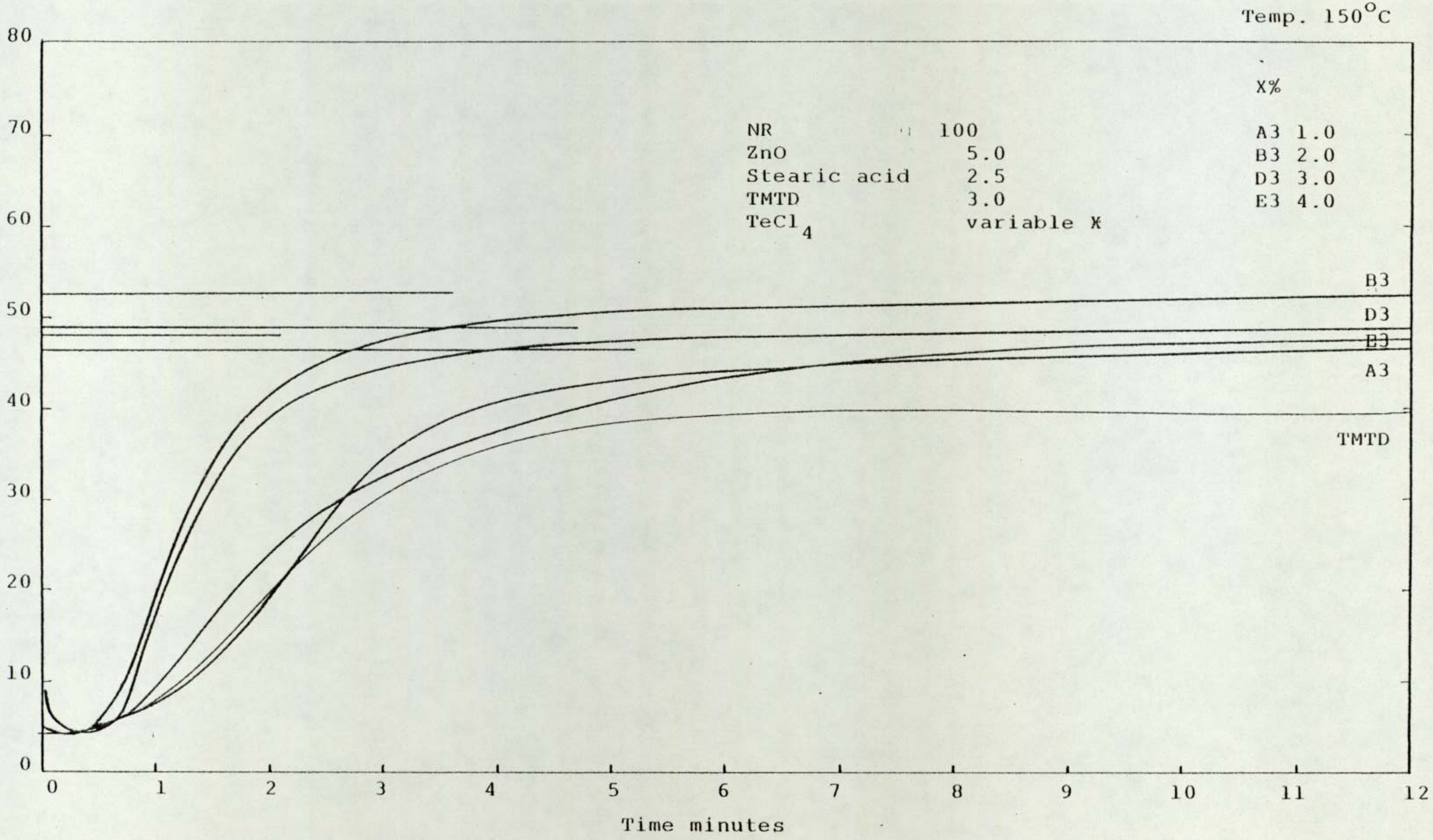
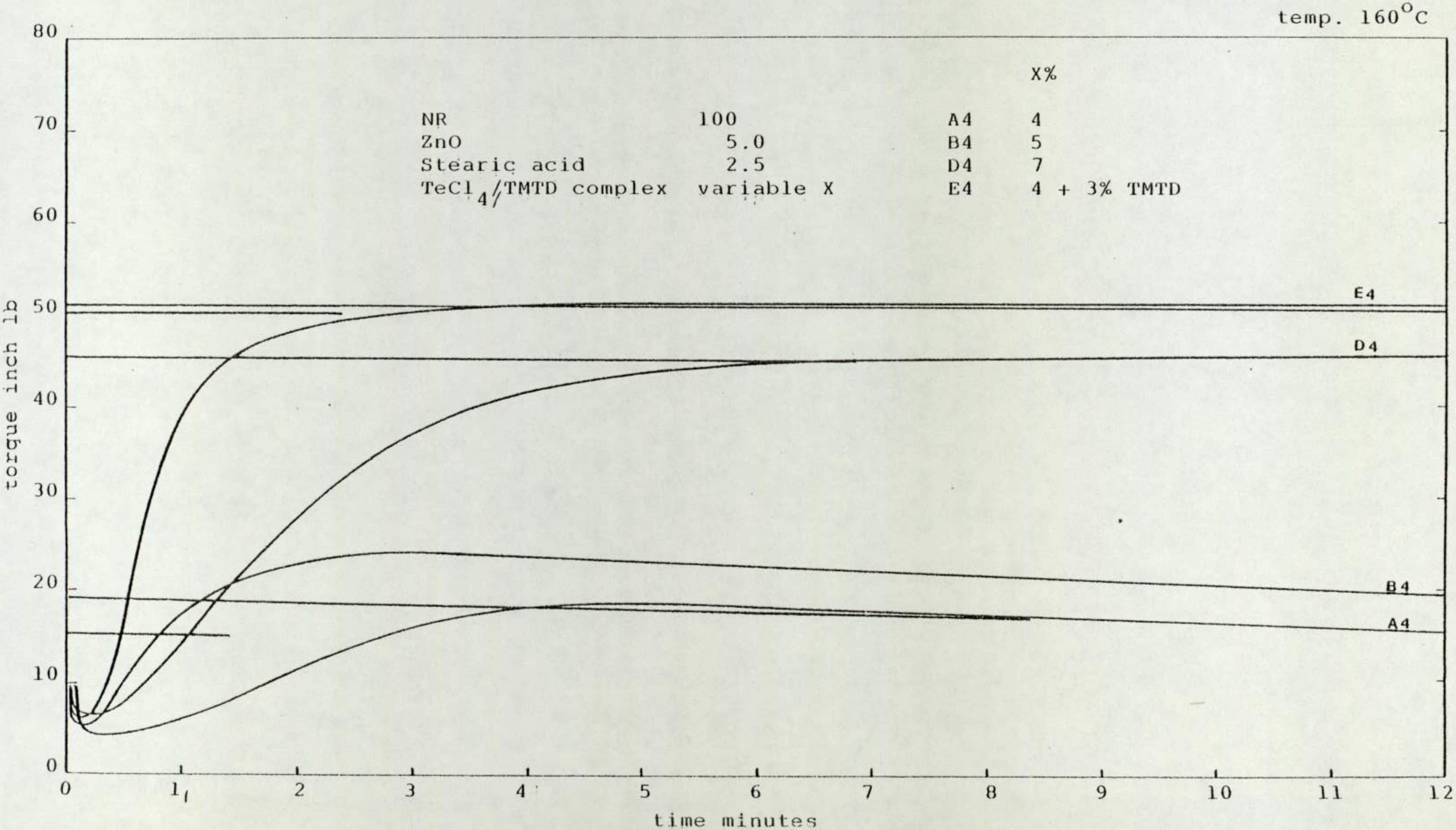
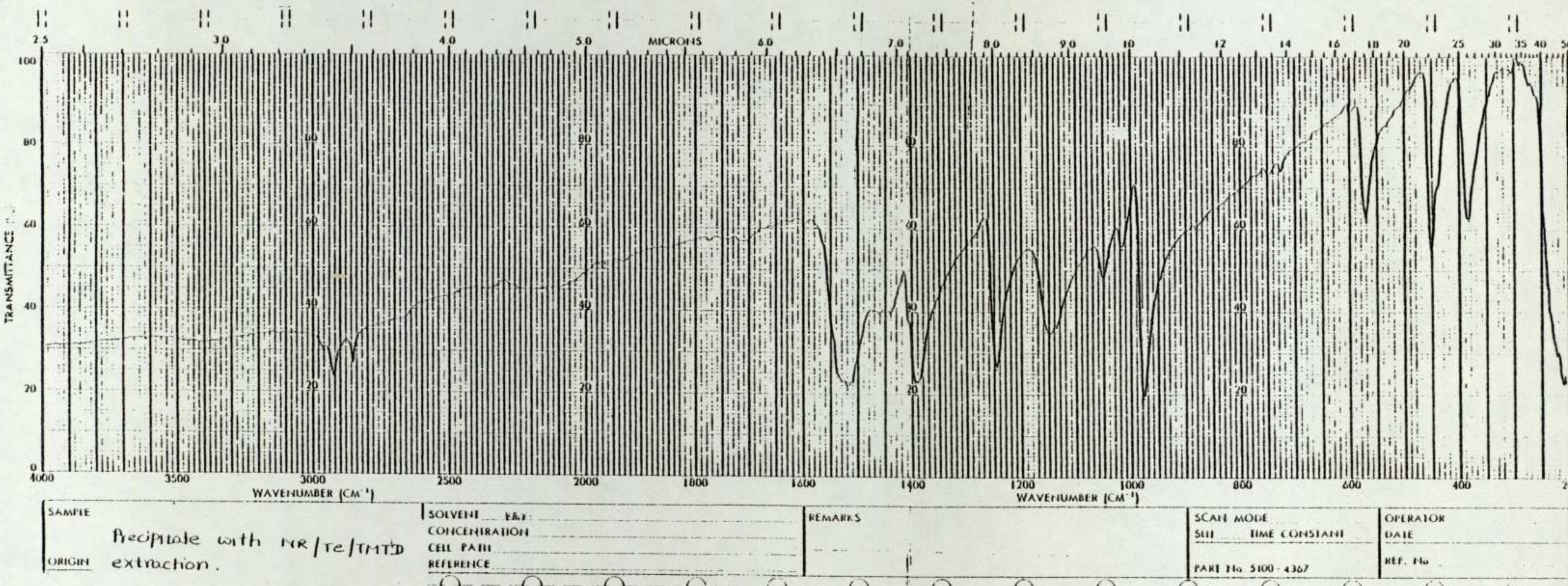

Temp. 150°C
X%
A3 1.0
B3 2.0
D3 3.0
E3 4.0
NR 100
ZnO 5.0
Stearic acid 2.5
TMTD 3.0
TeCl4 variable X
B3
D3
E3
A3
TMTD
torque inch lb
0
10
20
30
40
50
60
70
80
0
1
2
3
4
5
6
7
8
9
10
11
12
Time minutes

Figure 3.3d

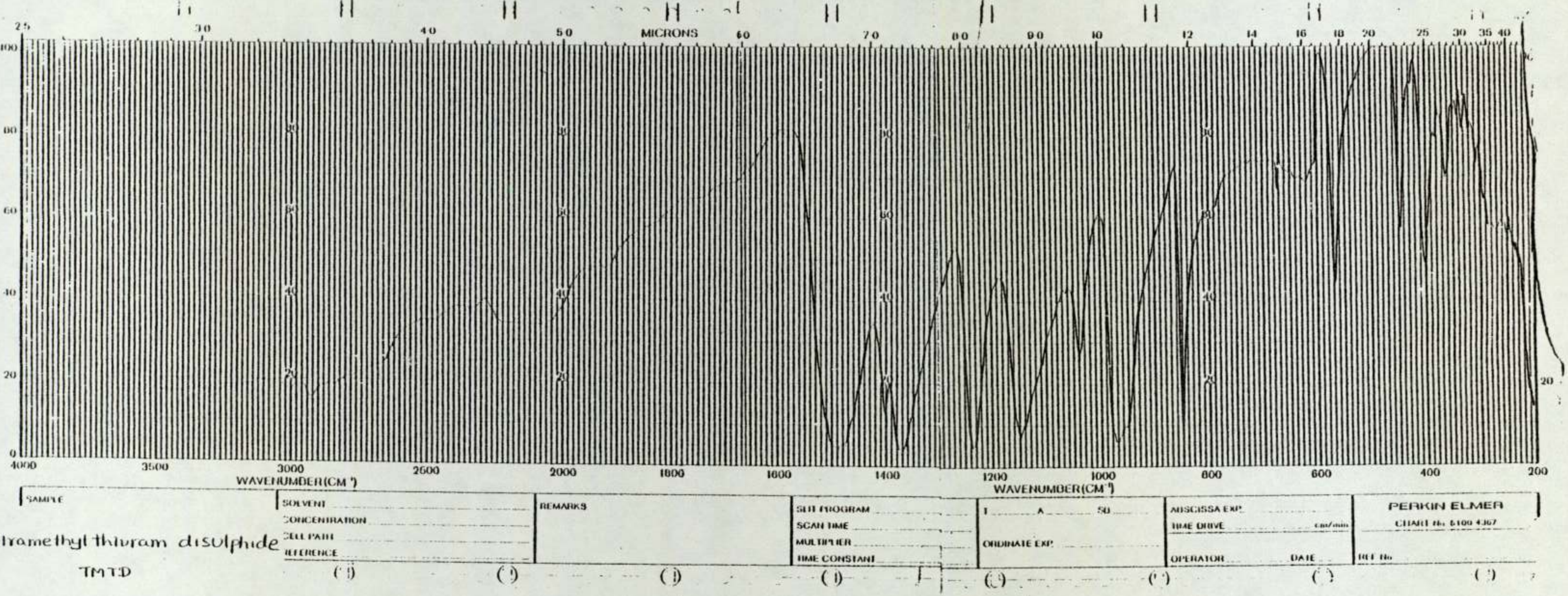

temp. 160°C
NR 100
ZnO 5.0
Stearic acid 2.5
TeCl4/TMTD complex variable X
X%
A4 4
B4 5
D4 7
E4 4 + 3% TMTD
E4
D4
B4
A4
torque inch lb
time minutes
0
10
20
30
40
50
60
70
80
0
1
2
3
4
5
6
7
8
9
10
11
12



SAMPLE Precipitate with NR/Te/TMTD

ORIGIN extraction.

Figure 3.4



Tetramethyl thiuram disulphide

TMTD

Figure 3.5

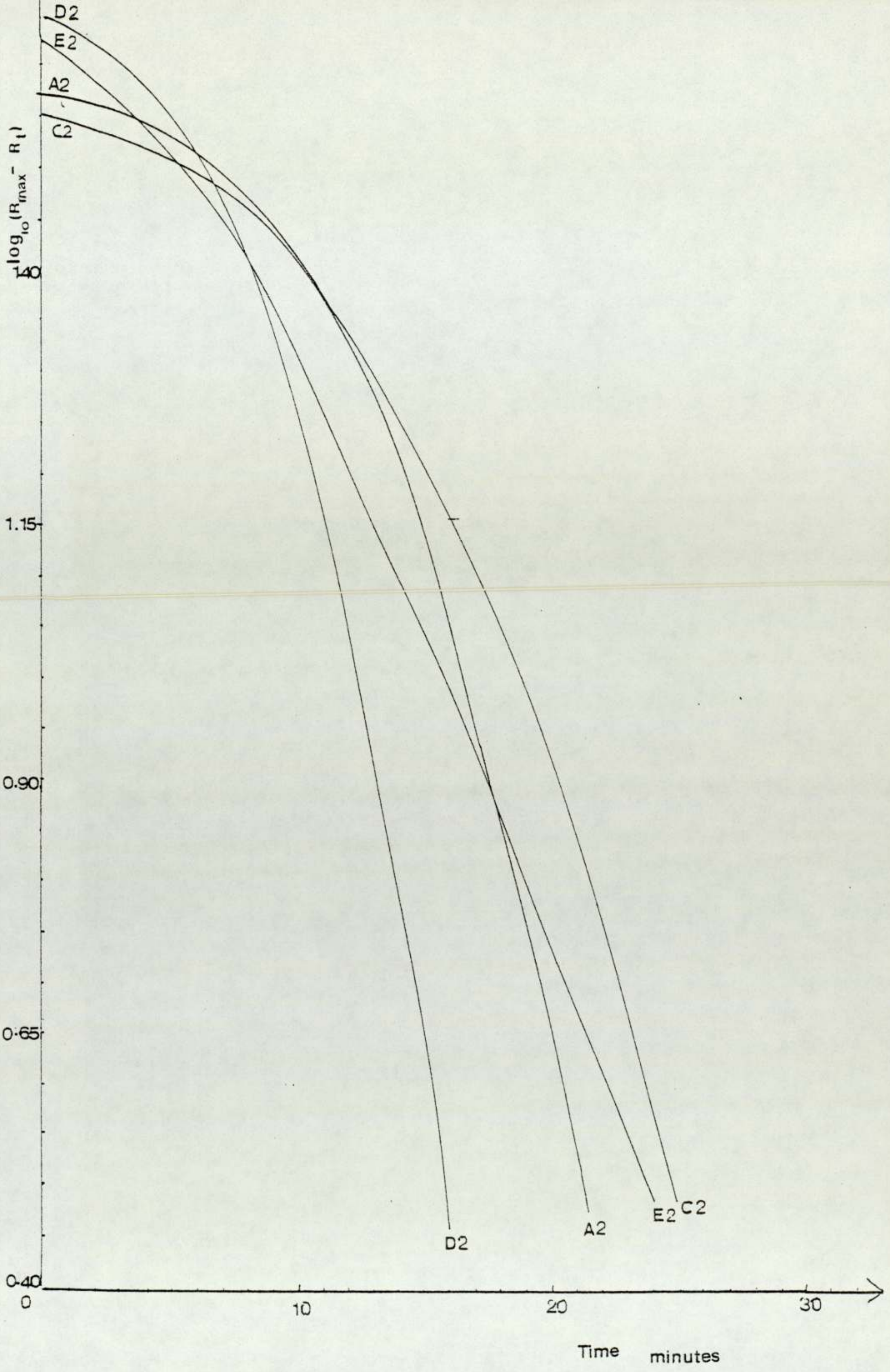

D2
E2
A2
C2
log₁₀(R_max − R_t)
1.40
1.15
0.90
0·65
0·40
0
10
20
30
D2
A2
E2
C2
Time minutes

Figure 3.6a

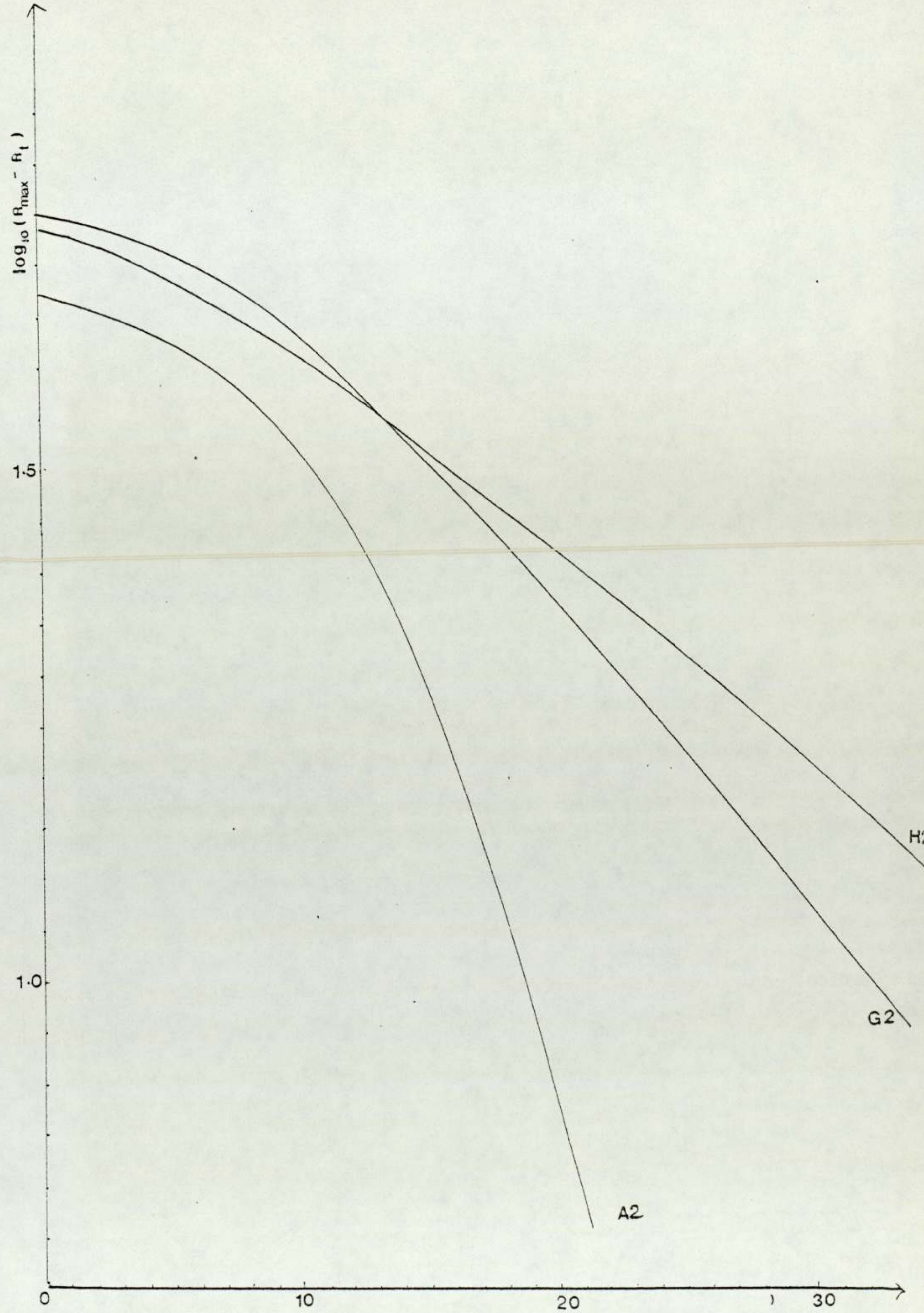


Figure 3.6b

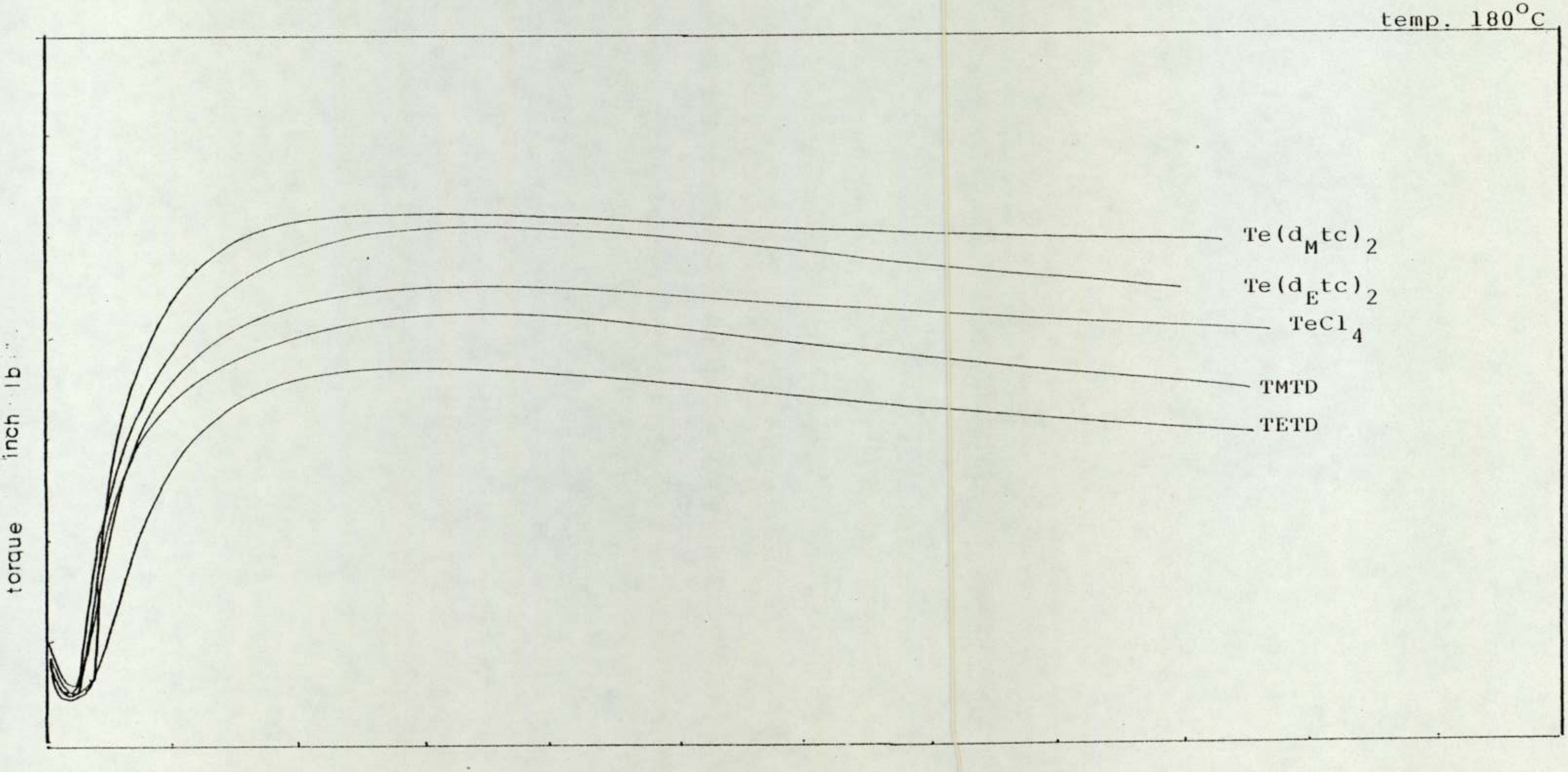

temp. 180°C
$Te(d_Mtc)_2$
$Te(d_Etc)_2$
$TeCl_4$
TMTD
TETD
torque inch lb
time minutes

Figure 3.7a

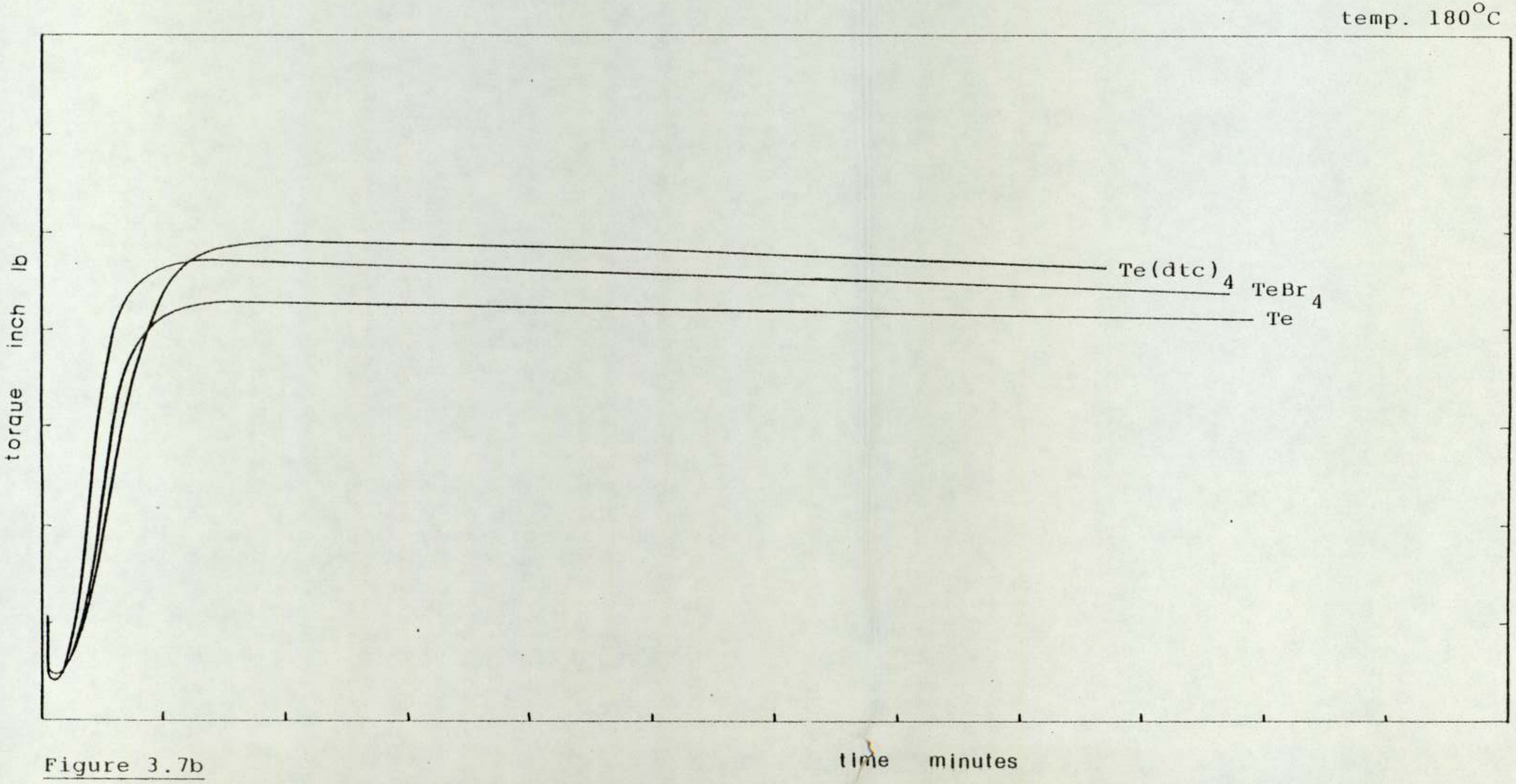


Figure 3.7b

The crosslink density and some physical properties of the vulcanizates are tabulated in Tables 3.9 and 3.10 respectively.

sample	average crosslink density of three samples ($g\ cm^{-3}$)
A2	6.505×10^{-5}
C2	6.785×10^{-5}
D2	8.820×10^{-5}
E2	8.783×10^{-5}
F2	8.590×10^{-5}
H2	10.261×10^{-5}
F1	4.14×10^{-5}
G1	3.90×10^{-5}

Table 3.9 Crosslink density of the vulcanizates (using swelling measurements in n-hexane at 25°C

3.4 Discussion

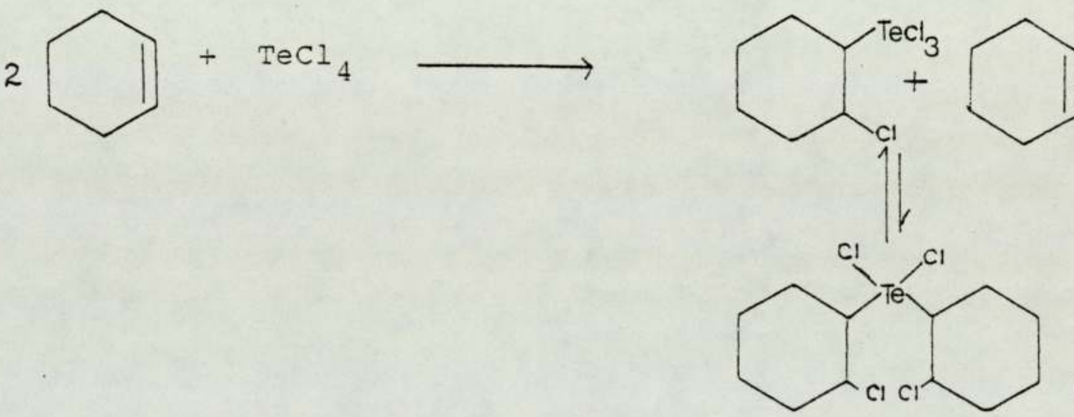
The reaction of tellurium tetrachloride with the alkenes produced elemental tellurium in most organic solvents used and also when the neat unsaturated compound was used. In some reactions unstable yellow precipitates formed, which decomposed with an increase in temperature above 0°C (Tables 3.2 and 3.3). However, in acetonitrile at 0°C, tellurium tetrachloride reacted with cyclohexene to give

Sample	100%MOD kg cm^{-2}	300% MOD kg cm^{-2}	Tensile strength kg cm^{-2}	Elongation at break cm
A2	3.30	10.94	210.53	650
C2	3.15	9.82	229.33	640
D2	4.90	29.70	267.52	620
E2	5.20	21.50	281.66	600
F2	6.25	30.25	310.11	680
F1	2.50	10.00	150.00	630
G1	2.60	10.70	197.80	700

Table 3.10

a stable crystalline product. The infra-red spectrum obtained for the product shows no band around 1650 cm^{-1} due to $\nu(C=C)$ indicating that the double bond is involved in the reaction. The new bands at 355 cm^{-1} and 250 cm^{-1} are probably due to $\nu_{Te-aliphatic}$ and ν_{Te-Cl} respectively.

The elemental analysis and the melting point of the pure compound shows that this is a 1:1 molar proportion addition reaction, not a 2:1 cyclohexene:tellurium tetrachloride addition as suggested by some early workers. Petragnani(44) in his studies showed that the addition product has a 1:1 molar ratio even in the presence of a great excess of cyclohexene. The results obtained in this work are in agreement with this observation.



Eq 3.1

However, under certain conditions which are not specified by the workers, the dichloride has been isolated and the crystal structure has been determined(48) (Figure 3.8).

The addition of tellurium tetrachloride to an alkene was suggested(45) to involve a cyclic telluronium intermediate

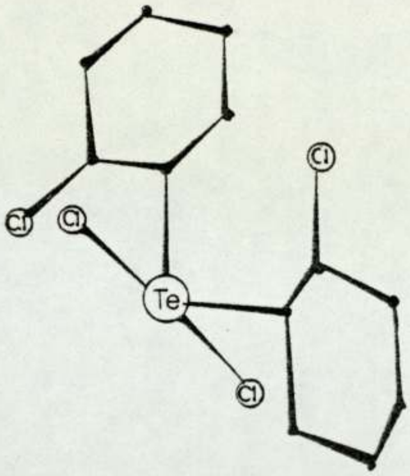
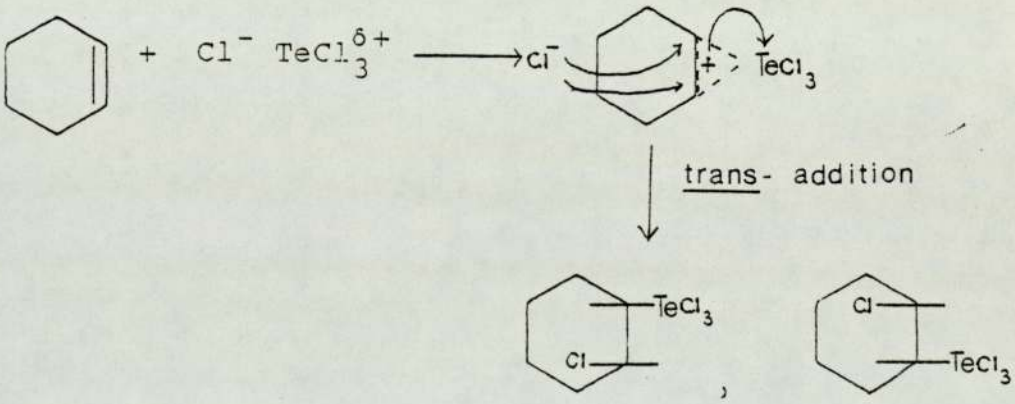


Figure 3.8

which could then be attacked by the chloride ion according to the following Equation 3.2, the mechanism suggested being a trans-addition.



But according to Bäckvall and Engman's recent research $^{(52)}$ on NMR coupling constants of the reaction product of E-1-deuterio-1-decene and tellurium tetrachloride, the addition product is cis- and the formation of the inverted alkene on reduction of trichloride with sodium sulphide suggests that the elimination is trans-.

Further, they pointed out that the cis-addition is favoured, probably due to the loosely coordinated bond between the electron rich chlorine atom attached to carbon and the electron deficient tellurium atom in solution, a phenomenon previously observed(54) for the oxygen atom in 8-ethoxy-4-cyclooctenyltellurium trichloride in solid state (Figure 1.13 in Chapter One).

The following reaction scheme shown in Figure 3.9 was suggested for the addition-elimination reactions as described above for tellurium tetrachloride addition to E-1-deuterio-1-decene in chloroform.

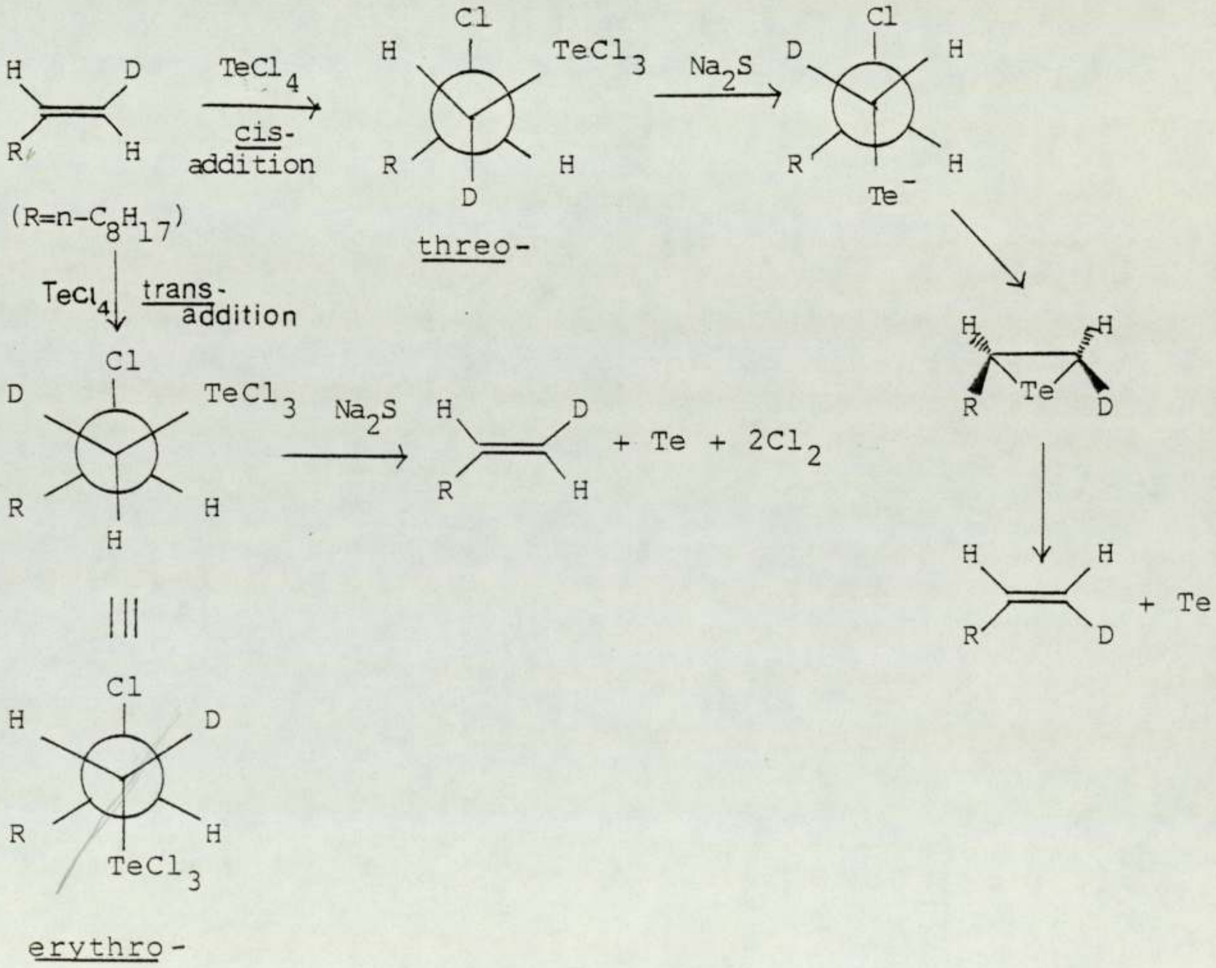


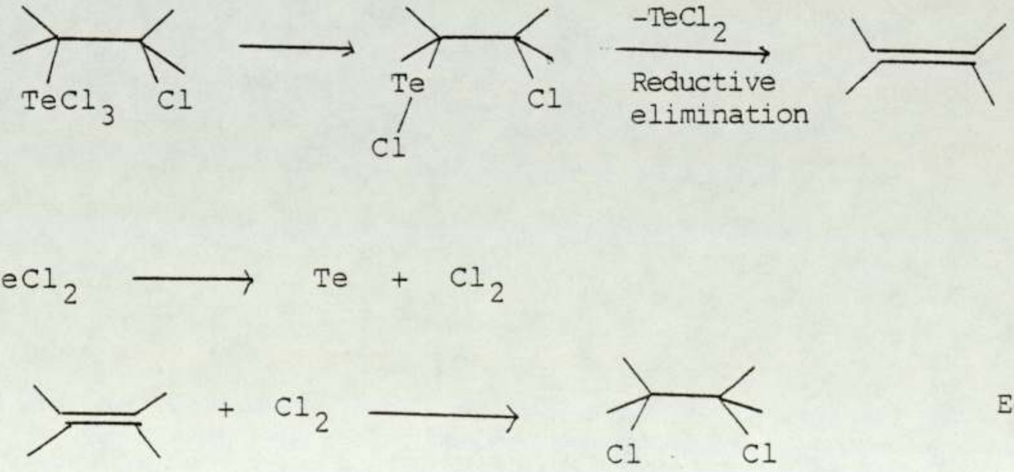
Figure 3.9

Further studies by the same workers(55) proposed that the major pathway of the addition reaction of tellurium tetrachloride to alkenes is a <u>cis</u>-addition with a competing radical chain reaction.

The presence of a weakly coordinating solvent such as acetonitrile could prevent the weak interaction of the chlorine atom attached to carbon and tellurium in $TeCl_3$-moiety in solution by coordinating to tellurium thus inhibiting easy elimination of tellurium from the trichloride.

The stereochemistry of the cyclohexyl ring, which hinders rotation around the C-C bond, together with the weak coordination with the solvent could stabilise the reaction product with cyclohexene.

The failure to isolate a reaction product with 2-methyl-2-pentene could be due to the decomposition of the unstable trichloride formed with the 2-methyl-2-pentene, which may undergo the following elimination of elemental tellurium and chlorinated 2-methyl-2-pentene (Equation 3.3)



$$TeCl_2 \longrightarrow Te + Cl_2$$

Eq. 3.3

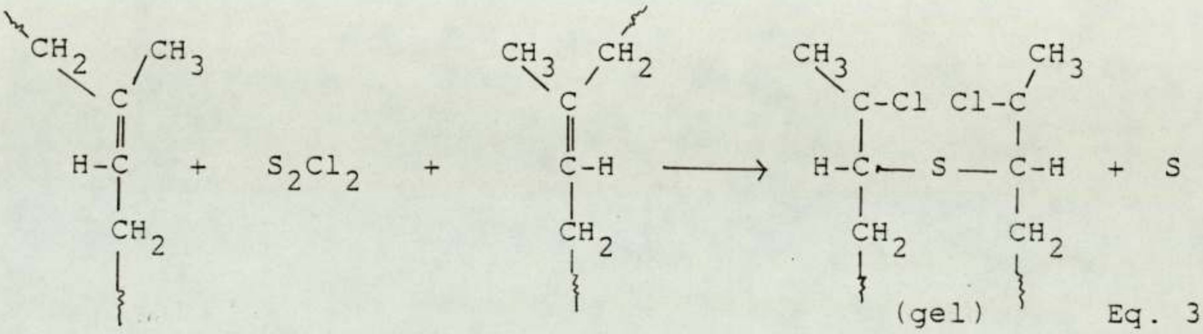
The reactivity of chlorine towards the alkene may also be a reason for the easy decomposition of the product and this supports the mechanism proposed. The removal of precipitated tellurium by centrifugation resulted in a colourless solution, that showed a peak corresponding to 2,3-dichloro-2-methyl-2-pentane in g.l.c. analysis.

The reaction of cyclohexene and tellurium tetrachloride in chloroform also could follow a similar decomposition resulting in the production of elemental tellurium and 1,2-dichlorocyclohexane.

The addition of tellurium tetrachloride to alkenes has been suggested to involve an ionic or radical(55) mechanism depending on the conditions of the reaction. The presence of a weakly coordinating solvent could stabilise the trichloride moiety - the ion or the radical by coordination e.g., through N in acetonitrile. Detailed study of the radical mechanism has not yet appeared in the literature.

Although the presence of tetrahydrofuran and acetonitrile prevented the elimination of the elemental tellurium, only in acetonitrile was a crystalline product isolated with cyclohexene.

When the model compound studies were expanded to the actual natural rubber molecules, the elimination of elemental tellurium was observed together with a gel formation in the solution. The disadvantage in model compound studies is that they do not provide any information on intramolecular reactions involving more than one double bond. Therefore the gelation observed could be due to the formation of crosslinks between the adjacent rubber molecules. This could be a similar observation to that made with the sulphur monochloride and natural rubber system which forms a gel(17) and results in crosslinking and the production of elemental sulphur as shown in Equation 3.4.



Eq. 3.4

The infra-red spectra of natural rubber and the black gel formed with tellurium tetrabromide are shown in Figure 3.2a and Figure 3.2b respectively.

The disappearance of the $\nu_{C=C}$ at 1600 cm^{-1} in the black gel suggests that the double bond is involved in the gelation. The band at 750 cm^{-1} in the black gel could be due to the stretching frequency of C-Cl.

The ^{125}Te Mössbauer spectrum obtained with the black gel formed with tellurium tetrachloride and natural rubber gave a well resolved spectrum with an isomer shift (δ).$(0.80 \pm 0.2)mms^{-1}$

with respect to $^{125}I/Cu$ and a quadrupole splitting (Δ), (7.36 ± 0.3) mms^{-1} (Figure 3.1).

Tellurium-125 Mössbauer spectroscopy, which examines the electronic environment of the tellurium nucleus directly, is a powerful means by which the fundamental nature of bonding and structure in solid organotellurium compounds may be investigated. The technique involves the recoil free emission of gamma-rays from excited state tellurium nuclei in a radioactive source and their absorption by ground state tellurium nuclei in the compound under investigation.

A typical Mössbauer spectrum consists of a plot of gamma-ray counts against the applied velocity which is measured in mm sec^{-1}. The magnitude of the applied velocity is called the chemical isomer shift, δ, and is a direct measure of the electron density at the nucleus. The chemical isomer shift data therefore provide information on oxidation states, co-ordination number and bonding characteristics. The symmetry of the electron density and ligand arrangement around tellurium atom is obtained from the measurement of the quadrupole splitting which arises with asymmetric electric fields. Under such circumstances the excited state energy level splits and a two line Mössbauer spectrum is recorded. The distance between the two peaks is called the quadrupole splitting, Δ, and gives information relating to the degree of distortion of the electronic and ligand array around the tellurium nucleus and, importantly, permits an evaluation of the relative populations of the tellurium 5s- and 5p-orbitals(89).

The initial ^{125}Te Mössbauer investigation of organotellurium compounds were performed in mid-1970's and involved the examination of a variety of alkyl- and aryl-derivatives of Te(II) and Te(IV)(87,90-93).

The isomer shifts of the organotellurium compounds lie in the order(87,90) tellurides<ditellurides<monohalides< dihalides<trihalides<tetrahalides<hexahalides.

The ^{125}Te Mössbauer parameters for some organotellurium(IV) chlorides are summarised in Table 3.11.

The chlorine atoms appear to remove some 5p- electron density from tellurium leading to an increase of deshielding of the 5s-electrons from the nucleus and hence increasing the value of δ.

Structural studies of the crystalline dihalides have shown(94,95,96) the tellurium atoms to be in distorted trigonal bipyramid coordination. In these structures the halogens occupy trans axial positions and the organic groups are situated in the equatorial plane in which the third position is occupied by a lone pair of electrons which may sometimes be involved in intermolecular bonding through bridging halogens.

Compound	δ *mms^{-1}	Δ **mms^{-1}	reference
Te metal	0.50$\pm$0.06	7.77$\pm$0.06	97
$(CH_3)_2TeCl_2$	0.58	9.4	87
$(C_6H_5)_2TeCl_2$	0.50	9.2	90
$(p\text{-}CH_3OC_6H_4)_2TeCl_2$	0.68	9.1	92
$(p\text{-}C_2H_5OC_6H_4)_2TeCl_2$	0.70	9.1	90
$(C_6H_4ClC{=}CH)_2TeCl_2$	0.57	8.0	90
$(C_6H_4)_2OTeCl_2$	0.68	8.0	90
$(p\text{-}CH_3OC_6H_4)TeCl_3$	0.9	9.2	90
$(p\text{-}C_2H_5OC_6H_4)TeCl_3$	0.91	9.4	87
$TeCl_4$	1.2	4$\pm$1.6	98
$TeCl_4(Py)$	0.86	4.5	90
$(NH_4)_2TeCl_6$	1.95	0.0	99

* δ with respect to I/Cu;error $\pm$0.08 unless otherwise stated
**Δ $\pm$0.1 unless otherwise stated

Table 3.11

The chemical isomer shift of the tetrachloride as shown in Table 3.11 is more positive than those of dichlorides and this is consistent with the chloride ligands removing predominantly p-electron density from the tellurium.

The quadrupole splitting arises due to the imbalance in the p-orbital electron population about tellurium and the trend may be rationalised if the bonding is envisaged as primarily involving the p-orbitals such that, V_{zz}, the principal component of the electric field gradient tensor, lies along the X-Te-X bond axis and is positive in sign. Thus the quadrupole splittings recorded from the trichlorides are the same as the corresponding dichlorides (Table 3.11). The data are consistent with the similar structures of these chlorides(100,101) in which the bonding is predominantly concerned with the involvement of p-orbitals, and a considerable amount of electron density is removed from the tellurium 5Pz-orbital leading to an electron deficit along that axis compared with the xy equatorial plane.

The quadrupole splitting of tellurium tetrachloride shows a more symmetric environment around tellurium atom and hence the coordination about the tellurium atom in the tetrachlorides must be significantly different from that in the trichlorides and dichlorides. The Mössbauer spectrum of the hexachlorotellurate anion does not show any splitting due to the regular octahedral environment around tellurium in $(NH_4)_2TeCl_6$ complex (Table 3.11).

The complexes $(C_6H_4ClC{=}CH)_2TeCl_2$ and $(C_6H_5)_2TeCl_2$ as shown in Table 3.11 have Mössbauer parameters $\delta=(0.57\pm0.08)$ and $\delta=(0.50\pm0.08)$ mms^{-1} and $\Delta=(8.0\pm0.1)$ and $\Delta=(9.2\pm0.1)$ mms^{-1}. The R groups attached to tellurium in the complex $(C_6H_4Cl{=}CH_2)_2TeCl_2$ containing double bonds and chlorine atoms seem to increase the isomer shift and decrease the quadrupole splitting. The black gel obtained with tellurium tetrachloride and natural rubber may have a similar environment with intramolecular tellurium-chlorine bonds and double bonds along the natural rubber chains resulting in a significantly different environment from the other well known dichlorides.

However, there is a possibility that the Mössbauer parameters obtained for the black gel, 0.80 ± 0.2 mms^{-1} and 7.36 ± 0.3 mms^{-1} for δ and Δ respectively, could be due to the elemental tellurium metal and dichlorides. Hence at this instance it is not possible to be certain of the formation of tellurium-carbon bonds in the natural rubber medium.

It is also not possible to see support for a second tellurium site in the ^{125}Te Mössbauer spectrum of the black gel as there is no significant broadening of the components of Δ (Figure 3.1) with a line width, $\Gamma_{\frac{1}{2}}$, of 6.24 mms^{-1}. In agreement with the model compound studies there is however positive evidence for the presence of elemental tellurium in the black gel and the literature value$^{(97)}$ of the linewidth for tellurium metal (6.21 ± 0.11) mms^{-1} is in the range of the value obtained for the black gel. However, being bonded to natural rubber, a second tellurium species may have a very low recoil free fraction thus not contributing significantly to the 80K spectrum.

Hence the slight broadening of the ^{125}Te Mössbauer spectrum of the black gel does not argue strongly for two significantly different types of tellurium species present in the black gel.

In an attempt to find the precentages of tellurium and chlorine bound to natural rubber, the black gel was treated with concentrated HNO_3 to remove any elemental tellurium present and the resultant yellow precipitate showed non-rubbery properties and which analysed to contain 14.8% tellurium and 8.9% chlorine.

Thus, at this instance, with the aid of the Mössbauer data obtained for the black gel, it is not unreasonable to suggest that the bound tellurium is present as dichlorides (N.B. Te:Cl=1:2.12) in the natural rubber medium hence the formation of tellurium-carbon bonds is implied.

The infra-red spectra of the yellow precipitates obtained with tellurium tetrachloride and tetrabromide with natural rubber solutions are similar to those of their black gels. The mass spectrum of the yellow precipitate obtained with tetrabromide clearly shows the characteristic fragmentation pattern of tellurium containing species at 362,294 and 257 m/e (based on ^{130}Te) values.

The yellow materials were resistant to corrosive chemicals like concentrated HNO_3, stable at room temperature and decomposed at 118°, hence showing properties of chlorinated rubber.

The formation of black gels was not observed with nitrile rubber solutions in chloroform. The infra-red spectrum of the thin film obtained by evaporating the emulsion formed, shows a possibility of a coordinating nitrile group in the nitrile rubber to tellurium via the nitrogen atom as there is an indication of a slight increase in $\nu_{C\equiv N}$ band at 2100 cm^{-1}. Therefore this may be evidence for the stabilisation of $TeCl_3$-moiety with the C≡N as described before for model alkenes in acetonitrile which stabilises the +2 oxidation state of tellurium.

Among the solid natural rubber vulcanizates, the samples that contain no tetramethylthiuram disulphide (TMTD), but contain bis and tetrakis (diethyldithiocarbamato)tellurium (II) and tellurium(IV) showed very effective crosslinking in the Shawbury curometer at 160°C as in Figure 3.10.

The effect of tellurium, tellurium tetrachloride, tellurium tetrabromide, p(ethoxyphenyl)tellurium trichloride and fresh tellurium powder is very little and the formation of weak crosslinks was observed. The shapes of the Shawbury cure curves obtained with these compounds are illustrated in Figure 3.11.

Elemental sulphur without any accelerator or activator failed to show as effective crosslinking as the tellurium dithiocarbamato-compounds with natural rubber, but was still better than the other tellurium compounds described. The type of curve obtained in the Shawbury curometer for sulphur only vulcanizate is shown in Figure 3.12.

Tellurium oxide did not show any crosslinking, probably due to the high stability of the compound (Figure 3.13).

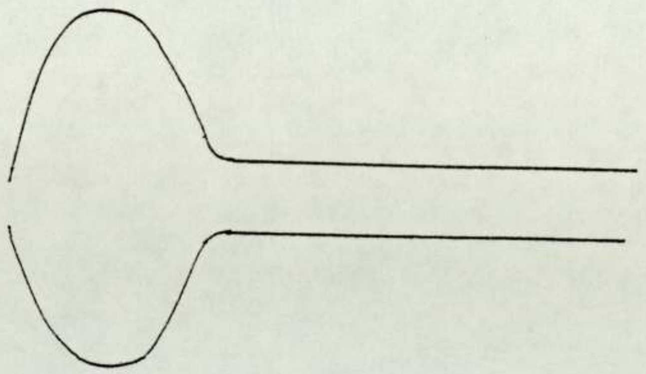


Figure 3.10 The type of curve obtained with samples El, Fl, Gl in Shawbury curometer

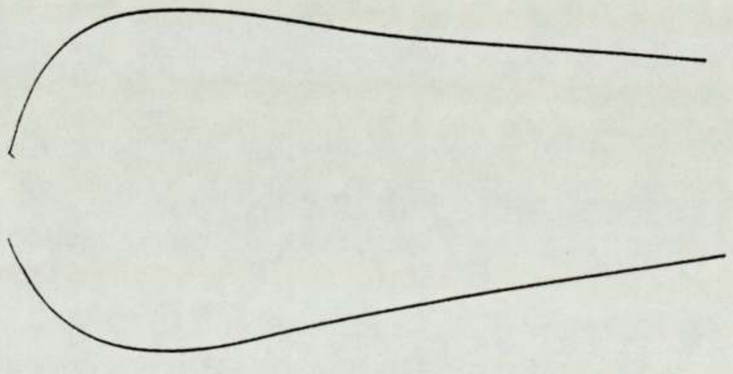


Figure 3.11 The type of curve obtained with samples Al, Bl, Cl, Dl and Il in Shawbury curometer

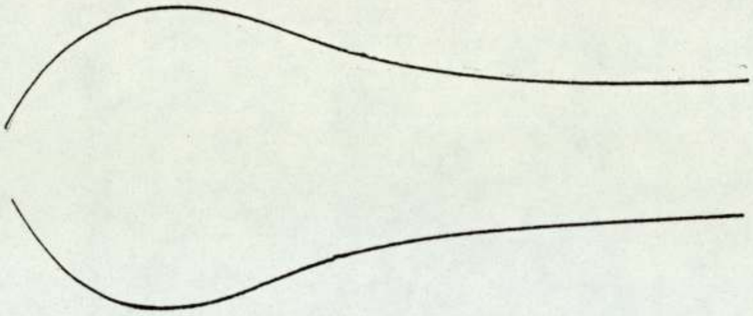


Figure 3.12 The type of curve obtained with sample J1 - elemental sulphur - in Shawbury curometer

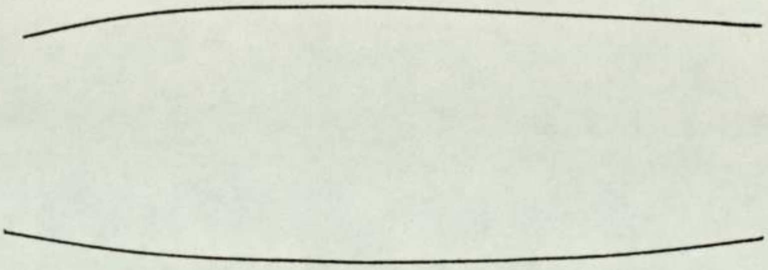


Figure 3.13 The type of curve obtained with sample H1 - tellurium oxide - in Shawbury curometer

The above figures show the different types of curves obtained in Shawbury curometer at 160°C.

According to the literature(34) tetrakis(diethyldithiocarbamato-)tellurium(IV) is the only dithiocarbamate salt that has been found to crosslink natural rubber in the absence of sulphur or TMTD.

This work shows that bis(dimethyl- and diethyl-dithiocarbamato-) tellurium(II) compounds are also good crosslinking agents without sulphur or TMTD.

The solid NR vulcanizates with tellurium, tellurium tetrachloride and tetrabromide and p(ethoxyphenyl)tellurium trichloride together with a sulphur containing compound, TMTD or TETD gave interesting observations. These samples, labelled C2-H2, I2, K2 and L2 in Table 3.5, increased the acceleration and the crosslink density of the vulcanizates when compared with the disulphides alone, as shown in the Monsanto rheographs (Figures 3.3a-3.3e).

Among these, D2, E2 and K2, the samples with tellurium tetrahalides gave the best enhanced acceleration and crosslinking as shown in the Figures. An attempt to use selenium tetrachloride instead of tellurium showed the same effect on the rubber vulcanizates when used together with TMTD. The acceleration of elemental tellurium and disulphide containing vulcanizates could be due to the formation of the corresponding bis(dialkyldithiocarbamato)-tellurium (II) since these compounds may be prepared by the reaction of elemental tellurium with disulphides at higher temperature, in boiling xylene. It has already been shown that these compounds are good accelerators as well as crosslinking agents.

The vulcanizate C2, containing tetramethylthiuram disulphide and elemental tellurium, was extracted with acetone and the solvent was evaporated to dryness in a rotary evaporator. The infra-red spectrum of the precipitate obtained is shown in Figure 3.4, which is similar to the infra-red spectrum of bis(dimethyldithiocarbamato)tellurium(II) but different from TMTD (Figure 3.5) supporting the above suggestion. Thus a comparison of Figures 3.4 and 3.5 shows a positive shift in ν_{C-N} at 1500 cm^{-1}, a negative shift in the band at 400 cm^{-1} and disappearance of the band at 850 cm^{-1}, due to the formation of bis(dimethyldithiocarbamato)tellurium(II).

Obviously the increase in crosslink density and the acceleration of the samples containing dithiocarbamates (F2, G2, H2 and L2) in Table 3.5 is due to the presence of two well known accelerators.

Among the samples with different proportions of tellurium tetrachloride (Table 3.6), the sample B3 with 2.0% tellurium tetrachloride gave the best curve in the Monsanto rheographs (Figure 3.3d). In the case of selenium, the samples containing 2.5% selenium tetrachloride gave the best rheograph.

The crosslink density of some samples in Table 3.6 are tabulated in Table 3.9 using the Flory-Rehner equation.

The information from the Monsanto rheographs was used to plot the $\log(R_{max} - R_t)$ vs. t graphs as shown in Figures 3.6a and 3.6b, which enabled the calculation of rate constants for the vulcanization reactions of some samples and these are tabulated in Table 3.8.

The tensile strength of these samples were also found together with the physical properties 100% and 300% modulus and the elongation at break as tabulated in Table 3.10.

All these results in Table's 3.8, 3.9 and 3.10 are in agreement with the observations made from the Monsanto rheographs.

In the study of heat stability of the tellurium containing samples, a comparison at 180°C (Figure 3.7) shows that the effect is almost the same as with TMTD, which is known to be a good heat stabiliser, but contrasts with TETD which is a poor heat stabiliser. However, it is known that in the presence of an antioxidant, the vulcanizate containing a little tellurium gives excellent heat stability(34).

A further set of reactions was carried out to study the effect of the enhancement of the acceleration and the crosslink density with tellurium tetrahalides with tetraalkylthiuram disulphides which will be discussed in detail in Chapter Four.

Samples containing tellurium tetrahalides, as the tellurium salt could react with any of the ingredients in the normal rubber vulcanizing mixture to enhance both crosslinking and acceleration. It was considered most likely that the tetrahalides had reacted with thiuram disulphides, which contain the essential group in thiourea, which is a compound well known for forming crystalline adducts with tellurium tetrahalides(68).

The reaction of tellurium tetrahalides and tetra(ethyl or methyl)thiuram disulphide resulted in stable tellurium complexes which are analysed and characterised as described in Chapter Four. Briefly, of the 4 sulphur atoms from the disulphide, 3 are contained in the complexes, leaving the fourth sulphur atom with the possibility of entering into the reaction medium in an active form.

Thus when triphenylphosphine, which could capture this sulphur, is used in vulcanization with NR, TMTD and tellurium tetrachloride gave no acceleration or enhanced crosslink density, this supported the above suggestion. This observation of the formation of triphenylphosphine sulphide also suggests that the sulphur is indeed involved in the acceleration and crosslinking of the NR containing tellurium tetrahalides.

CHAPTER FOUR

COORDINATION CHEMISTRY OF TELLURIUM WITH RUBBER ACCELERATORS

4.1 Introduction

This chapter is concerned with the study of tetraalkylthiuram disulphides (methyl-and ethyl-) with some tellurium (IV) compounds. As described in Chapter Three, tellurium tetrachloride enhances the acceleration and crosslink density of the vulcanization reaction of natural rubber when used with thiuram disulphides. It was decided that the structural variety possible for this observation is best demonstrated by reacting tellurium tetrachloride with thiuram disulphides, as mentioned in the previous chapter.

Since the complexes are derived from tellurium tetrachloride, it is convenient at this point to illustrate the main features of the structure of this compound.

4.2 Structure of Tellurium Tetrachloride

Both covalent structures, based on ψ-trigonal bipyramid ($TeCl_4$), and ionic structures ($TeCl_3^+ Cl^-$) have been proposed for tellurium tetrachloride in solid state by some early workers(102,103). Despite a large number of earlier attempts to determine the crystal structure, only the X-ray crystallographic method has been successful. Buss and Krebbs(104) have shown that tellurium tetrachloride comprises Te_4Cl_{16} units within the crystal lattice in which the tellurium is six coordinated, with both long (∿2.9Å) and short (~2.3 A) Te-Cl bonds, as shown below in Figure 4.1.

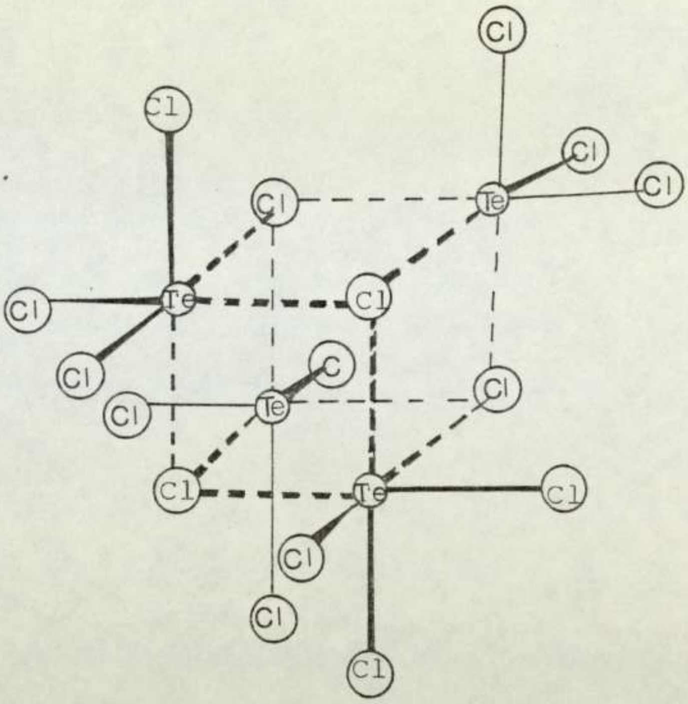


Figure 4.1

4.3 Experimental

4.3.1 Reaction of Tetramethylthiuram Disulphide (TMTD) with Tellurium Tetrachloride

Tetramethylthiuram disulphide (4.80 g, 20 m mol) dissolved in dry chloroform (50 cm^3) was added to a clear solution of tellurium tetrachloride (5.38 g, 20 m mol) dissolved in dry chloroform (50 cm^3) with vigorous stirring; immediately a yellow product separated out. The reaction was carried out under a nitrogen atmosphere. The product so formed was filtered, washed with carbon disulphide and ether and dried in *vacuo* over P_4O_{10}.

The precipitate was recrystallised from acetonitrile to afford yellow needles which melted at 198°C.

found C14.82 H2.50 N5.76 S21.20 Cl28.95 Te28.11%

$C_6H_{12}Cl_4N_2S_3Te$ requires C15.07 H2.51 N5.86 S20.10 Cl29.73 Te27.61%

4.3.2 Reaction of TMTD/Tellurium Tetrachloride Complex with Potassium Bromide

Potassium bromide (1.90 g, 16 m mol) dissolved in methanol (50 cm^3) was added to a solution of TMTD/tellurium tetrachloride complex (1.91 g, 4 m mol) in the same solvent (50 cm^3). Almost immediately on mixing of the reactants a brownish-orange product separated out. The reaction mixture was then heated just above the room temperature for 1 hour. The product was filtered, washed with methanol and ether and dried in vacuo over P_4O_{10}. (M.P. 173°C)

found C10.86 H1.84 N4.27 S14.88 Br47.38%

$C_6H_{12}Br_4N_2S_3Te$ requires C10.98 H1.83 N4.27 S14.64 Br48.81%

4.3.3 Reaction of TMTD/Tellurium Tetrachloride Complex with Potassium Iodide

The same procedure as above was adopted using potassium iodide (2.65 g, 16 m mol). The red-brown precipitate formed was filtered, washed with methanol and ether and dried in vacuo over P_4O_{10}. Recrystallisation of the product from benzonitrile afforded a fine crystalline material which melted at 193°C.

found C8.60 H1.43 N3.32 S11.82 Te16.01%

$C_6H_{12}I_4S_3N_2Te$ requires C8.53 H1.42 N3.31 S11.37 Te15.12%

4.3.4 Reaction of Tetraethylthiuram Disulphide (TETD) with Tellurium Tetrachloride

TETD (5.92 g, 20 m mol) dissolved in dry chloroform (50 cm^3) was added dropwise to a clear solution of tellurium tetrachloride (5.38 g, 20 m mol) dissolved in dry chloroform (50 cm^3) with vigorous stirring under nitrogen. A yellow product separated out immediately after mixing the reactants. The product was filtered, washed with carbon disulphide and ether and dried in *vacuo* over P_4O_{10}.

found C22.05 H3.58 N5.00 S17.24 Cl26.22%

$C_{10}H_{20}Cl_4N_2S_3Te$ requires C22.48 H3.74 N5.24 S17.99 Cl26.61%

4.3.5 Reaction of TMTD with p-Ethoxyphenyltellurium Trichloride

p-Ethoxyphenyltellurium trichloride, (pEtOPh)$TeCl_3$, was prepared by refluxing tellurium tetrachloride, phenetole and chloroform according to the literature method(105).
M.P. 182°C (lit. 182-183°C)

TMTD (2.40 g, 10 m mol) in dry chloroform (50 cm^3) was added in a dropwise manner to a solution of (pEtOPh)$TeCl_3$ (7.10 g, 20 m mol) in dry chloroform (50 cm^3) with vigorous stirring under nitrogen atmosphere. The fine powdery material formed was found difficult to filter without adding dry ether to the reaction mixture. The product was stirred with ether for a few minutes and filtered off and dried in <u>vacuo</u>-over P_4O_{10}. (M.P. 178°C)

found	C28.56 H3.15 N3.01 S10.66 Cl24.00%
$C_{22}H_{30}Cl_6N_2O_2S_3Te_2$ requires	C28.75 H3.26 N3.04 S10.45 Cl23.19%

4.3.6 Reaction of TMTD/Trichloride Complex with Potassium Bromide

Potassium bromide (2.14 g, 18 m mol) dissolved in methanol (20 cm^3) was added to a solution of TMTD/(p-EtOPh)$TeCl_3$ complex (2.75 g, 3 m mol) in the same solvent (50 cm^3). Heating the mixture just above room temperature with vigorous stirring afforded an orange-brown precipitate. The product was filtered off, washed with a little methanol and dried in <u>vacuo</u>-over P_4O_{10}. (M.P. 153°C)

found	C22.04 H2.52 N2.14 Br38.92%
$C_{22}H_{30}Br_6N_2O_2S_3Te_2$ requires	C22.27 H2.53 N2.36 Br40.49%

4.3.7 Reaction of TMTD/Trichloride Complex with Potassium Iodide

The same procedure as above was adopted using potassium iodide (2.98 g, 18 m mol). The reddish-brown precipitate obtained was filtered off, washed with a little ether and dried in *vacuo*. (M.P. 181°C)

found C17.78 H2.01 N1.91 S6.34%

$C_{22}H_{30}I_6N_2O_2S_3Te_2$ requires C17.99 H2.04 N1.90 S6.54%

4.3.8 An Attempt to React TMTD with Bis(p-ethoxyphenyl) Tellurium Dichloride $(pEtOPh)_2TeCl_2$

$(pEtOPh)_2TeCl_2$ was prepared according to a literature method.(105) TMTD (4.80 g, 20 m mol) in chloroform (20 cm^3) was added dropwise to a solution of $(pEtOPh)_2TeCl_2$ (11.3 g, 20 m mol) with stirring and refluxing. The reaction product was found unchanged even after refluxing for four hours.

4.3.9 Reaction of TMTD with Tellurium Tetrachloride in a Coordinating Solvent

The same procedure and the same amounts of reactants as used in the reaction of TMTD and tellurium tetrachloride in chloroform were used in this reaction, but using dry pyridine instead of dry chloroform as the solvent (the pyridine was redistilled before use in the reaction). The yellow product formed was filtered off immediately and washed with a little dry ether, dried over P_4O_{10} and submitted for analysis as soon as possible.

The reaction was repeated using the same amounts of reactants, but using chloroform (25 cm^3) and pyridine (0.319 g, 40 m mol). The reaction product was analysed fresh and was found to have the same stoichiometry as the above product.

The elemental analyses of the fresh sample, after 7, 14 and 27 days are tabulated below and the precipitate was found to absorb moisture, and decrease the percentages of C, H and N accordingly.

$C_{11}H_{17}N_3OS_3Te$ requires	C26.31	H3.38	N8.37	S19.13	Cl14.15%
found, fresh sample	C25.96	H3.29	N7.85	S18.72	Cl13.55%
after 7 days	C24.56	H3.05	N7.32	S19.15	Cl-
after 14 days	C22.84	H2.96	N7.15	S20.56	Cl-
after 27 days	C18.56	H2.91	N6.92	S21.58	Cl-

4.3.10 Reaction of Freshly Prepared TMTD/Tellurium Tetrachloride/Pyridine Complex with Potassium Bromide

Potassium bromide (1.90 g, 16 m mol) in methanol (25 cm^3) was added dropwise to a solution of TMTD/tellurium tetrachloride/pyridine complex (8.02 g, 16 m mol) in methanol

(25 cm^3) with stirring. Almost immediately on mixing the solutions, the reaction mixture turned orange. This was then heated slightly above room temperature for a few minutes and the product separated by filtration, washed with methanol and ether and dried in vacuo over P_4O_{10}.

found C14.18 H2.37 N5.17 S18.36 Br30.86%

$C_6H_{12}Br_2N_2OS_3Te$ requires C14.07 H2.34 N5.47 S18.76 Br31.27%

4.3.11 Reaction of TMTD/Tellurium Tetrachloride/Pyridine Complex with Potassium Iodide

Potassium iodide (2.65 g, 16 m mol) in methanol was treated as above with the tellurium tetrachloride/pyridine/TMTD complex (8.1 g, 16 m mol) to obtain a dark purple/black precipitate which was recrystallised from acetonitrile to afford shiny purple crystals which melted at 152°C.

found C11.90 H1.95 N4.55 S16.02%

$C_6H_{12}I_2N_2OS_3Te$ requires C11.88 H1.98 N4.62 S15.85%

4.3.12 Reaction of TMTD/Tellurium Tetrachloride/Triphenylphosphine in Benzene

To a clear solution of tellurium tetrachloride (5.38 g, 20 m mol) in dry benzene (25 cm^3) was added dropwise a mixture of TMTD(2.40 g,10 m mol) and triphenylphosphine

2.62 g, 10 m mol) in dry benzene with rapid stirring. The yellow precipitate obtained was filtered, dried over P_4O_{10}. (M.P. 156°C)

(When tellurium tetrachloride in benzene was added to triphenylphosphine in benzene without TMTD, a black precipitate was formed which, on analysis, was found to be elemental tellurium).

found C27.13 H2.58 N2.70 Te12.00%

$C_{24}H_{27}Cl_8N_2PS_4Te_2$ requires C27.66 H2.59 N2.68 Te12.25%

4.3.13 Reaction of TMTD/Tellurium Tetrachloride/Triphenylphosphine Complex with Potassium Iodide

To a solution of the complex (10.41 g, 10 m mol) as prepared above in methanol (50 cm^3) was added a solution of potassium iodide (1.6 g, 10 m mol) in methanol (15 cm^3) with stirring. The mixture afforded a dark brown precipitate which melted at 153°C.

found C11.83 H1.91 N4.71 S15.99%

$C_6H_{12}I_2N_2OS_3Te$ requires C11.88 H1.98 N4.62 S15.85%

4.3.14 Reaction of TMTD/Tellurium Tetrachloride Complex with Metal Salts

4.3.14.1 Reaction with Copper (II) Chloride

Copper chloride dihydrate (0.80 g, 5 m mol) was dissolved in acetone (15 cm^3) and to the resultant solution, the complex TMTD/tellurium tetrachloride (4.77 g, 10 m mol) in acetone (50 cm^3) was added with vigorous stirring; immediately a dark green product separated out and it did not change on subsequent heating at 35°C for 1 hour. The green product was filtered, washed with acetone, ether and dried in *vacuo*-over P_4O_{10}. (M.P. 132°C)

found	C13.45 H2.15 N5.08 S18.01 Cu5.33 Te22.95%
$C_{12}H_{24}Cl_{10}CuN_4S_6Te_2$ requires	C13.23 H2.20 N5.14 S17.64 Cu5.79 Te23.45%

4.3.14.2 Reaction with Cobalt (II) Chloride

The complex TMTD/tellurium tetrachloride (2.39 g, 5 m mol) in acetone (50 cm^3) was added to a solution of cobalt (II) chloride hexahydrate (2.38 g, 10 m mol) in acetone (30 cm^3) and the resultant mixture was heated slightly above room temperature with rapid stirring. The blue product separated out was filtered, washed with acetone, ether and dried in *vacuo*-over P_4O_{10}. (M.P. 206°C) found C14.98 H2.54 N5.92 Cl30.63 S20.48%

$C_6H_{12}Cl_4Co_2N_2S_3$ requires C15.38 H2.56 N5.98 Cl30.34 S20.51%

4.3.14.3 Reaction with Cobalt (II) Bromide

Aquated cobalt (II) bromide (3.27 g, 10 m mol) was dissolved in acetone (50 cm^3) and to this solution, the complex, TMTD/tellurium tetrachloride (2.39 g, 5 m mol) in acetone (50 cm^3), was added with stirring. The reaction mixture was heated slightly,when a blue precipitate was separated out. The precipitate was filtered, washed with acetone and ether and dried in vacuo-over P_4O_{10}.

found C11.08 H1.83 N4.52 Br50.03 S14.27%

$C_6H_{12}Br_4Co_2N_2S_3$ requires C11.14 H1.85 N4.33 Br49.53 S14.86%

4.3.14.4 Reaction with Mercury (II) Chloride

Mercury (II) chloride (2.72 g, 10 m mol) in acetone (50 cm^3) was added to a solution of TMTD/tellurium tetrachloride complex (2.39 g, 5 m mol) in acetone (50 cm^3). The reaction mixture was then stirred at room temperature for 30 minutes during which time a pale yellow precipitate was formed. The product was filtered, washed with acetone and a little methanol and dried in vacuo-over P_4O_{10}.

found C9.62 H1.63 N3.80 Cl18.86%

$C_6H_{12}Cl_4Hg_2N_2S_3$ requires C9.58 H1.59 N3.72 Cl18.91%

4.3.14.5 Reaction with Mercury (II) Bromide

The same procedure as above was adopted with mercury (II) bromide (2.60 g, 10 m mol). The yellow precipitate obtained was washed with acetone, methanol and dried in *vacuo*-over P_4O_{10}.

found C7.81 H1.32 N2.98 Br34.08%

$C_6H_{12}Br_4Hg_2N_2S_3$ requires C7.75 H1.29 N3.01 Br34.45%

4.3.15 Reaction of Selenium Tetrachloride with TMTD in Chloroform

TMTD (2.40 g, 10 m mol) dissolved in dry chloroform (20 cm^3) was added to a solution of selenium tetrachloride (4.42 g, 20 m mol) in dry chloroform (25 cm^3) under nitrogen atmosphere. Immediately after mixing the two solutions a dark yellow product separated out. The mixture was stirred for a further 30 minutes at 35°C and the product was filtered, washed with a little chloroform and ether, and dried in *vacuo*-over P_4O_{10}.

found C14.82 H2.45 N5.75 Cl15.83%

$C_6H_{12}Cl_2N_2O_3S_3Se_2$ requires C14.84 H2.47 N5.77 Cl15.90%

$C_6H_{12}Cl_2N_2OS_4$ could also be a possible empirical formula but the enhancing crosslink density and the acceleration with natural rubber vulcanizates containing TMTD and selenium tetrachloride certainly shows sulphur is entering the medium in a reactive form thus deleting this possibility.

4.3.16 Reaction of TMTD/Selenium Tetrachloride Complex with Water

To the complex (4.46 g, 10 m mol) as prepared above was added water (50 cm^3) and stirring commenced rapidly at 50°C. An orange precipitate separated out which was subsequently filtered, washed with water, ether and dried *in vacuo* over P_4O_{10} and then over concentrated H_2SO_4.

found	C 16.82	H 2.81	N 6.55%
$C_6H_{12}N_2O_4S_3Se_2$ requires	C 16.74	H 2.79	N 6.51%

4.3.17 Reaction of Selenium Dioxide/TMTD in Aqueous Hydrochloric Acid

To a solution of selenium dioxide (2.22 g, 20 m mol) dissolved in concentrated HCl (20 cm^3) was added a suspension of TMTD (2.40 g, 10 m mol) in water (25 cm^3) with rapid stirring. Almost immediately, an orange precipitate separated out, which was then filtered, washed with water, ether and dried *in vacuo* over P_4O_{10} and then over concentrated H_2SO_4.

found	C 15.51	H 2.62	N 5.93	Cl 14.80%
$C_6H_{12}N_2O_4S_3Se_2$ requires	C 16.74	H 2.79	N 6.51%	
$C_6H_{12}Cl_2N_2O_3S_3Se_2$ requires	C 14.84	H 2.47	N 5.77	Cl 15.90%

4.3.18 Reaction of Selenium Tetrachloride/TMTD Complex (Prepared in Chloroform) with Potassium Bromide

Potassium bromide (2.38 g, 20 m mol) dissolved in methanol (50 cm^3) was added to a solution of TMTD/selenium tetrachloride complex (4.46 g, 10 m mol) in the same solvent (50 cm^3). A brownish orange precipitate separated out upon heating the mixture slightly above room temperature. The product was filtered, washed with methanol, ether and dried in <u>vacuo</u>-over P_4O_{10}.

found	C 12.64	H 2.10	N 4.91	Br 27.64%
$C_6H_{12}Br_2N_2O_3S_3Se_2$ requires	C 12.54	H 2.09	N 4.87	Br 27.87%

4.3.19 Reaction of Selenium Tetrabromide/TMTD Complex in Chloroform

Fresh selenium tetrabromide was prepared by adding bromine (1.60 g, 10 m mol) in dry chloroform to a suspension of selenium (3.9 g) in dry chloroform under nitrogen, with rapid stirring. The excess bromine was flushed with nitrogen while heating the mixture at 40°C. To the fresh selenium tetrabromide so prepared, was added dropwise a solution of

TMTD (1.20 g, 5 m mol) with vigorous stirring. The orange precipitate formed was filtered, washed with dry ether and dried in vacuo-over P_4O_{10}.

found C 10.15 H 1.70 N 3.95 Br 44.28%

$C_6H_{12}Br_4N_2O_2S_3Se_2$ requires C 10.02 H 1.67 N 3.89 Br 44.56%

4.3.20 Reaction of Selenium Tetrachloride/TMTD Complex (Prepared in Dry Chloroform) with Potassium Iodide

Potassium iodide (3.32 g, 20 m mol) dissolved in methanol (50 cm^3) was treated with a solution of TMTD/selenium tetrachloride complex (4.46 g, 10 m mol) in the same solvent (50 cm^3) with stirring and heating at 40°C. The dark purple material obtained was filtered, washed with methanol, ether and dried in vacuo-over P_4O_{10}.

found C 11.00 H 1.80 N 4.25%

$C_6H_{12}I_2N_2O_3S_3Se_2$ requires C 10.77 H 1.73 N 4.19%

4.3.21 Reaction of Selenium Tetrachloride/TMTD in Pyridine

To a solution of selenium tetrachloride (4.42 g, 20 m mol) in dry pyridine (30 cm^3) was added dropwise a solution of TMTD (2.40 g, 10 m mol) in dry pyridine (30 cm^3) with rapid stirring under nitrogen. The orange precipitate formed was filtered, washed with dry ether and dried in vacuo-over P_4O_{10}.

found C 16.70 H 2.72 N 6.25%

$C_6H_{12}N_2O_4S_3Se_2$ requires C 16.74 H 2.79 N 6.51%

4.4 Results

4.4.1 Syntheses

A series of previously unknown tellurium complexes were synthesised directly from the reaction between tellurium (IV) compounds and TMTD. Some of the reactions were repeated with selenium tetrahalides using TMTD as the ligand to afford a new class of complexes which are different from the corresponding tellurium complexes. It seems that selenium tetrachloride easily forms oxychloride before reacting with the ligand, thus the final products always contain oxygen in the reactions with selenium tetrachloride. However, all the reactions seem to eliminate sulphur from TMTD, which is the essential element in NR vulcanization. The resulting ligand coordinates to tellurium or selenium giving complexes of which the structures and the properties were studied.

The above reactions were carried out using dry chloroform as the solvent. Interestingly when pyridine was used as the solvent for the tellurium tetrachloride reaction, pyridine seems to coordinate to central tellurium atom. The reaction product is moisture sensitive and looses the coordinated pyridine when reacted with KBr or KI.

When an alternative Lewis base, triphenylphosphine, was used in a benzene solution, a yellow complex containing two moles of tellurium tetrachloride was formed. It is known(106) that the reaction of tellurium tetrachloride with triphenylphosphine eliminates elemental tellurium. Hence, a mixture of TMTD and triphenylphosphine in benzene was added to a solution of tellurium tetrachloride in dry benzene.

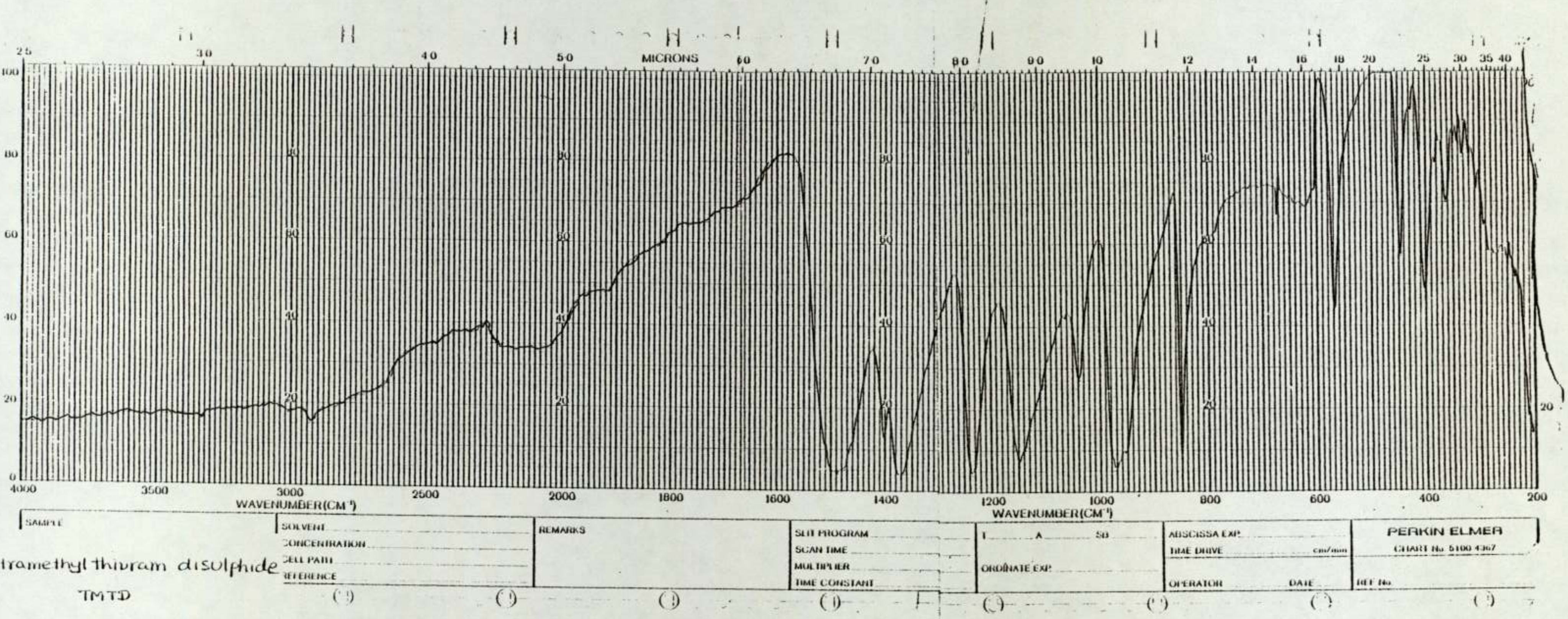
It was also of interest to observe that the complex derived from tellurium tetrachloride and TMTD reacts with other metal salts, hence salts of Co^{2+}, Cu^{2+} and Hg^{2+} were reacted with the complex and the products were characterised.

4.4.2 Vibrational Spectra

The infra-red spectra of TMTD, TMTM and the complex derived from TMTD and tellurium tetrachloride are shown in Figures 4.2a, 4.2b and 4.3. Figure 4.4 shows the far infra-red spectrum of the complex. This was recorded on a polyethylene disc, in a nitrogen environment.

The infra-red spectra of fresh and decomposed $RTeCl_3$/TMTD (where R=pEtOPh) is shown in Figure 4.8. Figure 4.9 shows the infra-red spectrum of pyridine and Figure 4.10 shows the TMTD/$TeCl_4$ complex derived from a pyridine medium.

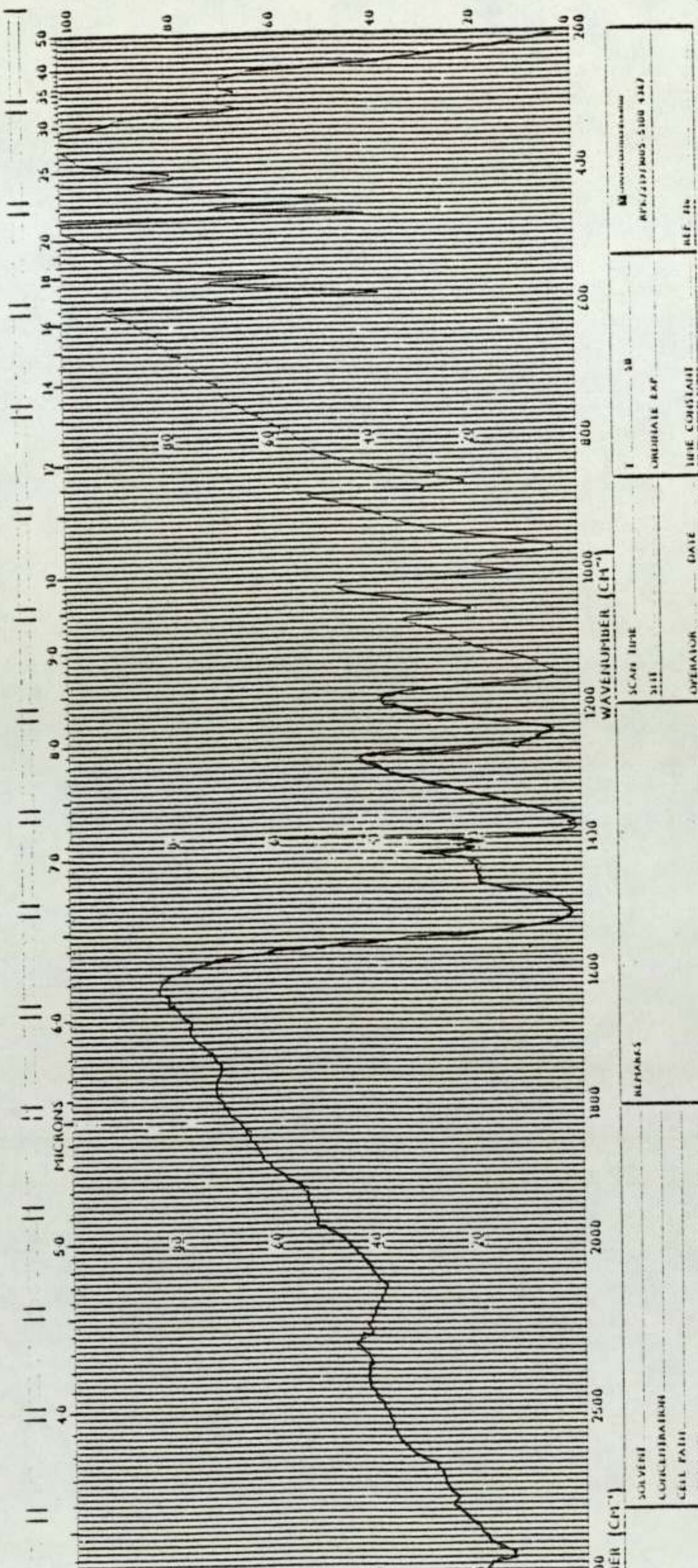
The infra-red spectra of Co^{2+} and Cu^{2+} complexes derived by reacting the $TeCl_4$/TMTD complex with Co^{2+} and Cu^{2+} salts



Tetramethyl thiuram disulphide

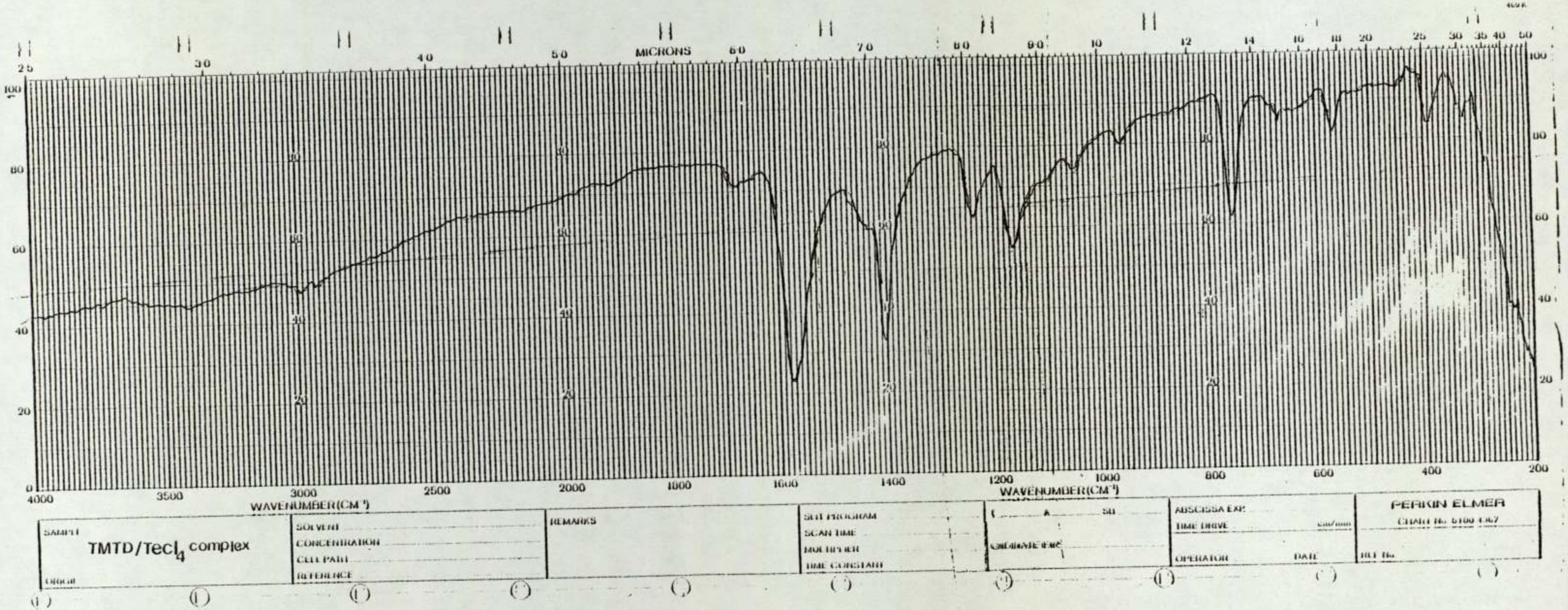
TMTD

Figure 4.2a



MICRONS
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)
SAMPLE
TMTM
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN TIME
SLIT
OPERATOR
DATE
TIME CONSTANT
ORDINATE EXP
REF. No

Figure 4.2b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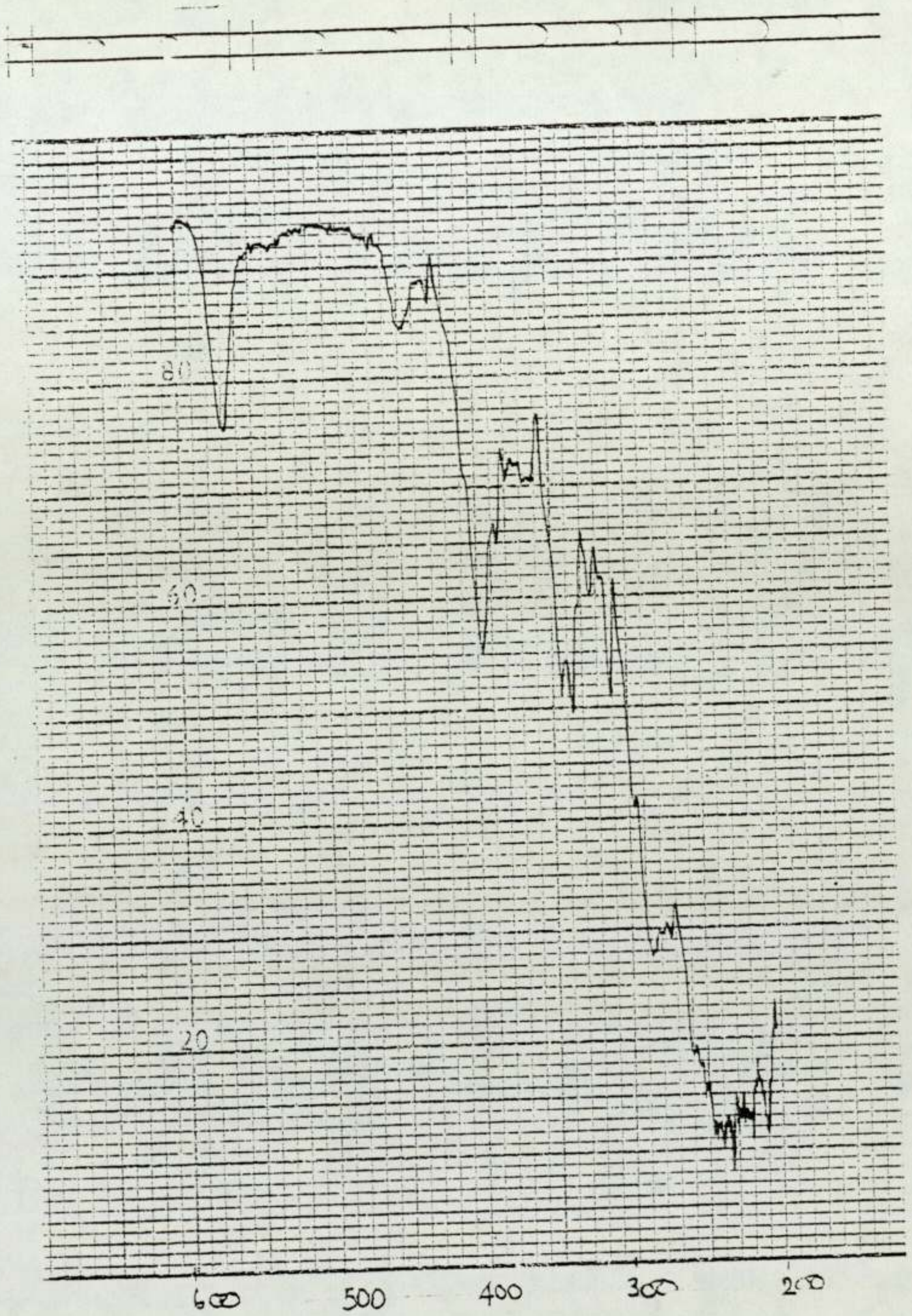
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER(CM⁻¹)
SAMPLE
TMTD/TeCl$_4$ complex
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SLIT PROGRAM
SCAN TIME
MULTIPLIER
TIME CONSTANT
ABSCISSA EXP.
TIME DRIVE
OPERATOR
DATE
PERKIN ELMER
REF. No.

Figure 4.3



TeCl$_4$ / TMTD Complex

Far-infrared spectrum

PK/216/1004 471-5027

Intek

Figure 4.4

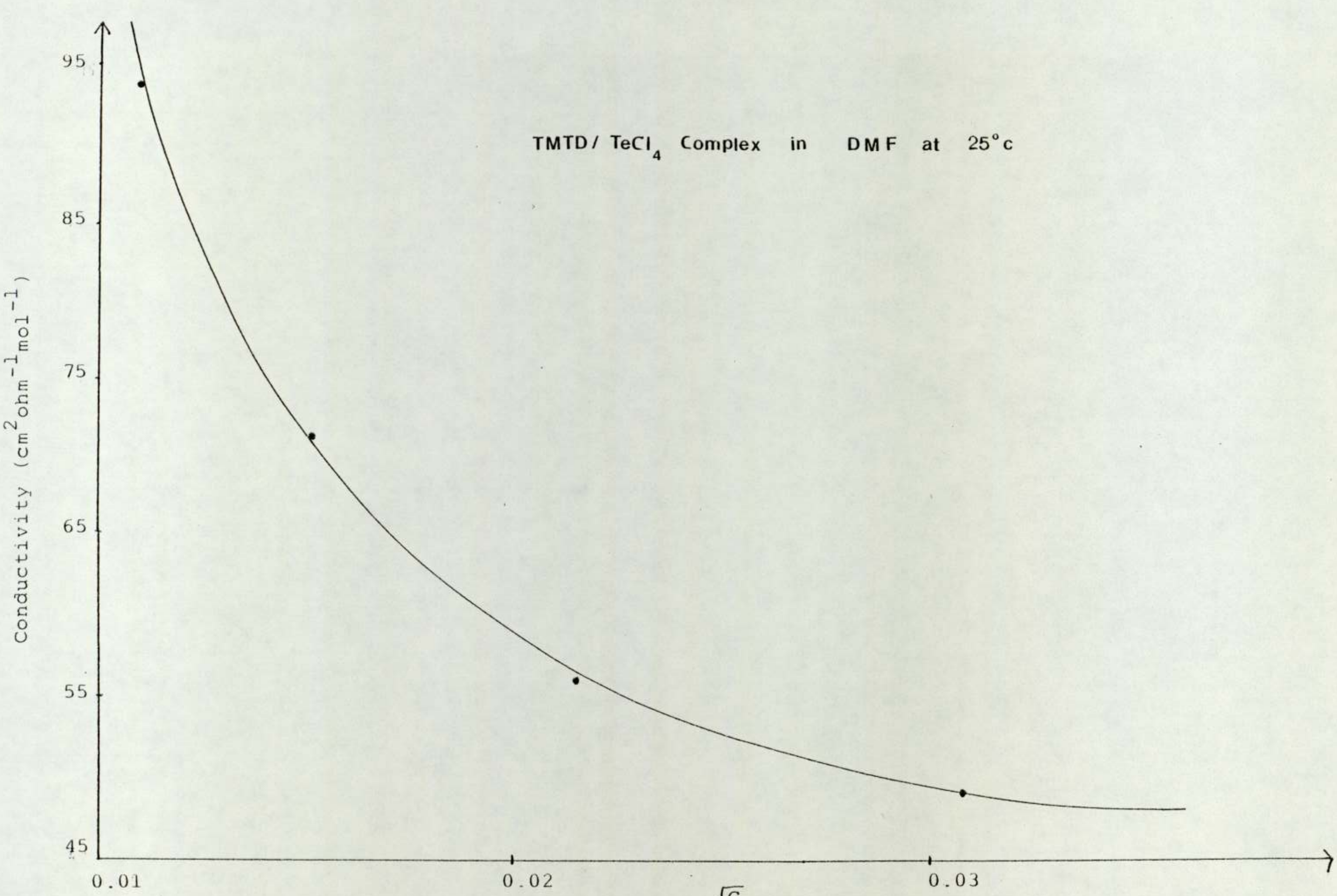

TMTD / TeCl$_4$ Complex in DMF at 25°c
Conductivity (cm^{2}ohm^{-1}mol^{-1})
95
85
75
65
55
45
0.01
0.02
0.03
$\sqrt{C}$

Figure 4.5

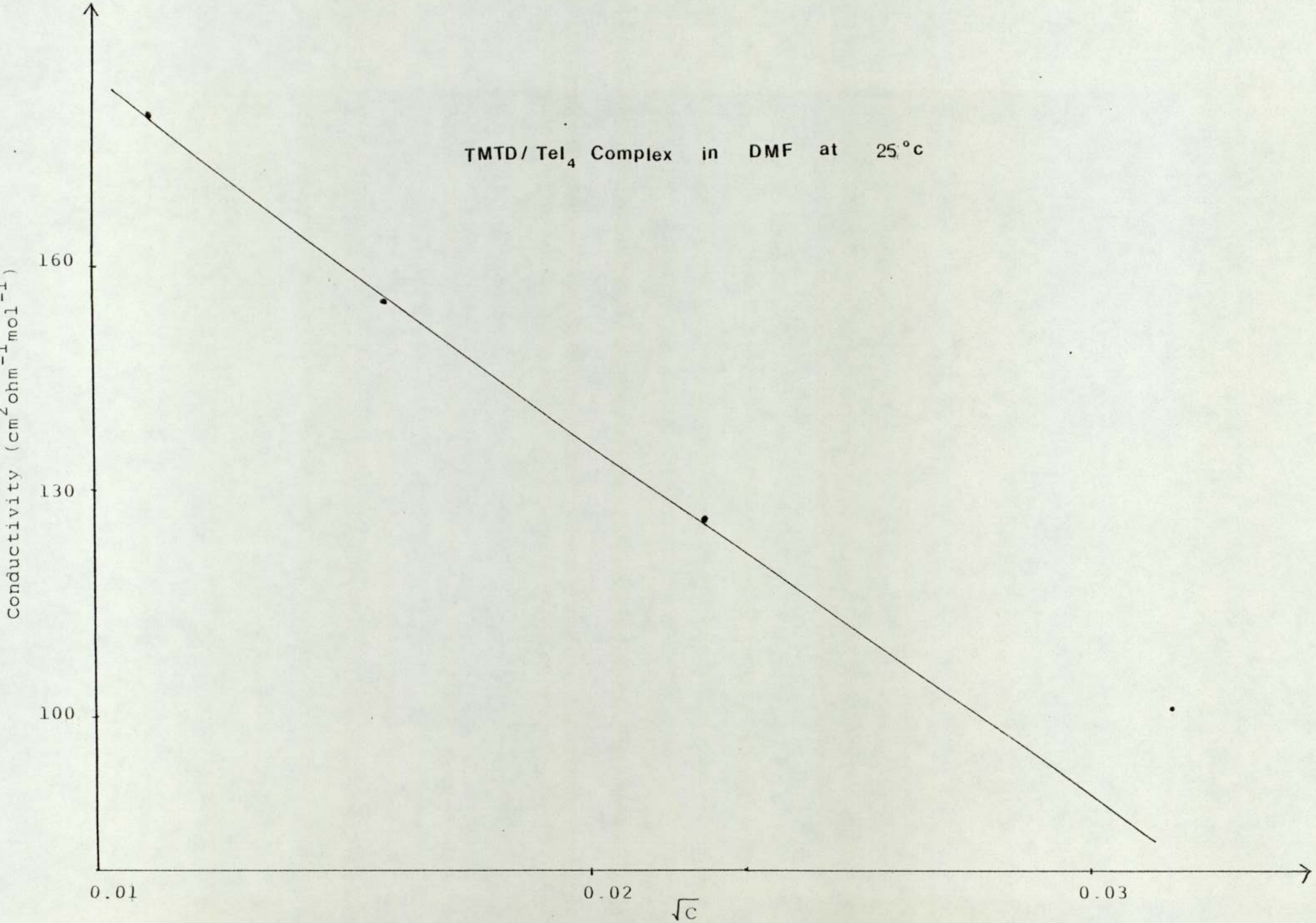

TMTD/ TeI$_4$ Complex in DMF at 25 °c

Figure 4.6

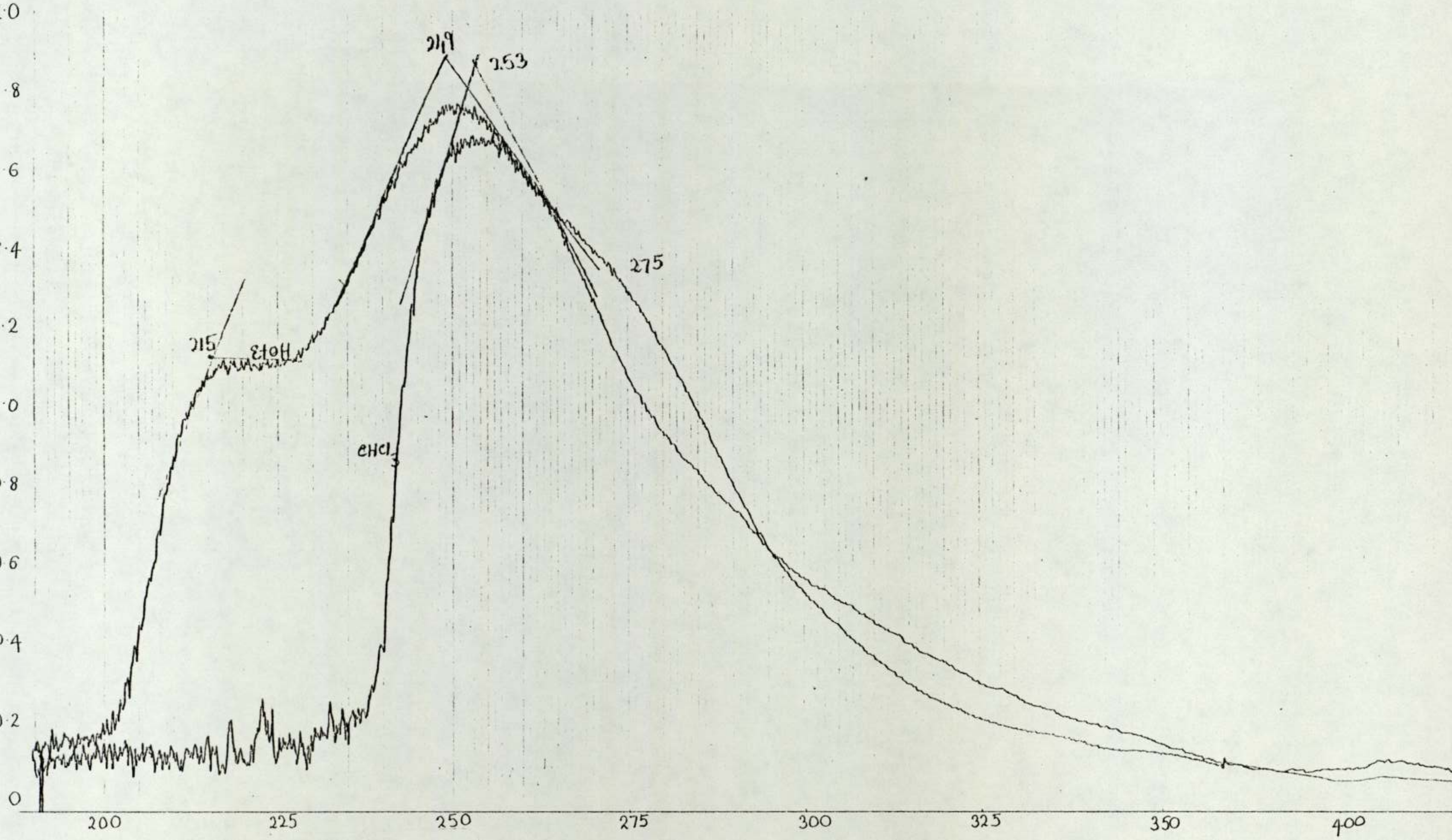


Figure 4.7 TMTD . TeCl$_4$ complex

(UV Spectrum)

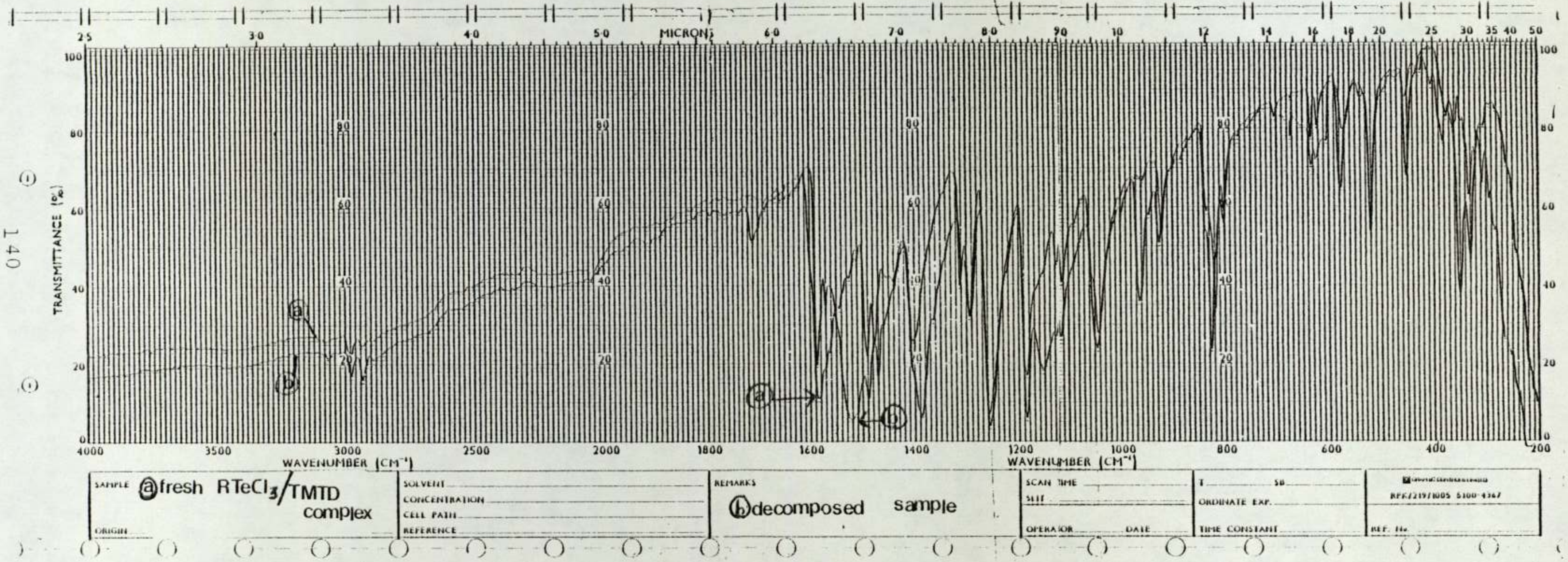

MICRONS
TRANSMITTANCE (%)
WAVENUMBER (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
2·5
3·0
4·0
5·0
6·0
7·0
8·0
9·0
10
12
14
16
18
20
25
30
35
40
50
0
20
40
60
80
100
a
b
SAMPLE a fresh RTeCl3/TMTD complex
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS b decomposed sample
SCAN TIME
SLIT
OPERATOR
DATE
T
SB
ORDINATE EXP.
TIME CONSTANT
RFK/219/1005 5100-4347
REF. No.

Figure 4.8

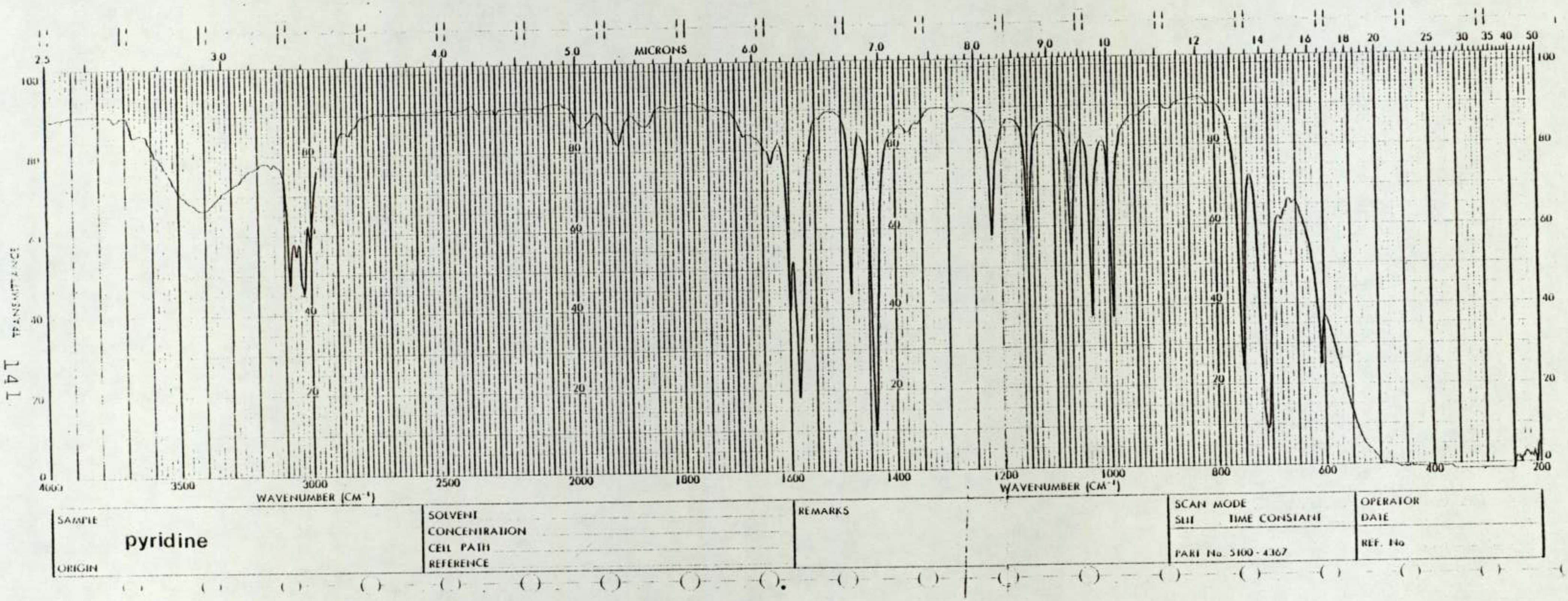
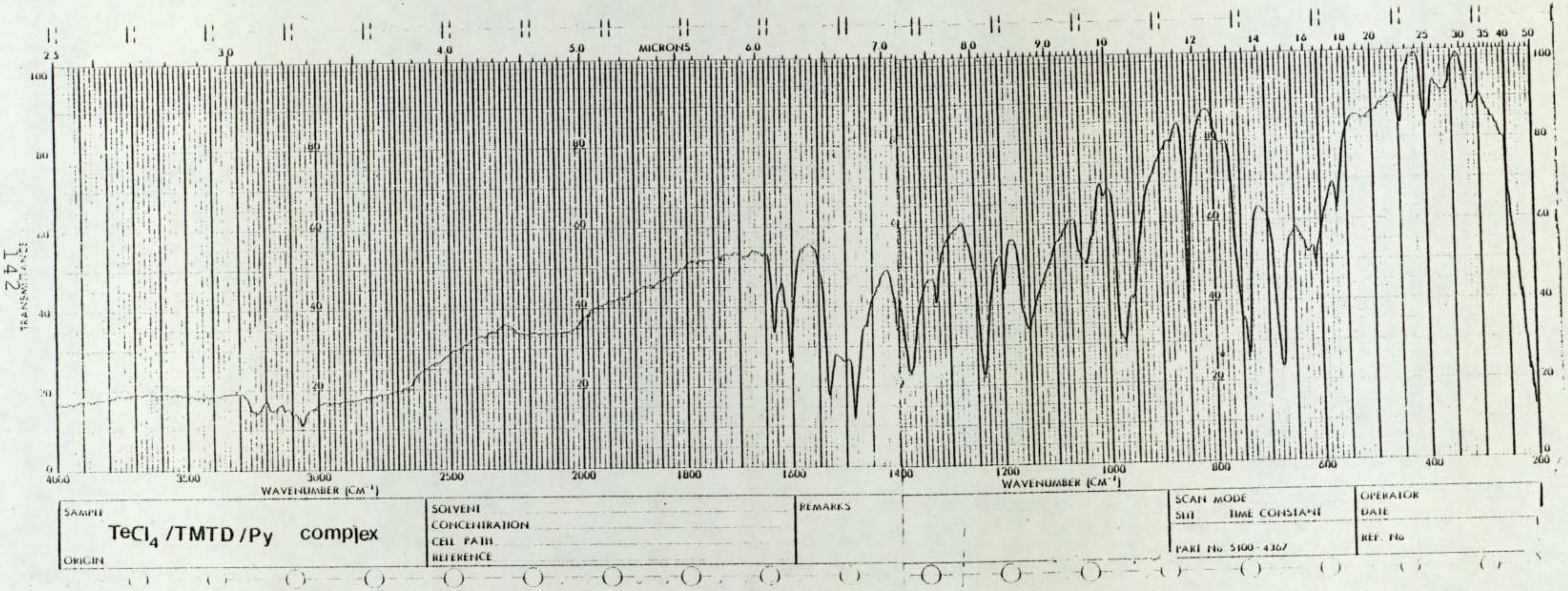

MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
WAVENUMBER (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
TRANSMITTANCE
100
80
60
40
20
0
SAMPLE
pyridine
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN MODE
SLIT
TIME CONSTANT
PART No. 5100 - 4367
OPERATOR
DATE
REF. No

Figure 4.9



SAMPLE $TeCl_4$ /TMTD/Py complex

Figure 4.10

are illustrated in Figures 4.11 and 4.12 respectively. The principal absorption bands for these complexes are tabulated in Table 4.5.

4.4.3 Conductivity Measurements

The conductivity data for the complexes derived from TMTD and $TeCl_4$ and its bromo- and iodo- derivatives in DMF at 25°C are tabulated in Table 4.1. The graphs of molar conductivity against $(concentration)^{\frac{1}{2}}$ for the chloro- and iodo-complexes are shown in Figures 4.5 and 4.6 respectively.

Table 4.2 shows the conductivity measurements for the other tellurium complexes and for the selenium complexes in DMF, whereas Table 4.6 shows the conductivity data for the transition metal complexes in acetonitrile at 25°C.

4.4.4 Mössbauer Data

The Mössbauer data for some hexahalo- and pentahalotellurates and for the complexes prepared with TMTD and tellurium tetrahalides are tabulated in Tables 4.3 and 4.4 respectively.

4.4.5 Magnetic Measurements

The solid state data for the Co^{2+} and Cu^{2+} complexes are gathered in Table 4.8.

4.4.6 Electronic Spectra

The absorption bands in the visible region for the Co^{2+} and Cu^{2+} chloride complexes are tabulated in Table 4.7.

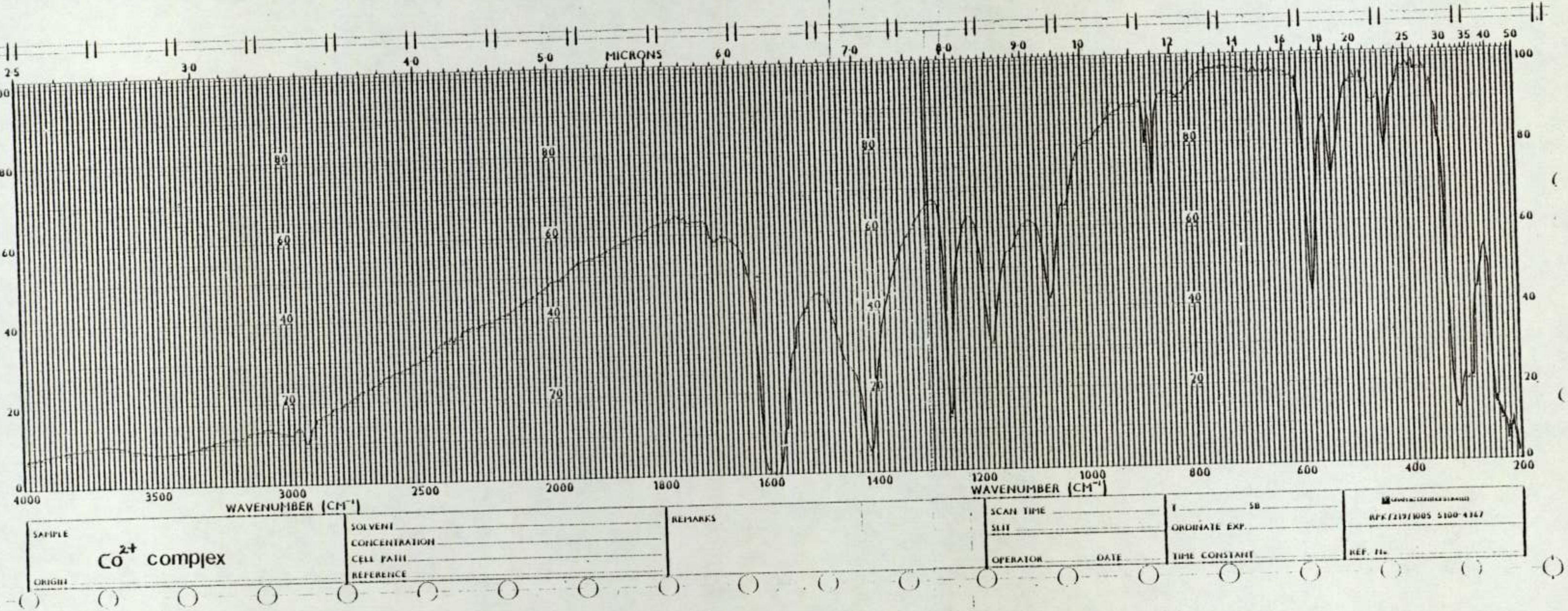

MICRONS
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
SAMPLE
Co^{2+} complex
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN TIME
SLIT
OPERATOR
DATE
ORDINATE EXP.
TIME CONSTANT
REF. No
RPF/219/1005 5100-4367

Figure 4.11

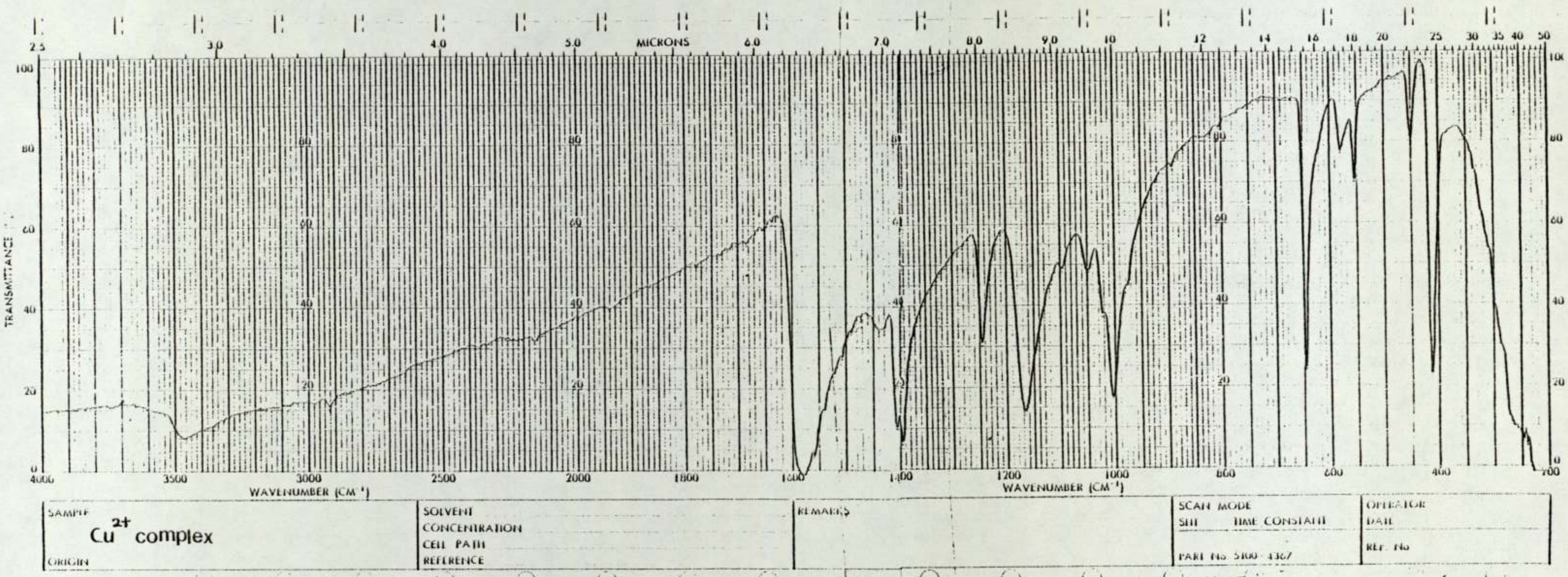

MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
TRANSMITTANCE
100
80
60
40
20
0
WAVENUMBER (CM⁻¹)
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
SAMPLE
Cu^{2+} complex
ORIGIN
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
SCAN MODE
SLIT
TIME CONSTANT
PART No 5100-4367
OPERATOR
DATE
REF. No

Figure 4.12

Concentration	$TeCl_4$/TMTD complex**	$TeBr_4$/TMTD complex***	TeI_4/TMTD complex
1.0×10^{-3}	49	52	103
0.5×10^{-3}	55	61	128
0.25×10^{-3}	70	93	157
0.125×10^{-3}	92	136	175

* The value characteristic for a 1:1 electrolyte in DMF at 25°C lies in the range 55-75 $cm^2 ohm^{-1} mol^{-1}$.

** The molar conductivity value for this complex in nitromethane (in which solvation is not very strong) gives a value 40 $cm^2 ohm^{-1} mol^{-1}$. The range for a 1:1 electrolyte in nitromethane is 70-90 $cm^2 ohm^{-1} mol^{-1}$.

*** The molar conductivity value for the bromo- complex in nitromethane shows a value of 67 $cm^2 ohm^{-1} mol^{-1}$. However, the values obtained here on dilution did not fit into either a characteristic curve of a weak electrolyte or a straight line of a 1:1 electrolyte.

Table 4.1 Conductivity measurements in DMF* at 25°C for the complexes derived from tellurium tetrahalides and TMTD

complex	molar conductivity measurement in DMF at 25°C	
$RTeCl_3$/TMTD complex	46	weak electrolyte
$RTeCl_3$/TMTD complex with KBr	98	approaching to a value of 1:2 electrolyte
$RTeCl_3$/TMTD complex with KI	160	1:2 electrolyte
$TeCl_4$/TMTD/pyridine complex	39	weak electrolyte
$TeCl_4$/TMTD/pyridine complex with KI	45	weak electrolyte
$TeCl_4$/TMTD/PPh_3 complex	58	1:1 electrolyte
$SeCl_4$/TMTD complex	28	weak electrolyte
$SeBr_4$/TMTD complex	91	approaching a value of 1:2 electrolyte
$SeCl_4$/TMTD complex with KBr	30	weak electrolyte

Table 4.2

Compound	δ* (isomer shift) ($\pm$0.08 mm s^{-1})	Γ (line width) ($\pm$0.1 mm s^{-1})
$(NH_4)_2TeCl_6$	1.72	6.8
$(n\text{-}Bu_4N)_2TeCl_6$	1.70	6.6
$(PhH)_2TeCl_6$	1.63	7.1
$(n\text{-}Bu_4N)_2TeCl_4Br_2$	1.54	6.5
$(Et_4N)_2TeCl_4Br_2$	1.46	7.6
$(Et_4N)_2TeCl_4I_2$	1.55	6.9
$(n\text{-}Bu_4N)_2TeBr_4I_2$	1.43	5.8
$(Et_4N)TeCl_5$	1.49	7.7
$(Et_4N)TeBr_4Cl$	1.44	7.0
$(Et_4N)TeBr_5$	1.41	7.2

* Isomer shift with respect to I/Cu source, and absorbers at 4.2K. All spectra were single lines.

Table 4.3 ^{125}Te Mössbauer parameters of some hexahalo- and pentahalotellurates.

Single line spectra (no observable quadrupole splitting)	δ *(isomer shift) ($\pm$0.23mms^{-1})	Γ (line width) ($\pm$1.0mms^{-1})	
TMTD/TeCl$_4$ complex	1.14	15.82	
TMTD/TeBr$_4$ complex	0.74	14.03	
TMTD/TeI$_4$ complex	1.53	12.79	
Two line spectra (observable quadrupole splitting)	δ *(isomer shift) (mms^{-1})	Δ (quadrupole splitting) (mms^{-1})	Γ (line width) (mms^{-1})
TMTD/TeCl$_4$ complex	0.84$\pm$0.55	6.33$\pm$0.90	6.69$\pm$0.7
TMTD/TeBr$_4$ complex	0.70$\pm$0.41	6.79$\pm$0.82	6.37$\pm$0.7
TMTD/TeI$_4$ complex	1.26$\pm$0.30	5.39$\pm$0.60	7.20$\pm$0.6

* δ with respect to I/Cu source and absorber at 77K.

Table 4.4 ^{125}Te Mössbauer parameters for the complexes prepared from TMTD and tellurium tetrahalides

Compound	$\nu_{(C=N)}$ cm^{-1}	$\nu_{(C=S)}$ cm^{-1}	Others
Complex with $CuCl_2$ ($CuL_2Te_2Cl_{10}$)	1575	1000(s)	260 $\nu_{(Cu-Cl)}$ 400(s)$\nu_{(Cu-N)}$
Complex with $CoCl_2$ (Co_2LCl_4)	1590	885(s) 875	316(vs) $\nu_{(Co-Cl)}$ 279(m) $\nu_{(Co-Cl)}$
Complex with $CoBr_2$ (Co_2LBr_4)	1590(s)	885(s) 880	275(s) $\nu_{(Co-Br)}$
Complex with $HgCl_2$ (Hg_2LCl_4)	1585(s)	875(s)	305(m) $\nu_{(Hg-Cl)}$ 326(m) $\nu_{(Hg-Cl)}$
Complex with $HgBr_2$ (Hg_2LBr_4)	1586(s)	872(s)	650 $\nu_{(C-S)}$

where $L=C_6H_{12}N_2S_3$

Table 4.5 Principal absorption bands in the infra-red spectra (KBr disc) cm^{-1} of the Co^{2+}, Cu^{2+} and Hg^{2+} containing complexes

complex**	molar conductance
complex with $CoCl_2$	57
complex with $CoBr_2$	60
complex with $CuCl_2$	179
complex with $HgCl_2$	20
complex with $HgBr_2$	25

* The range for a 1:1 electrolyte in acetonitrile is 90-130$cm^2ohm^{-1}mol^{-1}$

** All the complexes were prepared by reacting these salts with the complex derived from tellurium tetrachloride and TMTD

Table 4.6 Molar conductivity measurement in acetonitrile* at 25°C ($cm^2ohm^{-1}mol^{-1}$)

complex	ν (nm)	ε
$CoCl_2$ complex (Co_2LCl_4)	676 606	592 360
$CuCl_2$ complex (Cu_2LCl_4)	634	-

where $L=C_6H_{12}N_2S_3$

Table 4.7 Absorption bands in the visible spectra

complex	μ_{eff} (BM) at 298°K
complex with $CoCl_2$ (Co_2LCl_4)	4.48 ± 0.05
complex with $CoBr_2$ (Co_2LBr_4)	4.50 ± 0.05
complex with $CuCl_2$ ($CuL_2Te_2Cl_{10}$)	1.91 ± 0.05

where $L = C_6H_{12}N_2S_3$

Table 4.8 Solid state data

The electronic spectrum for the complex derived from $TeCl_4$ and TMTD is shown in Figure 4.7.

4.5 Discussion

Although all the complexes described in this chapter are derived from TMTD, it seems, as explained in the previous chapter, that one of the sulphur atoms from the disulphide is entering the reaction medium, leaving that monosulphide TMTM coordinating to tellurium (IV) atom forming stable complexes. Hence it is plausible to compare certain differences in the infra-red spectrum of TMTM rather than TMTD with the complexes derived from tellurium (IV) complexes with TMTD.

4.5.1 Tellurium Tetrachloride/TMTD Complex and its Bromo- and Iodo- Derivatives

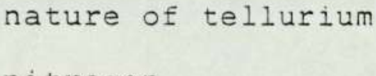
4.5.1.1 Infra-red Spectra

The vibrational analyses of compounds containing tellurium-sulphur bonds have been limited to compounds where thiourea, mercapto-acid and thiosulphate are ligands. Aynsley and coworkers(107) were the first research workers to study the spectra of compounds containing tellurium sulphur bonds.

Al-Turaihi(71) synthesised and characterised the reaction products of tellurium halides with a number of heterocyclic ligands as sulphur donors. Hendra and Javic(108) published the infra-red and Raman spectra of $Te(tu)_4Cl_2$, $Te(tu)_2Cl_2$ and $Te(tu)_2Br_2$ (where tu=thiourea) and a band at 225 cm^{-1} was assigned for the Te-S vibration.

The infra-red spectra of all the complexes derived from tellurium tetrahalides and TMTD are similar and are less complex than expected. This may indicate a more symmetric environment around the tellurium atom in the complexes. Certain important differences between the spectra of the complexes and the free ligand TMTM are discussed below.

The infra-red spectrum of the chloro- complex (derived from $TeCl_4$ and TMTD) (Figure 4.3), shows that the band at 1506 cm^{-1} in TMTM (Figure 4.2b)has shifted to a higher frequency, 1578 cm^{-1}, as expected upon complex formation. This may be due to the delocalization of the negative charge on nitrogen, thus increasing the double bond nature of the C-N bond.



$R_2N^{\delta-}$—$C^{\delta+}$=S—Te

Both nitrogen and sulphur in the ligand could act as co-ordinating centres but according to Pearson(109), the soft nature of tellurium atom would prefer soft sulphur to hard nitrogen.

The intensities of the band at 965 cm^{-1} and 582 cm^{-1} which are assigned as $\nu_{(C=S)}$ and $\nu_{(C-S)}$ respectively have greatly reduced in the complex. However, the new intense band appearing at 755 cm^{-1} could probably be a combination of decreased $\nu_{(C=S)}$ and increased $\nu_{(C-S)}$ vibrations in the complex, of which the structure will be discussed later.

Filippo and Preti(110) reported the preparation of metal complexes with a sulphur containing ligand, thiomorpholin-3-one($SCH_2CH_2NHCOCH_2$) and suggest that the increase in $\nu_{(C-O)}$ is due to the metal-sulphur bonding in the complexes. The weak band at 562 cm^{-1} in the free ligand has shifted to a lower frequency, and this weakening could result from electron withdrawal from the sulphur atom due to its coordination to the metal atom, assuming that this band arises mainly from the contribution of C-S stretching vibrations. They also pointed out that it is particularly difficult to assign the C-S vibrations according to the literature(111).

Though the vibrational spectroscopic technique is a powerful tool for structural investigations, some ambiguous and indecisive cases can occur for the interpretation of the far infra-red spectra of complex molecules. A very good example is shown by the studies of tellurium tetrachloride(102,113). Both covalent and ionic structures based on ψ-trigonal bipyramid(103) have been proposed for tellurium tetrachloride using infra-red data, although the X-ray crystallographic studies showed a cubane like structure(104).

The complex formed with TMTD and tellurium tetrachloride will simply have a structure with C_{2v} symmetry based on tellurium tetrachloride crystal structure. Thus the band appearing at 283 cm^{-1}, which has split into four, could be assigned as $\nu_{(Te-Cl)}$ (Figure 4.4). The far infra-red data were recorded as polyethylene discs, for all the complexes.

4.5.1.2 Molar Conductivity Measurements

Table 4.1 shows the molar conductivities of the tetrahalide complexes together with values characteristic for a 1:1 electrolyte in both DMF and nitromethane. The low conductivity value of the chloro- complex, about 40 $cm^2ohm^{-1}mol^{-1}$ in nitromethane suggests that it is a non-electrolyte (see Figure 4.5). However, this value is too high for a non-electrolyte, probably due to the partial solvolysis of the complex that may have taken place(112).

The molar conductance of tetrabromo- and tetraiodo- complexes in nitromethane and DMF respectively are found to be 67 and 103 $cm^2ohm^{-1}mol^{-1}$. These values show that the latter is fully dissociated in DMF. (Note: The range for a 1:1 electrolyte in nitromethane and DMF at 25°C are 70-90 and 55-75 $cm^2ohm^{-1}mol^{-1}$ respectively). Hence, it could be suggested that the iodo- complex is a 1:1 electrolyte in DMF(114).

The graphs of molar conductivity against $(\text{concentration})^{\frac{1}{2}}$

for the chloro- and iodo- complexes are shown in Figures 4.5 and 4.6.

4.5.1.3 Structures

Since the ligand exhibits two modes of coordination in these complexes, it is possible to suggest the structures shown in Figures 4.13(a-c). However, it is of interest to know whether the soft nature of tellurium will favour sulphur bonding and/or the greater electronegativity of nitrogen will be required to accommodate the electron density associated with the non-bonding molecular orbital in tellurium as shown in Figures 4.13b and 4.13c.

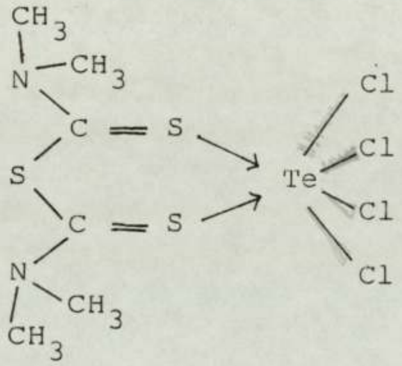


Figure 4.13a

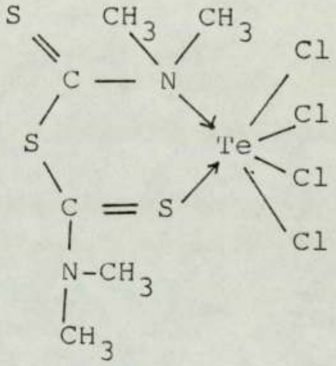


Figure 4.13b

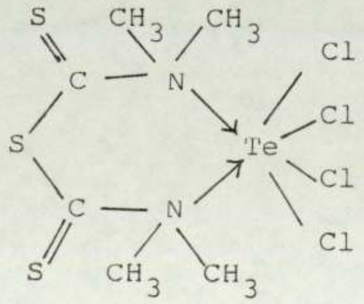


Figure 4.13c

Although it is not possible to be certain, it seems reasonable to argue that the structure shown in Figure 4.13a is most suitable for the chloro- complex when the following two factors are considered:

i. The infra-red spectrum of the complex with an increase in $\nu_{(C-N)}$ and the absence of free $\nu_{(C=S)}$.

ii. Even though it was not possible to obtain a better spectrum for ^{1}H NMR, it was good enough to identify only one type of ^{1}H in the complex, and the concentration of the solutions are fair enough to show if there is $^{125}Te-^{1}H$ coupling, which is not seen in the spectrum. It seems probable that there would be a greater chance of observing coupling if Figures 4.13b and 4.13c were applicable.

Thus these two points help to rule out the structures shown in Figures 4.13b and 4.13c.

The six-membered ring may be planar and strained if π electron delocalization is important (overall symmetry, C_{2v}). Alternatively, the ring may pucker (overall symmetry, C_s).

There is strong evidence that in hexahalotellurates tellurium (IV) is generally found in an octahedral environment. The demonstration by X-ray crystallographic examination of a number of hexahalotellurate (IV) salts(115-118) e.g., K_2TeBr_6(66), $(NH_4)_2TeBr_6$(116), Cs_2TeBr_2(116) and K_2TeI_6(117) indicates that the complex anion have regular octahedral symmetry. However, two instances of distorted $TeCl_6^{2-}$ have been reported(67,119).

The existence of these regular environments has been explained either in terms of the accommodation of the $5s^2$- electrons in a_{1g} antibonding orbitals(78), or in terms of the absence of distorting crystal field effects(120,121). Donaldson and Silver(122) have suggested that the intense colour of salts of TeX_6^{2-} may be attributed to the population of conduction bands in the solid, thus when the $5s^2$- pair plays no steric role, electron density may be forced into conduction bands which probably involve halogen d orbitals.

The complexes obtained by the reaction of tellurium tetrahalides with TMTD are coloured suggesting these complexes may have a regular octahedral environment around tellurium (IV).

Mössbauer spectroscopy is in principle a good way of determining the stereochemical activity of s- electrons since participation of the s- orbital in a hybrid set suitable for inducing stereochemical activity from the lone pair should reduce δ below values typical of the hexahalotellurates or species such as $[TeCl_4Br_2]^{2-}$ which are octahedral. However, the range of δ values is small for tellurium (IV) compounds and the errors are often large, hence conclusions must be drawn with care.

The Mössbauer data of the complexes obtained with TMTD and tellurium tetrahalides could either be fitted to single peaks with very large line widths ($\sim$15 mms^{-1}) or two peaks with observable quadrupole splittings ($\sim$7 mms^{-1}).

When the conductivity data of the iodo- complex is considered, it gives strong evidence that this complex is ionic and a strong electrolyte (Figure 4.6). Hence the structure of the iodo- complex could be viewed as a five-coordinated and hence a square pyramidal structure(62) with a stereochemically active lone pair. Thus for the iodo- complex a two line Mössbauer spectrum is acceptable. Some reported Mössbauer isomer shifts and line widths for five-coordinated pentahalo- and organo-tetrahalo- complexes(Table 4.3) by Jones et al(123) are in good agreement with the isomer shift and quadrupole splitting obtained for the iodo- complex (Table 4.4).

The acceptance of two line spectra may not be good when comparing the chloro- and bromo- complexes since the far-infra-red spectrum shows the presence of four tellurium-chlorine bonds in the chloro- complex, and the non-electrolyte properties of the chloro- and bromo- complexes, suggest non-ionic structures in their solid states. Hence, if two line spectra for these two complexes are applicable, five-co-ordinated structures, with the possibility of a monodentate sulphur ligand, must be considered. This situation could be achieved either by forming a S-Te coordination bond through the sulphur atom attached to two carbon atoms (thio-ether) as shown in Figure 4.14a or by a sulphur atom in one of the C=S bonds as shown in Figure 4.14b.

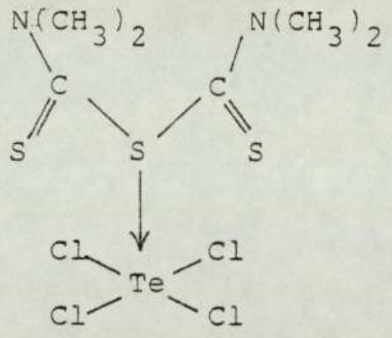


Figure 4.14a

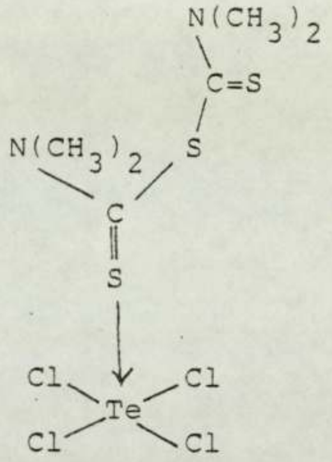


Figure 4.14b

However, these types of monodentate ligands are not consistent with the observed high frequency infra-red data.

The Mössbauer data could also be fitted to a single line for the chloro- and bromo- complexes. In which case the possibility of octahedral structures for these two complexes may be considered. However, the large line widths, which are much higher than the other known hexahalotellurates are disappointing. Therefore the quality of the Mössbauer data of these complexes at 77K is evidently too poor to be the basis of a definite choice of structures. On balance, other data available favour the six-coordinate structure presented earlier in the Chapter.

4.5.1.4 Electronic Spectra

The identification based on a single pair of UV and visible spectra may be ambiguous due to the limited characteristic features available from these spectra. The electronic absorption peaks of many compounds are not greatly influenced by structural features of attached non-absorbing groups, and as a consequence, only absorbing functional groups can be identified. Unfortunately, however, the solvents cut off regions which may also hinder features of the compounds under study.

The electronic spectra obtained for the complex derived from TMTD and tellurium tetrachloride are shown in Figure 4.7.

An inspection of data in literature sources(124) shows that there are some trends in the shifts of the bands probably connected with the nature of the central atom. For the sake of comparison, the spectra are restricted to those taken in chloroform and ethanol for which more data are available.

Jørgenson(125) conducted a detailed study of the electronic spectra of dithiocarbamato-complexes neglecting the effect of M→Sπ bonding. The S→M π bonding (π antibonding) was related to the availability of the lone pairs on the sulphur atoms. Therefore as the C-S bond order increases, the availability of lone pairs on sulphur atoms decreases and S→M π bonding decreases in importance.

The band at 39 kk ascribed as $\pi \rightarrow \pi^*$ transition located mainly in the C=S group. This band is reported for all the dithiocarbamato-complexes and shows a slight red solvent shift and high intensity. Its position is not much affected by the presence of the central atom (39 ± 3 kk). Hence the band at 39 kk should be an essentially intraligand $\pi \rightarrow \pi^*$ transition as suggested by Jørgenson.

The complex derived from TMTD and tellurium tetrachloride has a strong band at 39.5 kk which is in agreement with similar complexes. Thus this band should be the indication of $\pi \rightarrow \pi^*$ in the complex. The $\pi \rightarrow \pi^*$ transition should show a red shift when the solvent is changed from a non-polar to a polar type due to solvation and/or hydrogen bonding between the non-bonding electrons of the thiocarbonyl group of the solute and the solvent molecules(126). The spectra obtained with the free ligand TMTM in chloroform and ethanol are in agreement with this statement, but the chloro- complex in chloroform and ethanol shows no difference or a slight blue shift with the increase in polarity of the solvent, thus showing the reduced availability of non-bonding electrons on sulphur. This supports the idea that the sulphur atoms are coordinated to the tellurium.

The other peaks which may be due to $n\rightarrow\pi^*$ and $n\rightarrow\sigma^*$ transitions are not discussed here due to the uncertainty of the cut off regions of the solvents used.

4.5.1.5 Mass Spectra

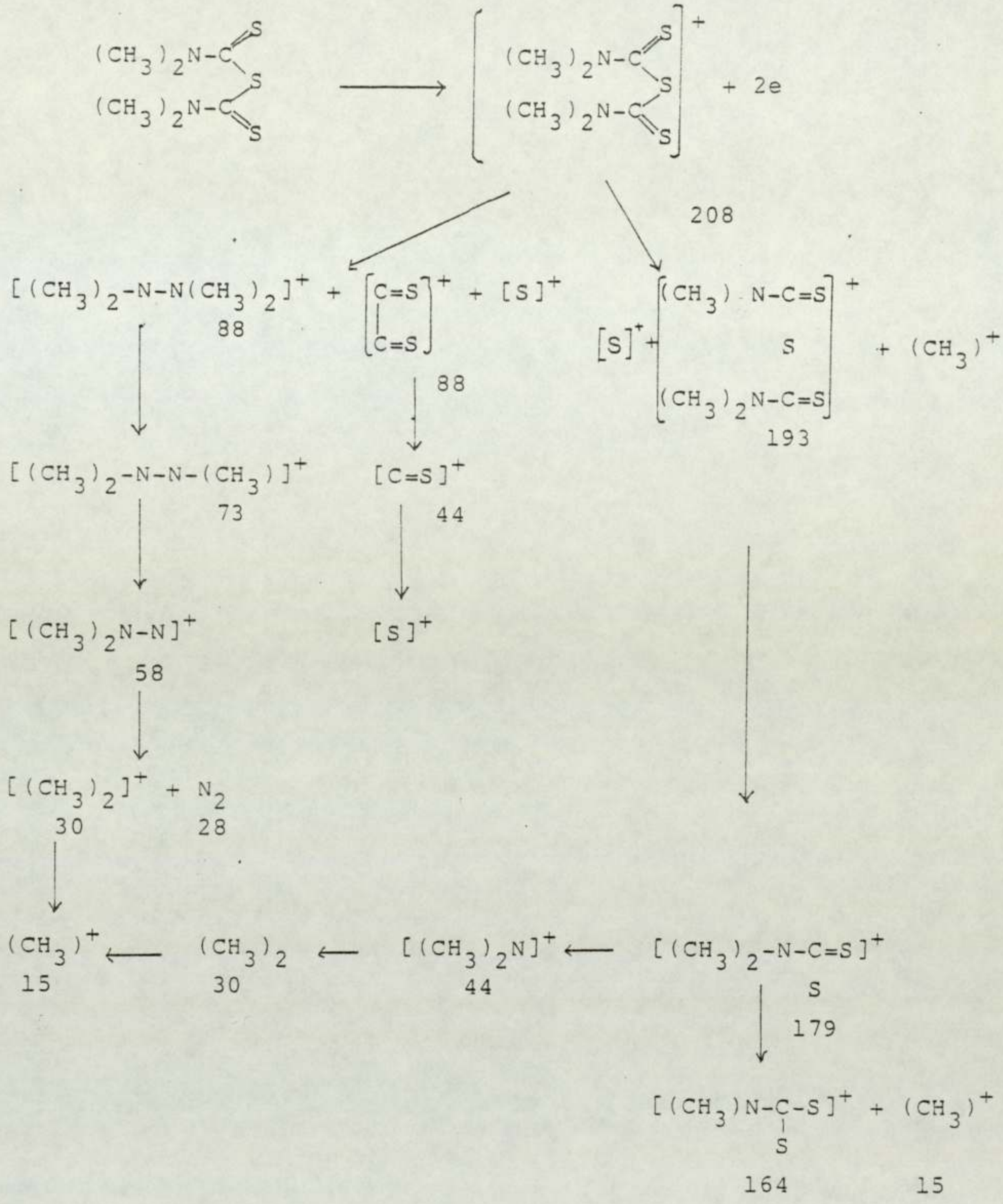
The fragmentation patterns of the TMTM and tetrachloro-complex are shown in Figure 4.15 and Figure 4.16 respectively. In general, the ligand is decomposed more easily than the tellurium tetrahalides and therefore it is not surprising that the complex has an extremely weak or even absent molecular ion peak.

The clusters around m/e 256, 192, 128, 64 and 32 could be the fragmentation patterns of the pyrolysed polyatomic sulphur, S_8, in the chamber. These clusters are also seen in the mass spectrum of TMTM.

4.5.2 TMTD and (p-Ethoxyphenyltellurium)trihalide Complexes

4.5.2.1 Infra-red Spectra

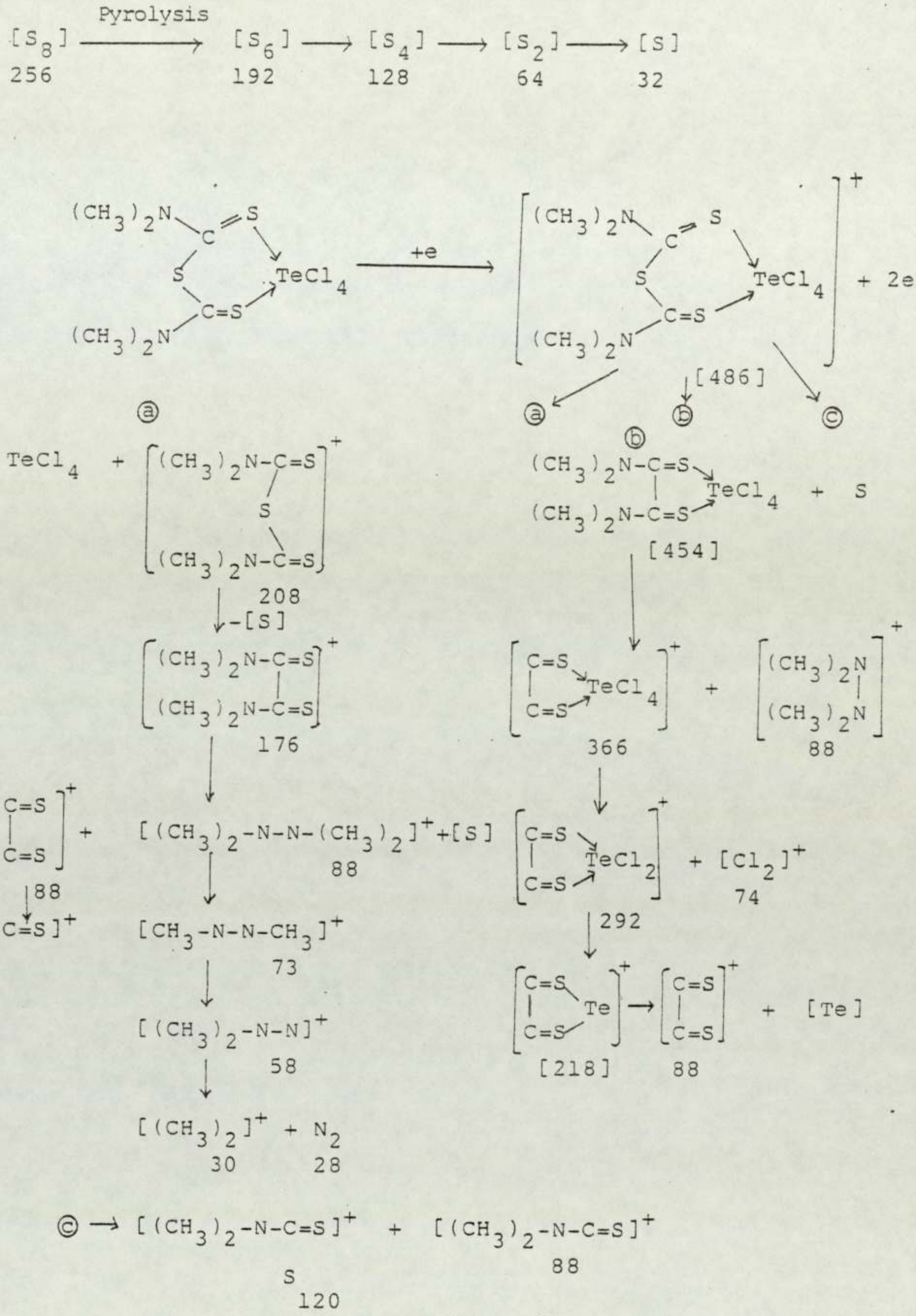
The vibrational spectra of complexes formed with TMTD and (p-ethoxyphenyl)tellurium trihalides, in general, show all



Quoted m/e values are referenced to ^{130}Te, ^{37}Cl, ^{12}C, ^{1}H, ^{14}N and ^{32}S.

Major peaks in the mass spectrum of the complex derived from TMTM.

Figure 4.15



Quoted m/e values are referenced to ^{130}Te, ^{37}Cl, ^{12}C, ^{1}H, ^{14}N and ^{32}S. The square brackets indicate the m/e values not observed in the spectrum.

Figure 4.16 Major peaks in the mass spectrum of the complex derived from TMTD and $TeCl_4$

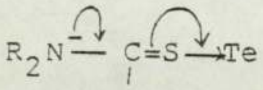
the bands due to trihalides and the dithiocarbamato- group. The bands at 1500 cm^{-1} and 872 cm^{-1} in TMTD have shifted;one to a higher frequency, 1580 cm^{-1}, and one to a lower frequency, 820 cm^{-1} respectively, in the complex formed with trichloride (Figure 4.8). In the triiodide complex these bands are shifted to 1540 cm^{-1} and 830 cm^{-1} respectively, indicating weaker electron donation from the S in C=S to the central tellurium atom.

Assignment of bands below 200 cm^{-1} to $\nu_{(Te-Cl)}$ modes must be made with caution due to ligand vibrations. However, after eliminating the ligand bands, the bands at 318 and 298 cm^{-1} in the trichloride complex are probably due to $\nu_{(Te-Cl)}$ modes. These two positions have been reported as $\nu_{(Te-Cl)}$ modes above 200 cm^{-1} by McWhinnie et al(101) for trichlorides. The other two bands above 200 cm^{-1}, at 334 and 326 cm^{-1} may have overlapped with the ligand vibrations.

The bands below 400 cm^{-1} were also examined as polyethylene discs and after eliminating the above vibrational modes, the absorptions in the 258-205 cm^{-1} region are all likely to be associated with $\nu_{(Te-S)}$ vibrations.

The infra-red spectrum of the trichloride complex recorded a few months after preparation shows the bands due to $\nu_{(C-N)}$ and $\nu_{(C-S)}$ approaching their original positions found in the free ligand spectrum. The band at ∿990 cm^{-1} in the

TMTM (Figure 4.2b) which is assigned to $\nu_{(C=S)}$ is clearly reappearing on this spectrum. This band is not seen in the freshly prepared complex probably due to the decrease in the bond order in C=S bond upon coordination i.e., when the coordination bond is formed with tellurium, the availability of the lone pair electrons on the sulphur atoms decreases resulting in a decrease in the double bond character of the C=S bond.



However, the triiodide complex is quite stable probably due to the ionic nature of the complex as discussed below.

4.5.2.2 Molar Conductivity

Molar conductance of trichloride, tribromide and triiodide complexes in DMF at 25°C are found to be 46, 98 and 160 $cm^2 mol^{-1} ohm^{-1}$ respectively. The values of tribromide and triiodide complexes show that these complexes are fully dissociated in DMF showing characteristic properties of 1:1 and 1:2 electrolytes. The value for the trichloride complex however, is low for it to be considered as a 1:2 electrolyte.

It could be suggested that the steric factors facilitate the formation of ionic tribromide and triiodide complexes.

4.5.2.3 Structures

The sulphur atoms of the ligand could exert a stronger trans-bond lengthening effect than does chlorine and a five-coordinated tellurium complex with one long Te-Cl is therefore likely with the TMTD/(p-ethoxyphenyl) tellurium trichloride complex. A similar argument could be made with tetrachloro-complex having two long Te-Cl bonds.

Different degrees of Lewis acidity may readily account for the possible structures suggested for tetrachloro- and trichloro- complexes. The lower Lewis acidity of the trichloride points to the fact that it may accept only one sulphur atom from the ligand. Therefore the structure could be a dimer, which is in very good agreement with the elemental analysis, as illustrated in Figure 4.17.

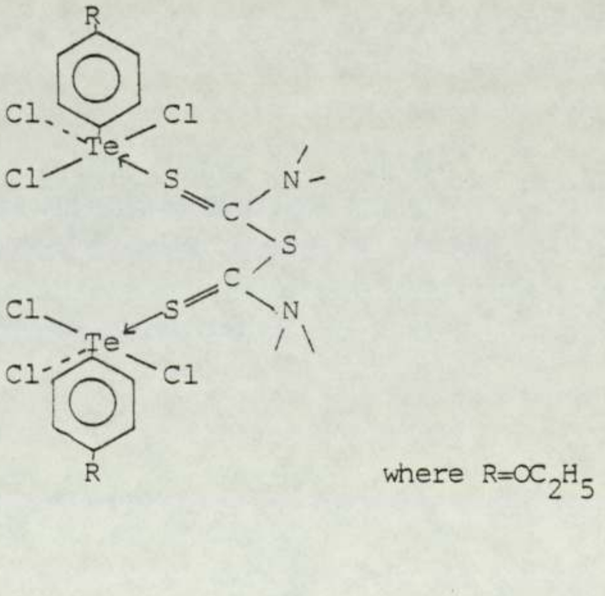


Figure 4.17

The poor solubility in common organic solvents supports the polymeric nature of the trichloride complex. The proposed structure is also in accordance with the theory of Wynne and Pearson$^{(127)}$, that the five-coordinate tellurium atom will have no halogens in positions trans- to the phenyl groups.

The conductivity data show values characteristic for 1:2 electrolytes for the bromo- and iodo- complexes, hence suitable ionic structures could be proposed for these two complexes as shown in Figure 4.18.

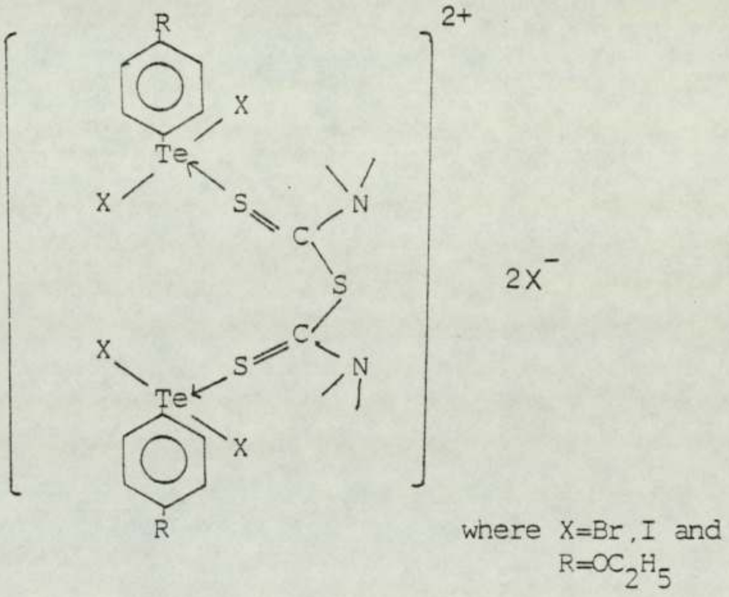


Figure 4.18

However, the equilibrium shown below could easily occur from solvolysis in all these compounds hence showing higher values for the molar conductivities.

$$\text{Dimer} \rightleftharpoons \text{RTeX}_2(\text{S}_2)^+ + \text{RTeX}_4^- \quad \text{where X=Cl,Br,I}$$

4.5.2.4 Mass Spectra

The crystal structures of (p-ethoxyphenyl)tellurium trihalides show(128) these materials are dimeric. The mass spectra obtained(129) for these show the fragmentation at higher m/e ratio than the monomer molecules. These ions could only occur from the dimeric molecules by breaking the tellurium-halogen bonds and forming tellurium-tellurium bonds.

The mass spectra obtained for the complexes prepared with TMTD and trihalides do not show the fragmentation pattern at higher m/e ratio as seen for trihalides alone. This observation helps us to speculate that the structures of the complexes do not contain halogen bridged tellurium atoms as for the trihalides.

Generally, the ligand is more easily decomposed than the trihalides, thus no peak due to the molecular ion is observed in all three cases.

4.5.3 A Comment on the Attempted Reaction of Bis(p-ethoxyphenyl)tellurium Dichloride with TMTD

The reaction of TMTD with bis(p-ethoxyphenyl)tellurium dichloride, R_2TeCl_2, failed to give a coordinated complex.

The failure in this reaction could mainly be due to the weak Lewis acidity of the compound. The contraction of the lone pair electrons on tellurium with two chlorine atoms is rather difficult, thus the availability of the lone pair on the tellurium atom will help to repel the incoming electron donation from the two sulphur atoms in the ligand. Thus the decreased tendency for the formation of a coordinated complex is not surprising.

4.5.4 TMTD/Tellurium Tetrachloride/Pyridine Complex and Its Bromo- and Iodo- Derivatives

4.5.4.1 Infra-red Spectra

The absorption bands between 2200 and 1900 cm^{-1} have been assigned(130) to be due to $\nu_{(=N^{+}-H)}$, immonium group which is likely to form in pyridine containing reactions. However, the complex formed with TMTD/tellurium tetrachloride in pyridine did not show these bands, suggesting that no protonation of pyridine has taken place in the reaction.

All the bands due to pyridine (Figure 4.9) and the ligand are clearly seen with slight shifts due to coordination in the complex, with tetrachloride (Figure 4.10). The spectra of the bromo- and iodo- complexes do not show any band due to pyridine. All three spectra clearly indicate the presence of a $\nu_{(Te=O)}$ band at 600 cm^{-1}.

The band at 1500 cm^{-1} in TMTM due to $\nu_{(C-N)}$ has shifted to 1520 cm^{-1} upon coordination in the complexes. This shift is smaller when compared with the $\nu_{(C-N)}$ shift in TMTD, tellurium tetrachloride complex in chloroform. The $\nu_{(C-S)}$ at 872 cm^{-1} has shifted to 760 cm^{-1} indicating coordination through sulphur atoms. The bands at 1599 cm^{-1} due to ring stretching vibrations and 700 cm^{-1} due to C-H out of plane deformation(130) vibrations of the pyridine ring are shifted to 1635 cm^{-1} and 685 cm^{-1} upon coordination.

The resulting chloro- complex will thus contain two chlorine atoms, one oxygen atom and a coordinated nitrogen atom from pyridine that will increase the electron density on tellurium. This may reduce the drift of electrons from the C-N bond in the ligand. Hence the slight shift in $\nu_{(C-N)}$ would be expected in these compounds, Figure 4.19 contributes to the above idea.

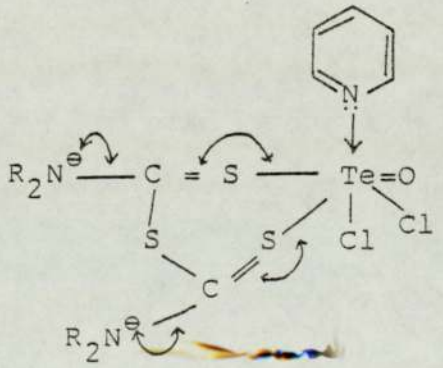


Figure 4.19

The bromo- and iodo- complexes show no pyridine bands in their infra-red spectra but the shift in $\nu_{(C-N)}$ is still seen in both cases. In these two complexes, the presence of lower electronegative bromo- and iodo- ligands and the oxygen will not much affect the electron density on tellurium thus only a slight shift in $\nu_{(C-N)}$ is observed. The presence of a Te=O band at 600 cm^{-1} is seen in both cases. The bands at 252-200 cm^{-1} region could probably be due to $\nu_{(Te-S)}$ vibrations.

4.5.4.2 Molar Conductivity

The molar conductivity data tabulated in Table 4.2 shows that all three complexes are weak electrolytes in DMF at 25°C.

4.5.4.3 Structures

On the basis of infra-red spectra, elemental analysis, mass spectra and conductivity data, the following structures, Figure 4.20 for tellurium tetrachloride and TMTD in pyridine; and Figure 4.21 for bromo- and iodo- complexes, could be suggested.

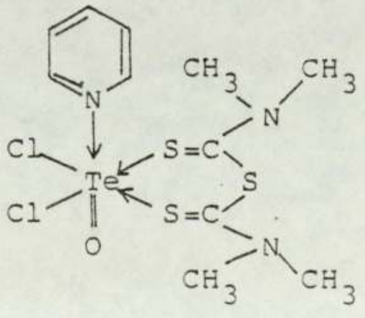
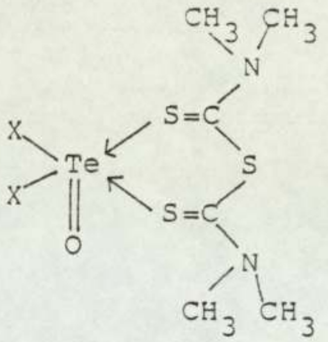


Figure 4.20



where X=Br,I

Figure 4.21

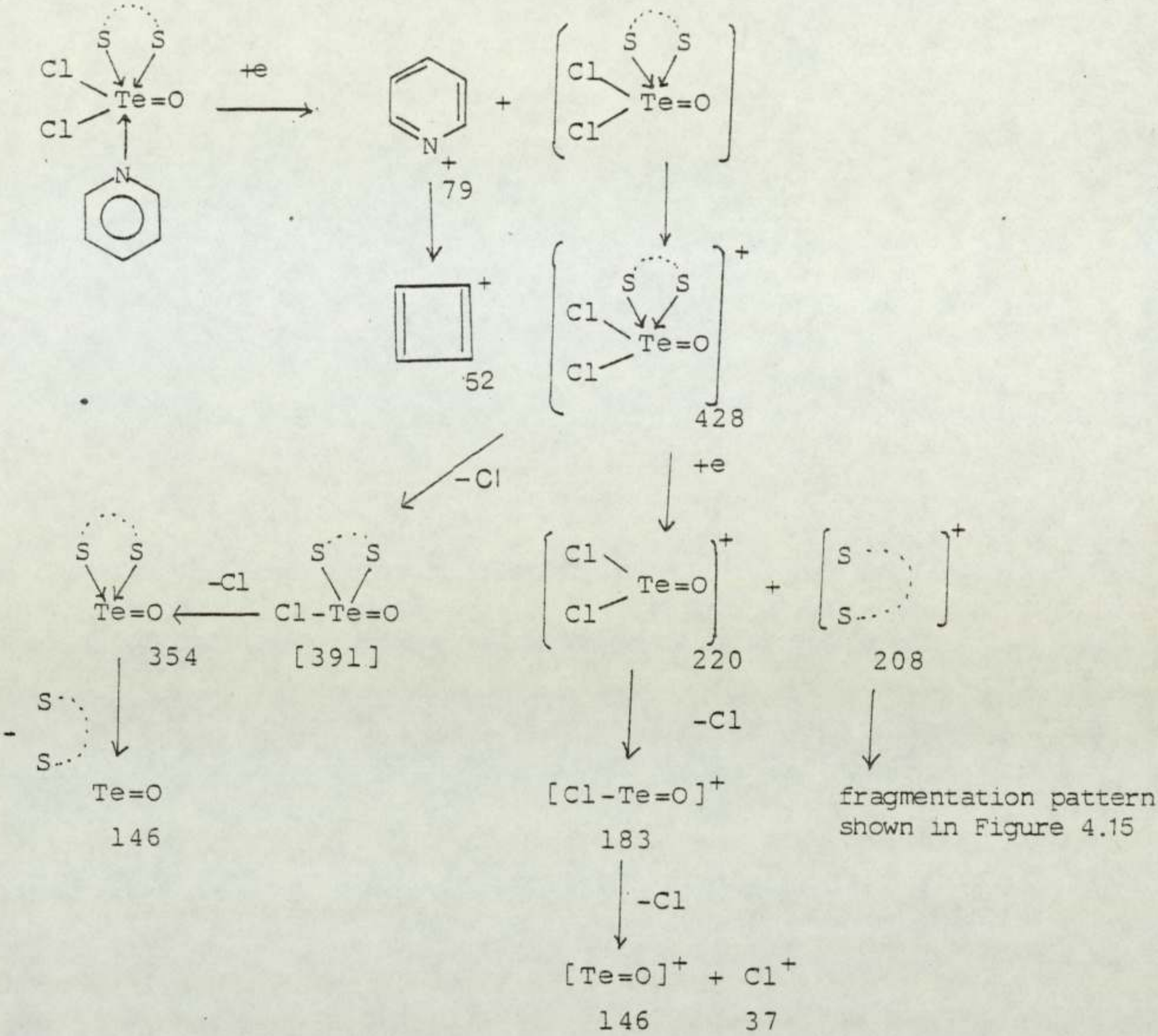
4.5.4.4 Mass Spectra

The fragmentation patterns of the TMTD.tellurium tetrachloride pyridine complex and its bromo- and iodo- derivatives are shown in Figures 4.22 and 4.23 respectively.

The mass spectra of the pyridine containing chloro- complex contains very intense peaks at 79 and 52. The relative intensities of the other peaks are less than 10% when compared with these two peaks. Thus the mass spectrum of this complex at 70 eV is found to be difficult to tabulate.

4.5.5 TMTD/Tellurium Tetrachloride/Triphenylphosphine Complex and Its Iodo- Derivative

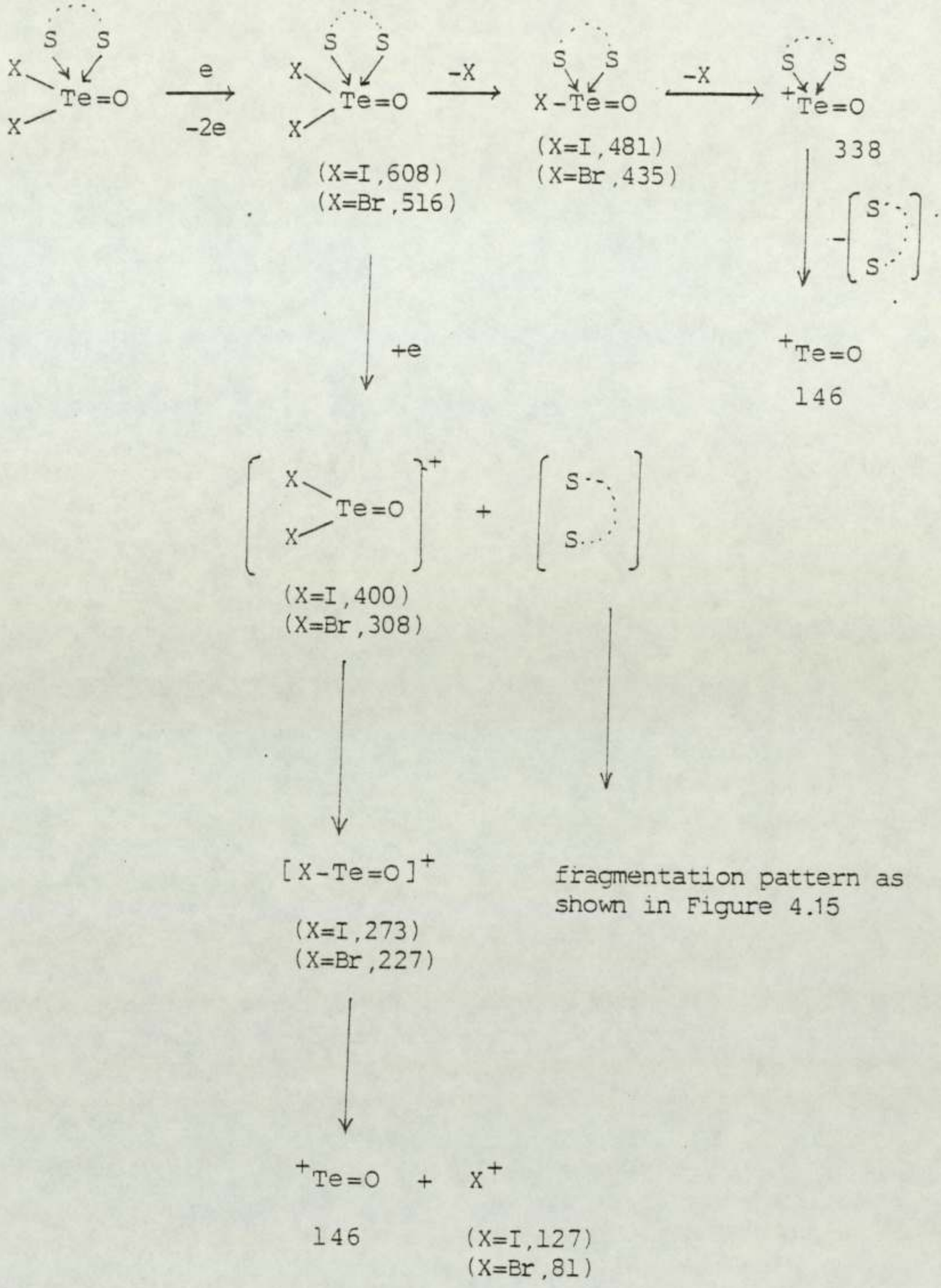
The interaction of TMTD, tellurium tetrachloride in the presence of triphenylphosphine in benzene solution produces a yellow complex with two molecules of tellurium tetrachloride.



fragmentation pattern shown in Figure 4.15

Quoted m/e values are referenced to ^{130}Te, ^{37}Cl, ^{12}C, ^{1}H, ^{14}N and ^{32}S.

Figure 4.22 Major peaks in the mass spectrum of the complex derived from TMTD/$TeCl_4$ in pyridine



Quoted m/e values are referenced to ^{130}Te, ^{81}Br. ^{37}Cl. ^{12}C, ^{1}H, ^{14}N and ^{32}S.

Figure 4.23 Major peaks in the mass spectrum of the complex derived from TMTD/$TeCl_4$ in pyridine with KBr and KI

4.5.5.1 Infra-red Spectra

The infra-red spectrum of the triphenylphosphine complex generally shows the vibration bands due to the ligand, TMTM and triphenylphosphine. The band at 1500 cm^{-1} in TMTM due to $\nu_{(C-N)}$ has shifted to a higher frequency, 1575 cm^{-1}, and the band at 872 cm^{-1} due to $\nu_{(C-S)}$ to a lower frequency, on coordination to tellurium. The new band at 642 cm^{-1}(131) clearly indicates the formation of triphenylphosphine sulphide. The bands in the region 1450-1435 cm^{-1} and 1005-995 cm^{-1} which have been suggested to be characteristic of a phosphorous-phenyl linkage(132) are not affected in the complex with sulphur attached to phosphorous.

The infra-red spectrum of the iodo- derivative shows the absence of all the triphenylphosphine sulphide bands. The coordination with two sulphur atoms in the ligand is still seen and the spectrum is identical with the iodo- derivative of the pyridine complex discussed earlier. The band at 600 cm^{-1} indicates the presence of Te=O in the complex.

4.5.5.2 Molar Conductance

Conductivity measurement in DMF, 58 $cm^2mol^{-1}ohm^{-1}$ shows the triphenylphosphine containing complex is a 1:1 electrolyte and the iodo- complex shows a very close value, 38 $cm^2mol^{-1}ohm^{-1}$, to that of the iodo- derivative of the pyridine complex,

$39.1\ cm^2mol^{-1}ohm^{-1}$ in DMF, a typical value for a weak electrolyte.

4.5.5.3. ^{31}P NMR

The ^{31}P NMR in DMSO shows the presence of one type of phosphorous atom in the complex. Due to the poor solubility, no other information could be obtained from the spectrum.

4.5.5.4 Structures

On the basis of elemental analysis, conductivity measurement, ^{31}P NMR and infra-red data, the following structures as shown in Figures 4.24 and 4.25 could be suggested for these complexes. The mass spectrum of the triphenylphosphine containing complex is too complicated to be analysed. As seen from Figure 4.24, there is no reason why the nitrogen could not be coordinated to the five-coordinate tellurium atom which is already interacting with triphenylphosphine sulphide, to satisfy the most probable coordination number for tellurium tetrachloride.

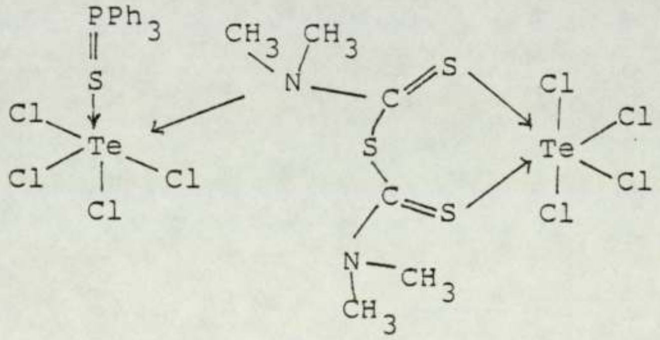
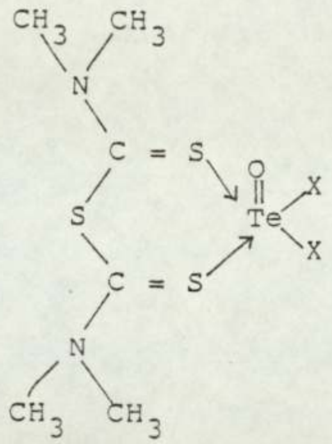


Figure 4.24



where X=Br,I

Figure 4.25

4.5.6 Reactions of Tellurium Tetrachloride/TMTD Complex with Some First Row Transition Metal Salts

One aspect of these reactions which has been of interest is the mode of bonding of two different metal atoms to the ligand, through nitrogen and sulphur atoms. According to the concepts of Pearson(109), the nitrogen is a hard centre and sulphur is a soft centre. Consequently, nitrogen bonding is expected with hard (Class a) metal ions while sulphur bonding should take place with those of soft (Class b). Further, bridging of two metal ions of form MNCSM' is well known(134,135).

However, the qualitative tests, mass spectra and analytical data clearly indicate that no tellurium species is present in the reaction product of tellurium tetrachloride complex with cobalt (II) chloride, bromide and mercury (II) chloride and bromide. The reactions with these metal salts have resulted in some stable coordination compounds with the corresponding metal coordinating to the ligand in the tellurium complex, liberating tellurium tetrachloride into the reaction medium. The nature of these compounds will be discussed in the following section. Further, it is known that tellurium tetrachloride could easily react with acetone thus giving good evidence for the above suggestion. When the reaction of cobalt (II) salts were carried out in methanol, pale yellow products were obtained which appeared to be impure and unstable.

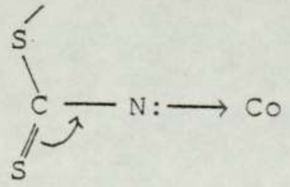
The reaction of the tetrachloride complex with copper (II) chloride however, resulted in a complex containing both tellurium and copper.

The properties of the metal complexes are in fact dependent upon the nature of the metal ion and also the ligands. Many types of ligands are known(135) and the properties of their derived metal complexes have been investigated. Of major importance in the transition metal coordinated complex is the presence of an incomplete d-shell in which the energies of the d orbitals are split, the magnitude of splitting being determined by the ligand field strength, Δ, and the stereochemistry of the complex.

4.5.6.1 Complexes of Cobalt (II)

4.5.6.1.1 Infra-red Spectra

The complexes of Co(II) salts were easily prepared and the infra-red spectra of the complexes obtained from the reaction of cobalt (II) chloride and bromide with tellurium tetrachloride/TMTD complex show very strong absorptions due to $\nu_{(C-N)}$ at values (Table 4.3) higher than the tellurium complex. The new band appearing at 880 cm^{-1} could be a negative shift in $\nu_{(C=S)}$ in the free ligand. This downwards shift may arise due to the reduced double bond character in C=S, caused by the coordination of the metal atom to the ligand. The reappearance of this band, which is absent in the tellurium complex, may also indicate the presence of a free C=S bond in the ligand, thus implying coordination through nitrogen has probably taken place, as shown below in the diagram.



The sharp bands at 540 cm^{-1} and 580 cm^{-1} could illustrate the absorptions due to C-S stretching vibrations. The far infra-red spectrum of the chloro- complex shows two absorptions at 316 cm^{-1} and 279 cm^{-1} which may be assigned to $\nu_{(Co-Cl)}$ (136) (Figure 4.11).

4.5.6.1.2 Electronic Spectra

Both Co(II) complexes have a deep blue colour and the chloro-complex shows two bands at 676 and 606 nm with ε values 592 and 360 respectively. These values are too high to infer an octahedral environment around the Co^{2+} ion.

Ferguson(137) has discussed the spectra of some Co(II) compounds which are free from severe distortion and resemble true tetrahedral stereochemistry and concluded that splitting of the band at higher frequency, ~700 nm can best be explained in terms of a lowering of symmetry e.g., $CoCl_4^{2-}$.

However, the band at 672 nm in the Co(II) complex shows no splitting, thus ruling out the possibility of ionic $CoL_2^{2+}CoCl_4^{2-}$ structure for the chloro- complex.

4.5.6.1.3 Magnetic Measurement

The observed magnetic moments for the cobalt complexes at room temperature are (4.48±0.05)BM and(4.50±0.05)BM for chloro- and bromo- compounds respectively. These are considerably in excess of the spin only value (3.89 BM), but in the range of normal values obtained for other tetrahedral Co(II) complexes $CoCl_4^{2-}$, 4.59 BM; $CoBr_4^{2-}$, 4.69 BM and CoI_4^{2-}, 4.77 BM(80).

4.5.6.1.4. Structure

The conductivity data in acetonitrile (Table 4.6) shows the two Co(II) complexes are weak electrolytes thus ionic formulae could be easily ruled out. So, suitable dimeric, neutral structures Co_2LX_4, where X=Cl, Br must be found for these compounds.

Three simple possibilities exist, two structures where the two coordinating centres, nitrogen and sulphur, are coordinating onto two cobalt atoms, and the other with halogen bridges. These possibilities are illustrated in Figures 4.26a, 4.26b and 4.26c.

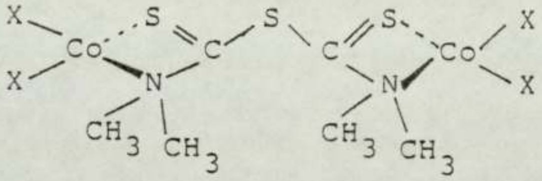


Figure 4.26a

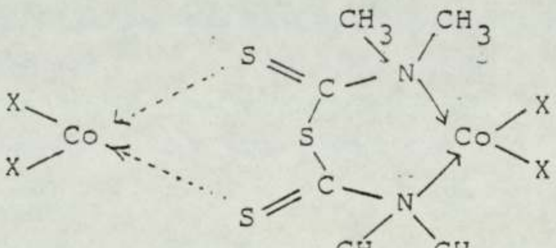
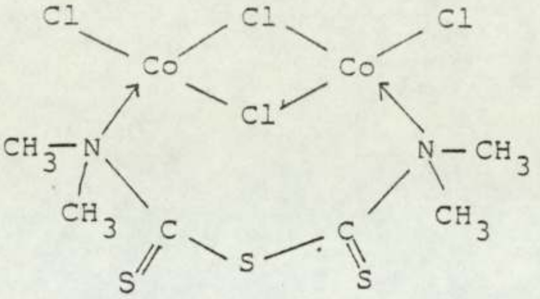


Figure 4.26b



where X=Cl,Br

Figure 4.26c

The magnetic moments observed for the chloro- and bromo-complexes are high for the compounds to be antiferromagnetic and hence a chlorine bridged structure as shown in Figure 4.26c is unlikely.

Hence the two possible formulations for the Co(II) complexes are the structures illustrated in Figures 4.26a and 4.26b.

Attempts were made to obtain ^1H NMR data for the complexes, but due to poor solubility properties they were unsuccessful.

In general, the mass spectra of the complexes were similar to that of free ligand and none of the complexes displayed the parent ion peak corresponding to their molecular weight. Apart from this information, the mass spectra of these complexes have not aided the structure-elucidation of these complexes, hence these data are not presented.

4.5.6.2 Complexes of Mercury (II) Salts

Both Hg(II) chloride and bromide react with the tellurium tetrachloride/TMTD complex under similar conditions to yield analogous products.

4.5.6.2.1 Infra-red Spectra

The infra-red spectra of both complexes are indeed similar, and indicate the presence of coordinated ligand.

The far-infra-red spectrum of the Hg(II) chloride complex indicates two absorption bands at 326 cm^{-1} and 305 cm^{-1} which were absent in the bromide complex and hence may be attributed to $\nu_{(Hg-Cl)}$. The far-infra-red spectrum in the case of the bromo- complex showed several ill-defined bands and hence nothing could be attributed with certainty to $\nu_{(Hg-Br)}$.

4.5.6.2.2 Conductivity Measurement

Both these complexes are non-electrolytes in solution and are diamagnetic.

4.5.6.2.3 Structure

These complexes agree well with the dimeric formulations as suggested for the cobalt(II) complexes. Thus, the mercury(II) complexes could represent dimeric structures with chlorine bridges as shown in Figure 4.27. ^{199}Hg NMR shows only one peak, supporting this structure.

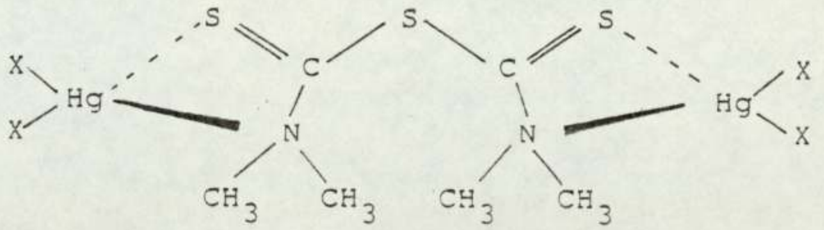


Figure 4.27

4.5.6.3 Complexes of Copper(II)

Ahrland et al$^{(138)}$ have classified the Cu(II) ion as a borderline case between Class a and Class b metals. The Cu(II) ion is a typical transition metal in respect of the formation of coordination complexes but less typical in its reluctance to take up a regular octahedral or tetrahedral stereochemistry. The 3d^9 outer electronic configuration of the Cu(II) ion lacks cubic symmetry and hence yields distorted forms of the basic stereochemistries.

4.5.6.3.1 Infra-red Spectra

The $\nu_{(C-N)}$ of the complex formed between Cu(II) chloride and tellurium tetrachloride/TMTD appears at slightly higher frequency than in the tellurium complex alone. The new sharp band appearing at 650 cm^{-1} could be an indication of C-S stretching vibrations. The far-infra-red spectrum of the Cu(II) chloride complex shows a sharp band at 410 cm^{-1} which is absent in all the other complexes and may indicate Cu-N stretching vibrations. The broad band around 260 cm^{-1} probably indicates the presence of Cu-Cl vibrations.

4.5.6.3.2 Electronic Spectra

The electronic spectrum of the green coloured copper(II) complex gives a sharp band at 634 nm. However, due to relatively low symmetry of the environment in which Cu^{2+} is characteristically found, detailed interpretations of the spectra and magnetic properties are somewhat complicated, even though Cu^{2+} is the equivalent of a one-electron case.

4.5.6.3.3 Magnetic Measurement

The value of μ_{eff} of the Cu(II) complex (1.91±0.05 BM), lies within the normal range generally observed for Cu^{2+} complexes(80).

4.5.6.3.4 Structure

Interestingly, the complex has shown the presence of tellurium and it analyses reproducibly to the stoichiometry $CuL_2Te_2Cl_{10}$, where $L=C_6H_{12}N_2S_3$. The conductivity measurement of the complex in acetonitrile shows a value 179 $cm^2ohm^{-1}mol^{-1}$ a value acceptable for a 1:2 electrolyte in acetonitrile. Hence, a suitable ionic formula must be found for this complex.

It is known that when Cu(II) is in six-coordination, the 'octahedron' is severely distorted, the typical distortion being an elongation along one 4-fold axis, so that there is a planar array of four short Cu-L bonds and two trans-long ones. In the limit, of course, the elongation leads to a situation indistinguishable from square coordination, as found in many discrete complexes of Cu(II). Thus the case of tetragonally distorted 'octahedral' coordination and square coordination cannot be sharply differentiated.

In view of the above information, it is conceivable that the Cu(II) complex could have a structure as shown below in Figure 4.28.

$(CuL_2)^{2+}(TeCl_5)_2^-$ where L =

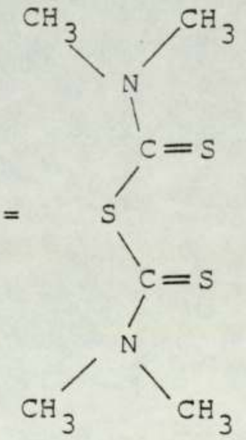
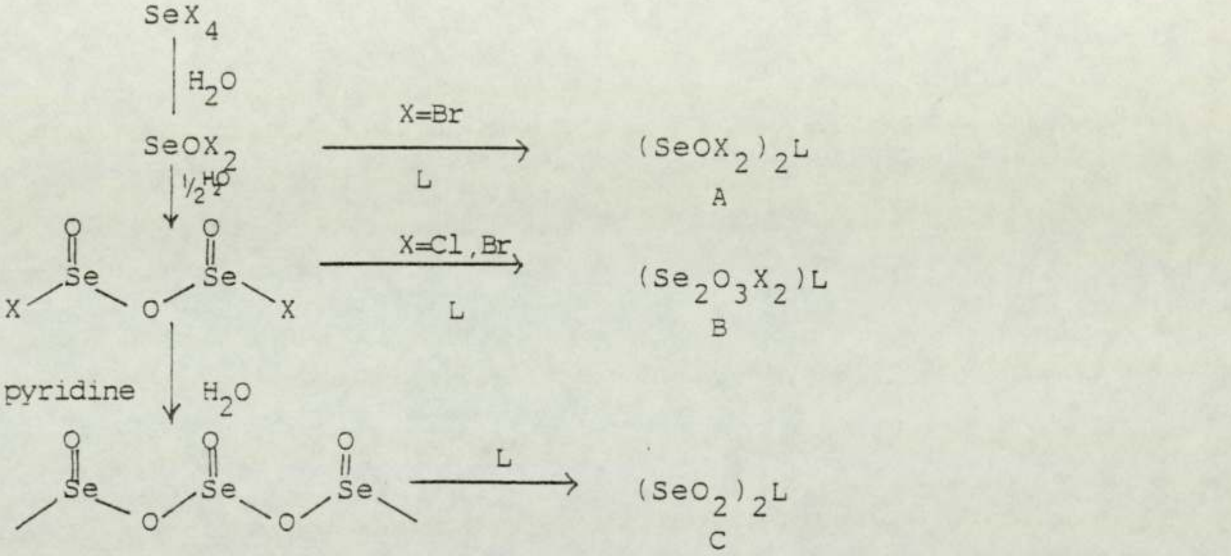


Figure 4.28

In the course of study of the reactions of selenium tetrahalides with TMTD, it appears that selenium tetrahalides are much more readily hydrolysed than tellurium tetrahalides under the reaction conditions used.

The summary of the complexes obtained is shown in Figure 4.29 below.



where L=TMTM; i.e., monosulphide

Figure 4.29

Under inert atmosphere with freshly prepared tetrabromide the complex A was isolated. Further hydrolysis of $SeOX_2$ (where X=Cl, Br) could result in B, again stabilized with the monosulphide. However, in the presence of a base e.g., pyridine, further hydrolysis seems to occur leading to the separation of a complex C in which selenium dioxide is coordinated.

The reactions of tellurium tetrahalides followed a different scheme as shown below in Figure 4.30.

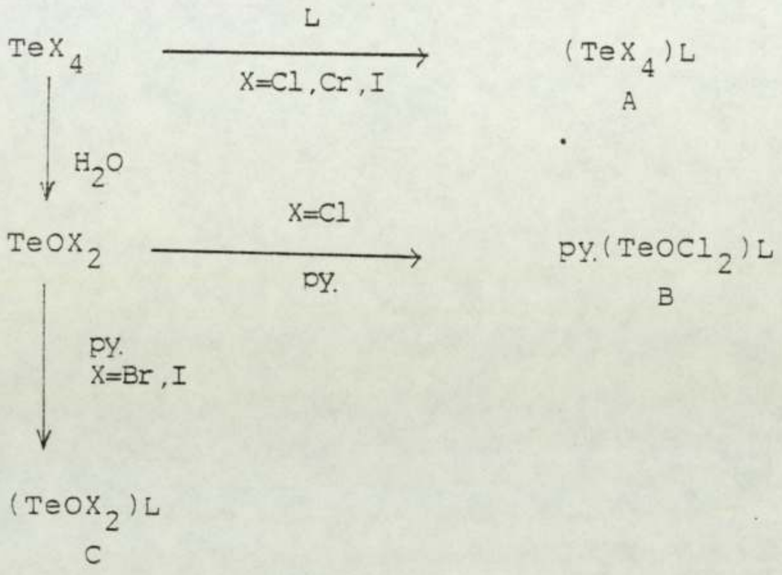


Figure 4.30

Only in the presence of a base tellurium tetrachloride hydrolyses to give a complex B with pyridine coordinating to tellurium and tetrabromide and iodide hydrolyse to give complex C stabilized by the monosulphide.

4.5.7 Selenium Tetrachloride/TMTD Complex and Its Bromo- and Iodo- Derivatives

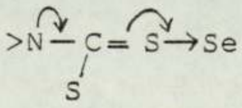
It was thought that selenium tetrachloride could follow the same mechanism as for the tellurium tetrachloride reaction with TMTD. Thus it was of interest to carry out a few reactions with selenium tetrahalides and TMTD, following the reactions carried out with tellurium tetrahalides.

It was encouraging that selenium tetrachloride and bromide gave the same effect when used together with TMTD in NR vulcanization, increasing the acceleration and enhancing the crosslink density of the vulcanizates, thus suggesting the possibility of the release of active sulphur atoms into the reaction media.

The analytical data and some physical data used in the structure elucidation of the complex formed with selenium compounds and TMTD are discussed below.

4.5.7.1 Infra-red Spectra

The vibrational spectra of all the complexes obtained with selenium tetrahalide and TMTD show the characteristic upward shifts in $\nu_{(C-N)}$ upon complex formation through S atoms of the ligand. The new band appearing at 905 cm^{-1} could probably be due to a negative shift in $\nu_{(C=S)}$ that occurs at 965 cm^{-1} in the free ligand.



The $\nu_{(C-H)}$ region of the complexes show identical bands to the tellurium complexes thus implying the symmetry of the coordinated ligand molecule could be the same as in the tellurium complexes. The broad band at 380 cm^{-1} could probably be an indication of Se=O stretching vibrations.

Unlike tellurium, the complexes of Se_2Cl_2 and Se_2Br_2 have been reported and the spectroscopic data based on assignments for C_{2v} symmetry, have been interpreted$^{(139)}$.

4.5.7.2 Conductivity Measurement

The conductivity of the chloro- complex, 28 $cm^2ohm^{-1}mol^{-1}$ in DMF at 25°C, shows that the compound is a weak electrolyte, thus eliminating the possibility of an ionic compound.

The conductivity of the corresponding bromo- complex furnished a value of 30 $cm^2ohm^{-1}mol^{-1}$ in DMF suggesting that this too is a weak electrolyte. However, the complex formed with fresh selenium tetrabromide/TMTD shows a different value, 91 $cm^2ohm^{-1}mol^{-1}$, a value approaching a 1:2 electrolyte (Table 4.2), hence, formation of an ionic complex is more likely in this case.

4.5.7.3 Mass Spectra

The mass spectra of all complexes clearly indicate the presence of two selenium atoms.

The fragmentation pattern of the bromo- complex gives particularly intense peaks, this probably being due to the most abundant isotopes of selenium, 78 (25.52%) and 80 (49.82%) and bromine 79 (50.53%) and 81 (49.47%) lying in the same region.

Although attempts to assign all the peaks in the spectra were not successful, the assignments of two selenium atoms and probably two halogen atoms in the complexes prepared with selenium tetrachloride give valuable evidence for structure elucidation. Further, the characteristic fragmentation pattern of the ligand confirms the presence of the unaltered ligand skeleton in the complexes.

4.5.7.4 Structure

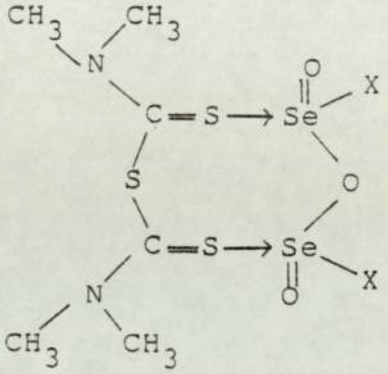
Although the same conditions were used and care was taken to avoid oxygen as in the case of the tellurium tetrachloride reaction, selenium tetrachloride seems to give a different product with TMTD.

The main feature common to both systems is the possibility of eliminating active sulphur to the reaction medium.

The elemental analyses of the complex prepared with selenium tetrachloride/TMTD and its bromo- and iodo- derivatives, show a stoichiometry $Se_2LO_3X_2$, where $L=C_6H_{12}N_2S_3$ and

X=Cl, Br, I. However, the figures obtained for the percentage of sulphur seem to vary, probably due to the presence of selenium interfering with the sulphur analyses.

On the basis of infra-red, mass spectra and conductivity measurements the most suitable structure for these complexes could be that shown below in Figure 4.31.



where X=Cl,Br,I

Figure 4.31

It seems that selenium tetrachloride absorbs moisture, and as observed, much more rapidly than tellurium tetrachloride, thus the possibility of formation of oxychloride before reacting with TMTD is not unlikely even though care was taken to avoid this situation.

Further, the complex formed with tellurium tetrachloride/TMTD shows no reaction with water, the complex formed with selenium tetrachloride/TMTD has been shown to interact with water losing the two remaining chlorine atoms. The product formed shows a stoichiometry Se_2LO_4. thus suggesting a structure as shown in Figure 4.32 is a suitable model for the hydrolysed product.

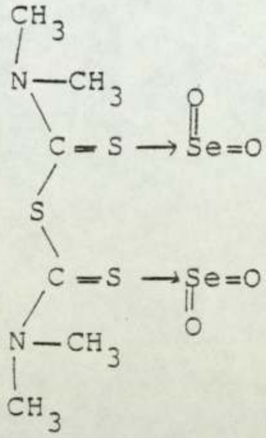


Figure 4.32

The freshly prepared selenium tetrabromide when reacted with TMTD gave a complex with a different stoichiometry; the analytical data fits well with the stoichiometry $Se_2LO_2Br_4$. Therefore in the case where the starting material is less susceptible to moisture, the structure would be as follows (Figure 4.33):

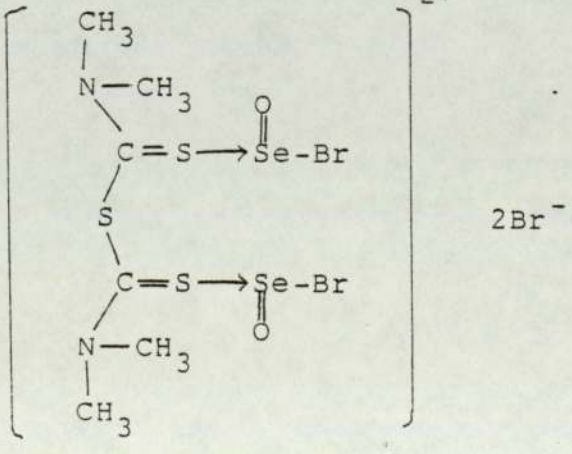


Figure 4.33

The interaction of four large bromine atoms close to each other may be the reason for the high conductivity value observed for this complex (Table 4.2).

4.5.8 Reaction of Selenium Tetrachloride/TMTD in Pyridine

The reaction carried out in pyridine failed to show any bands due to pyridine in its infra-red spectrum or any fragmentation pattern characteristic of pyridine in its mass spectrum. It is not surprising that in the presence of a base, pyridine, further hydrolysis could result in a complex with a stoichiometry Se_2LO_4, thus a structure similar to that shown in Figure 4.30 could be proposed for this complex.

CHAPTER FIVE

SYNTHESIS AND PROPERTIES OF ORGANOTELLURIUM COMPOUNDS DERIVED FROM TERMINAL DIHALOALKANES

5.1 Introduction

As mentioned previously in Chapter 3, attempts to react tellurium and tellurium compounds with model alkenes failed to show the formation of tellurium-carbon bonds in most of the reactions, indicating the difficulty in crosslinking natural rubber (NR) molecules with tellurium and its compounds.

A modified NR e.g., brominated NR, $(C_6H_{10}Br_2)_n$, could be an alternative rubber to study the crosslinking with tellurium compounds as it is known that various diorganyl ditellurides R_2Te_2, react with compounds of the type $Br(CH_2)_nBr$ (n=1, 3, 4) in the presence of an alkaline alcoholic solution of sodium or potassium borohydride(140,141).

Diorganyl-ditellurides are convenient, stable starting materials for various tellurium compounds and metal complexes. ^{125}Te Mössbauer data of diphenyl-ditelluride $(C_6H_5)_2Te_2$, suggests that the involvement of intramolecular tellurium associations, in addition to short Te-C and Te-Te bonds gives rise to highly coloured diaryl-ditellurides as shown by the red coloured $(C_6H_5)_2Te_2$ in which the Te-Te bond is 2.7 Å and the intramolecular contacts are 4.2 Å(142). However, Thavornyutikarn(129) has shown that there are other factors that could affect the colour of the compounds, and even though it has been suggested(143) that some decomposition of diaryl-ditellurides to free radicals occurs in solution, the ditelluride is undissociated in organic solvents. Thus the electron spin resonance spectrum of a solution of diphenyl-ditelluride in benzene did not indicate any radical species present. Also, the diffuse reflectance spectrum of diphenyl-ditelluride and visible spectrum of a solution in chloroform are similar, indicating that the species in the solid and in solution are similar.

The reaction of a diorganyl-ditelluride, R_2Te_2 with aqueous alkaline sodium tetrahydroborate affords a solution with the chemical properties of NaTeR'. and a large number of aromatic ditellurides have been reduced to aryl-sodium tellurides in this way (Equation 5.1)

$$\left.\begin{aligned} \mathrm{RTe\text{-}TeR} &\xrightarrow[\mathrm{1M\ NaOH/EtOH}]{\mathrm{NaBH_4}} \mathrm{2NaTeR} \\ \mathrm{2NaTeR} &\rightleftharpoons \mathrm{RTe^-} + \mathrm{Na^+} \end{aligned}\right) \quad \text{Eq. 5.1}$$

The compounds R-C≡C-TeNa have been prepared (144) by the addition of elemental tellurium to the sodium acetylide, prepared by treatment of sodium or sodium amide with acetylenic hydrocarbons in liquid ammonia. Tellurium inserts into the C-Na bond as shown below in Equation 5.2.

$$\mathrm{RC{\equiv}C\text{-}Na} + \mathrm{Te} \xrightarrow{\mathrm{liq\ NH_3}} \mathrm{R\text{-}C{\equiv}C\text{-}TeNa} \qquad \text{Eq. 5.2}$$

The alkynyl-sodium tellurides have never been isolated, but have been found to react with alkyl-halides to give alkynylalkyl-tellurides. Thus methyl-iodide is reacted with alkyl-thioethynyl-sodium tellurides and ethynyl sodium telluride in liquid ammonia to give alkylthioethynyl-methyl-tellurides(145,146) and ethynyl-methyl-telluride(147) respectively as shown below.

$$\text{R-C}\equiv\text{C-TeNa} + \text{CH}_3\text{I} \xrightarrow{\text{liq NH}_3} \text{R-C}\equiv\text{C-TeCH}_3 + \text{NaI} \qquad \text{Eq. 5.3}$$

where $R=R_3S$, C_3H_7S and H

The preparation of diaryl-tellurides, RTeR' (R,R' = C_6H_5, C_6H_5; C_6H_5, $4CH_3C_6H_5$; $4CH_3OC_6H_5$, $4CH_3C_6H_5$), has also been claimed(148) by reacting RTeNa with the appropriate diazonium tetrafluoroborates, $R'N_2{}^+BF_4{}^-$.

Some years ago, it was suggested by McWhinnie and coworkers(149) that the oxidative addition reaction of diorganotellurides with methyl-iodide went through an intermediate which was a charge-transfer complex as shown in Figure 5.1.

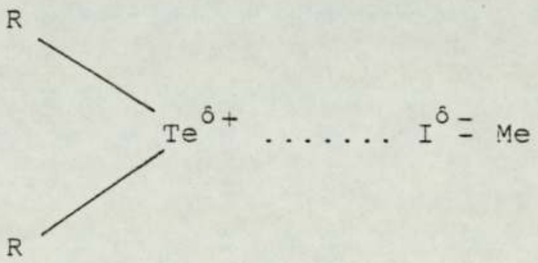
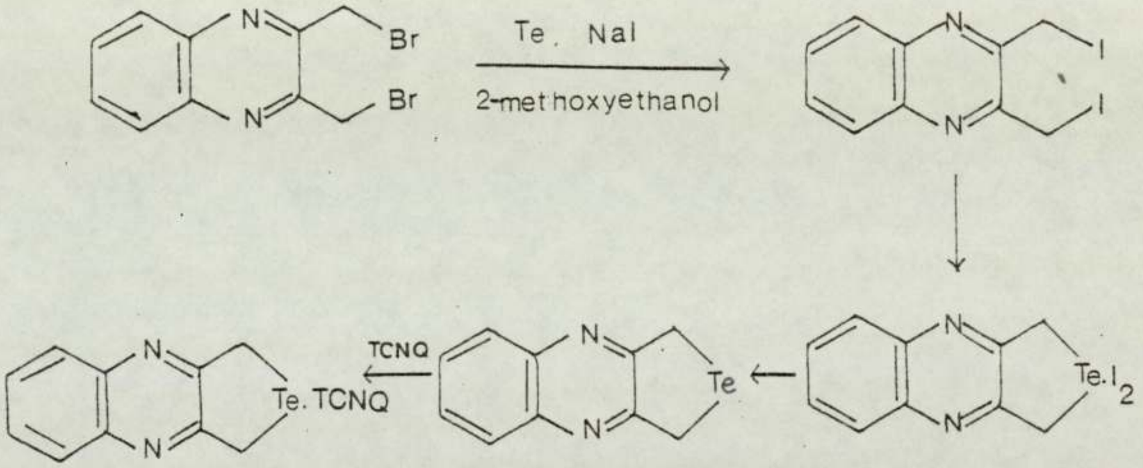


Figure 5.1

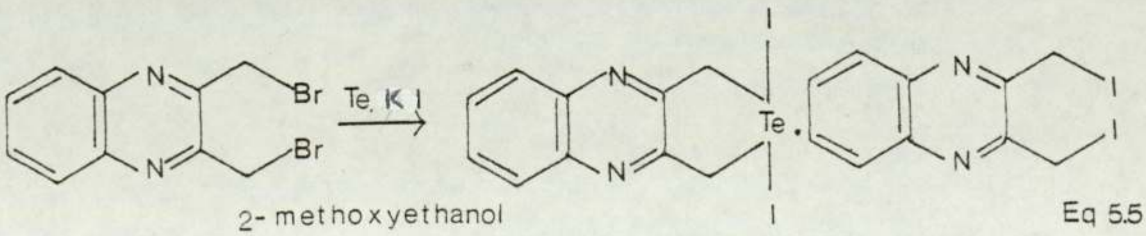
Charge-transfer compounds have been demonstrated for organotellurium complexes with 7, 7, 8, 8-tetracyanoquindimethane (TCNQ)(150). Also the reaction product of 2.3-bis(bromomethyl)quinoxaline with tellurium and sodium iodide on reduction gave a violet crystalline material, 3.4-quinoxalino-1-tetracyclopenta-1-1-diiodide, which produced a black crystalline charge-transfer complex with TCNQ as illustrated in Equation 5.4.



Ⓐ Violet

Eq 5.4

When 2,3-bis(bromomethyl)qiunoxaline is reacted with tellurium and potassium iodide, a yellow 1:1 adduct of 3,4-quinolino-1-telluracyclopentane-1-1-diiodide and 2.3-bis-(iodomethyl)quinoxaline is isolated.



Eq 5.5

Ⓑ Yellow

McCullough and coworkers(49 .151,152.153.154) have demonstrated that in $RTeI_2$, R_2TeI_2 and $RTeI_3$ type compounds, a variety of intermolecular Te..I and I..I contacts exist and they postulated a correlation between colour and the type and degree of secondary bonding.

The compounds obtained in Equations 5.4 and 5.5, namely compounds A and B, are violet and yellow suggesting weak bonding in the crystal structure and strong intermolecular bonding respectively, according to McCullough's suggestion.

The crystal structure has also been determined for the yellow complex (B) and is illustrated in Figure 5.2.

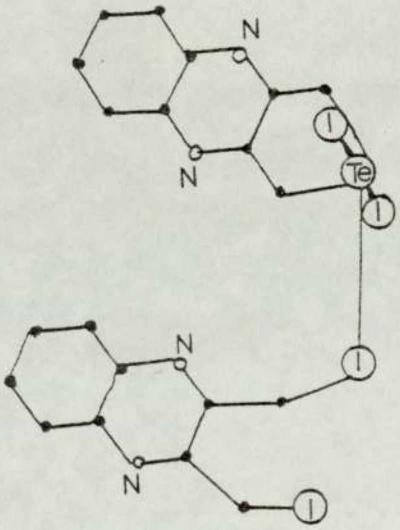


Figure 5.2

5.2 Experimental

The reactions with $RTe^{\ominus}$ anion were carried out by two different methods, one using mixed organic solvents and the other in the presence of a phase transfer catalyst.

5.2.1 Preparation of the Starting Materials

Preparation of diphenyl ditelluride Ph_2Te_2

Ph_2Te_2 was prepared according to Gunther's method(155).
M.P. 63°C Lit. 65°C

found %	C 35.2	H 2.60
$C_{12}H_{10}Te_2$ requires %	C 34.8	H 2.41

Preparation of bis(p-ethoxyphenyl)ditelluride

The ditelluride was prepared by the literature method(105) as described briefly.

$(pEtOPh)TeCl_3$ was prepared by refluxing tellurium tetrachloride, phenetol and chloroform under dry nitrogen for 2 hours. M.P. 182°C Lit. 182-183°C

Bis(p-ethoxyphenyl)ditelluride was obtained by reduction of the above trichloride at 0°C with potassium metabisulphite

($K_2S_2O_5$)   M.P. 105°C   Lit. 107 - 108°C

found %	C 38.3	H 3.50
$C_{16}H_{18}O_2Te_2$ requires %	C 38.6	H 3.60

Preparation of the phase transfer catalyst, benzyltri-n-butylammonium bromide $Bu_3N(CH_2Ph)BrQ^+Br^-$

Benzyl bromide (12 ml) was added to tri-n-butylamine (24 ml). The mixture was stirred at room temperature for 2 hours. A white solid, benzyltri-n-butylammonium bromide, was formed.

5.2.2 Preparation of $(RTe)_2(CH_2)_nX_2$ (where n=1) Complexes

5.2.2.1 The Method of Mixed Solvents - Method A

Bis(p-ethoxyphenyl)ditelluride (6.2 mmol) in benzene (2.5 cm^3) and ethanol (7.5 cm^3) was heated to reflux. To this solution, sodium tetrahydroborate (10 mmol) in 1 mol dm^{-3} sodium hydroxide (8.5 cm^3) was added dropwise. The reaction mixture became colourless on completion of the addition. Dihalomethane (bromo-/iodo-) (2 mmol) in benzene (5 cm^3) was then added and the warm mixture was stirred for 30 minutes. The mixture was then poured into water (100 cm^3) and the organic layer was extracted with diethyl ether (2 x 100 cm^3). A yellow precipitate was separated out in 75%

yield, was filtered off, washed with diethyl ether and dried in vacuo. Recrystallisation from acetonitrile gave yellow needles.

Dichloromethane gave white fibrous material which was found difficult to identify.

The analytical data for the compounds formed from the reaction between RTeNa and organic dihalides are given in Table 5.1 where R=(pEtOC_6H_4) and (C_6H_5).

5.2.2.2 In the Presence of a Phase Transfer Catalyst - Method B

Bis(p-ethoxyphenyl)ditelluride (1 mmol) in benzene (50 cm^3) was treated with a solution of sodium tetrahydroborate (10 mmol) and benzyltri-n-butylammonium bromide (2 mmol) in 1 mol dm^{-3} sodium hydroxide (20 cm^3). The mixture was stirred for 2 hours during which time the colour of the ditelluride was lost. Dihalo-(iodo-/bromo-)methane (2 mmol) was added and stirring continued for 4 hours at 30°C. Diethylether was then added and the mixture was set aside. A yellow precipitate was obtained in 60% yield and was separated, washed with diethyl-ether and dried in vacuo. Recrystallisation from acetonitrile gave compounds described in method A.

Complex	Found %		Required %		M.P. ^{o}C	Colour
	C	H	C	H		
$[(pEtOC_6H_4)\ Te]_2CH_2.CH_2I_2$	27.2	2.90	27.8	2.80	118	deep yellow
$[(pEtOC_6H_4)Te]_2CH_2.CH_2Br_2$	30.0	3.11	31.5	3.21	152-154	cream
$[(C_6H_5)Te]_2CH_2.CH_2I_2$	24.00	2.15	24.30	2.02	-	deep yellow
$(pEtOC_6H_4)Te(CH_2)_4Br$	37.2	4.40	37.4	4.40	258-260	white
$(pEtOC_6H_4)Te(CH_2)_4Cl$	41.9	5.10	42.3	4.90	228-230	white
$PhTe(CH_2)_4Br$	37.9	3.0	35.1	3.80	280	white
$PhTe(CH_2)_4Cl$	39.9	4.10	40.4	4.37	240	white
$P(EtOC_6H_4)Te(CH_2)_3Br$	36.0	3.80	35.5	4.00	260-262	pale yellow

ref for the telluronium salts - (140)

Table 5.1 Analytical data (along with melting points and colour) for new organotellurium compounds.

N.B. In both methods when n=4, R=pEtOC$_6$H$_5$ or (Ph) and X=Cl, Br white precipitate were obtained on cooling the warm reaction mixture$^{(140)}$.

The analytical data of all the compounds are tabulated in Table 5.1 together with their melting points.

5.2.3 Preparation of Palladium Complexes with $(RTe)_2CH_2.CH_2X_2$

A dihalomethane complex $(RTe)_2CH_2.CH_2X_2$ (prepared as above) (1 mmol) was added dropwise to a dichlorobis(benzonitrile) palladium(II) $Pd(PhCN)_2Cl_2$ (1 mmol) in chloroform at room temperature. The solution was stirred under nitrogen for 30 minutes. The red-brown precipitate so obtained was filtered off and vacuum dried. Analytical data for the complexes prepared are given below.

$Pd(PhCN)_2Cl_2$ with $(RTe)_2CH_2.CH_2I_2$ complex where R=pEtOPh

found	C 29.17	H 2.90	Cl 11.27%
$C_{17}H_{20}Cl_2O_2PdTe_2$ requires	C 29.62	H 2.90	Cl 10.31%

$Pd(PhCN)_2Cl_2$with $(RTe)_2CH_2.CH_2Br_2$ complex where R=pEtOPh

found	C 28.00	H 2.85	Cl 9.75%
$C_{17}H_{20}Cl_2O_4PdTe_2$ requires	C 28.30	H 2.77	Cl 9.85%

5.2.4 Reaction of RTe$^{\ominus}$ Anion with *Vic*-dibromo-Compounds

Method A in Section 5.2.2 was repeated with 2,3-dibromo-2-methyl-2-pentane and 2,3-dibromo-2-methyl-2-butane, each of 1 mmol instead of 2 mmol dihalomethane as used in Method A.

Addition of *vic*-dibromo-compound immediately changed the colourless solution to a dark red solution together with a red-orange precipitate indicating the formation of ditelluride in the reaction mixture. The precipitate was filtered off and the filtrate was subjected to g.l.c. analysis. In each case peaks due to the corresponding alkenes were observed in the g.l.c.

2-iodo-2-methyl-2-butane also gave similar results eliminating 2-methyl-2-butene and ditelluride.

5.2.5 Reaction of RTe$^{\ominus}$ with Dichlorocycloalkanes

The reaction of dichlorocarbene with cyclohexene was achieved by the following method$^{(156)}$;

Cyclohexene (9.6 g, 44 mmol) and chloroform (11 cm^3, 135 mmol) and tributylbenzylammonium bromide (0.15 g, 0.44 mmol) were stirred at 50°C while aqueous sodium hydroxide (13.5 g in 27 cm^3, 337 mmol) was added over a period of 15 minutes.

After 2 hours iced water (50 cm^3) was added and the mixture was acidified with sulphuric acid (10%) and extracted with diethyl ether (3 x 25 cm^3). The combined ether layer was washed with water, then saturated sodium chloride, dried and the solvent removed. The viscous liquid obtained was characterised by infra-red spectroscopy.

7,7-dichloromonocarane (3.30 g, 20 mmol) thus prepared was then added to an emulsion of bis(p-ethoxyphenyl) ditelluride (4.96 g, 10 mmol) in benzene (50 cm^3), benzyltributylammonium bromide (0.45 g, 1.76 mmol), sodium hydroxide (50%) (100 cm^3) in dropwise fashion with vigorous stirring at 50°C. A white precipitate formed when petroleum ether (60-70°C) was added to the cold mixture.

The precipitate was analysed by elemental analysis, infrared and mass spectrometry.

5.3 Results

The elemental analysis of the compounds obtained with $RTe^{\ominus}$ ($R=PhpEtOC_6H_4$) and $X(CH_2)_nX$ (where X=Cl, Br, I and n=1, 3, 4) are tabulated in Table 5.1. Tables 5.2 and 5.3 show the mass spectroscopic data for $[(pEtOPh)Te]_2CH_2.CH_2I_2$ and $(PhTe)_2CH_2.CH_2I_2$ respectively.

Figures 5.3, 5.4 and 5.5 show the major peaks in mass spectra $[(pEtOPh)Te]_2CH_2CH_2I_2$, $(PhTe)_2CH_2CH_2I_2$ and $RTe(CH_2)_4X$ (where

$X=Cl$, Br and $R=pEtOC_6H_4$). Table 5.4 summarises the ^{125}Te Mössbauer data for reaction products of $NaTe(C_6H_4OEt\text{-}p)$ with dibromoalkanes. The ^{13}C and ^{125}Te NMR data for 1-telluracyclopentane derivatives in DMSO are tabulated in Table 5.5.

The infra-red spectra of $(pEtOC_6H_4Te)_2CH_2.CH_2I_2$, CH_2I_2 and $(pEtOC_6H_4Te)_2CH_2.CH_2Br$ are shown in Figures 5.6, 5.7 and 5.8 respectively.

The ^1H NMR spectra for $(pEtOC_6H_4Te)_2CH_2.CH_2I_2$ and $(pEtOC_6H_4)Te(CH_2)_4Br$ in DMSO are shown in Figures 5.9 and 5.10. ^{13}C NMR for $(pEtOC_6H_4)Te(CH_2)_4Br$ and the ESR spectrum of $(pEtOC_6H_4Te)_2CH_2.CH_2I_2$ are illustrated in Figures 5.11 and 5.12 respectively.

Figure 5.20 and Figure 5.21 illustrate the infra-red spectra of the complexes $Pd(PhCN)_2Cl_2$ and $(RTe)_2CH_2.PdCl_2$. Figure 5.22 shows the infra-red spectrum of $(RTeO)_2CH_2PdCl_2$ and Figure 5.23 shows that of $(RTeO)_2O$. Figure 5.25 gives the major peaks in the mass spectrum of $(RTeO)_2O$.

5.4 Discussion

The experiments were carried out by using a solution of diorgano-ditelluride R_2Te_2 (where $R=Ph$, $pEtOC_6H_4$) in one portion of benzene and three portions of ethanol as desc-

m/e	Species	Relative Intensity
516	$(pEtOC_6H_4)_2Te_2(CH_2)^+$	30.5
502	$(pEtOC_6H_4)_2Te_2^+$	6.1
372	$(pEtOC_6H_4)_2Te^+$	100
268	$CH_2I_2^+$	29.0
265	$(pEtOC_6H_4)Te(CH_2)^+$	90.7
251	$(pEtOC_6H_4)Te^+$	100
242	$(pEtOC_6H_4)_2^+$	98.1
223	$(p\text{-}HOC_6H_4)Te^+$	100
93	$OC_6H_5^+$	100
78	C_6H_6	100
45	OC_2H_5	95.3

A relative to ^{1}H ^{12}C ^{130}Te ^{127}I ^{16}O

Table 5.2 Mass spectroscopic data for $[(p\text{-}EtOC_6H_4)Te]_2CH_2.CH_2I_2$

m/e	Species	Relative Intensity
428	$(PhTe)_2(CH_2)^+$	22.4
414	$Ph_2Te_2^+$	weak
348	$Ph(CH_2)TeI^+$	51.0
284	Ph_2Te^+	100
268	$CH_2I_2^+$	100
221	$PhTeCH_2^+$	99.0
207	$PhTe^+$	100
154	Ph_2^+	95.3
141	CH_2I^+	99.0
77	Ph^+	100

A relative to ^{1}H ^{12}C ^{130}Te ^{127}I

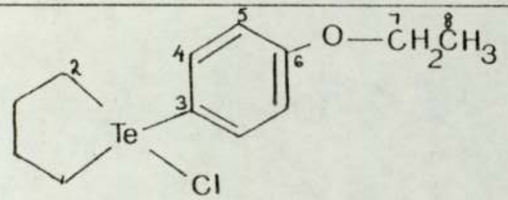
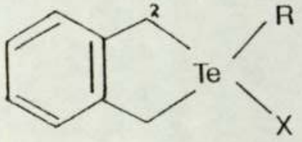
Table 5.3 Mass spectroscopic data for $(PhTe)_2(CH_2)CH_2I_2$

Compound	δ^a	Δ^b	$\Gamma_{\frac{1}{2}}$
$[(pEtOC_6H_4)Te]_2CH_2.CH_2Br_2$	0.53	7.58	6.33
$(pEtOC_6H_4)Te(CH_2)_3Br$	0.36	5.58	5.68
$(pEtOC_6H_4)Te(CH_2)_4Br$	0.38	5.50	5.43

a ± 0.08 mms^{-1} vs $^{125}Sb/Cu$

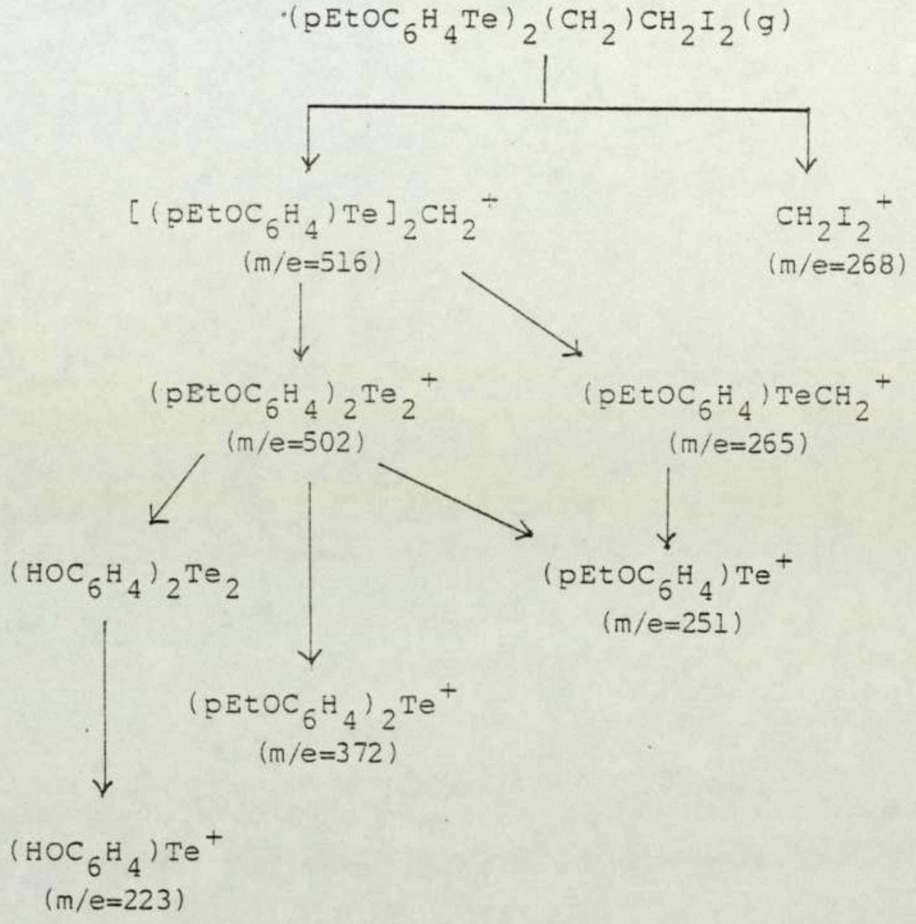
b Quadrupole splitting (± 0.1 mms^{-1})

<u>Table 5.4</u> ^{125} Mössbauer data (mms^{-1}) for reaction products of $NaTe(C_6H_4OEt\text{-}p)$ with dibromoalkanes(141)

Compound	$\delta(^{13}C)$ <u>vs</u> $SiMe_4$	$\delta(^{125}Te)$ <u>vs</u> Me_2Te
	31.43(C^1), 35.68(C^2), (C^3), 134.66(C^4), 115.73(C^5), 160.11(C^6), 63.21(C^7), 14.33(C^8)	761
* 	34.4(C^2)(R=Me, X=I) 34.3(C^2)(R=allyl, X=Br)	651(R=Me, X=I) 688.3(R=allyl, X=Br) 722(R=benzyl, X=Br)

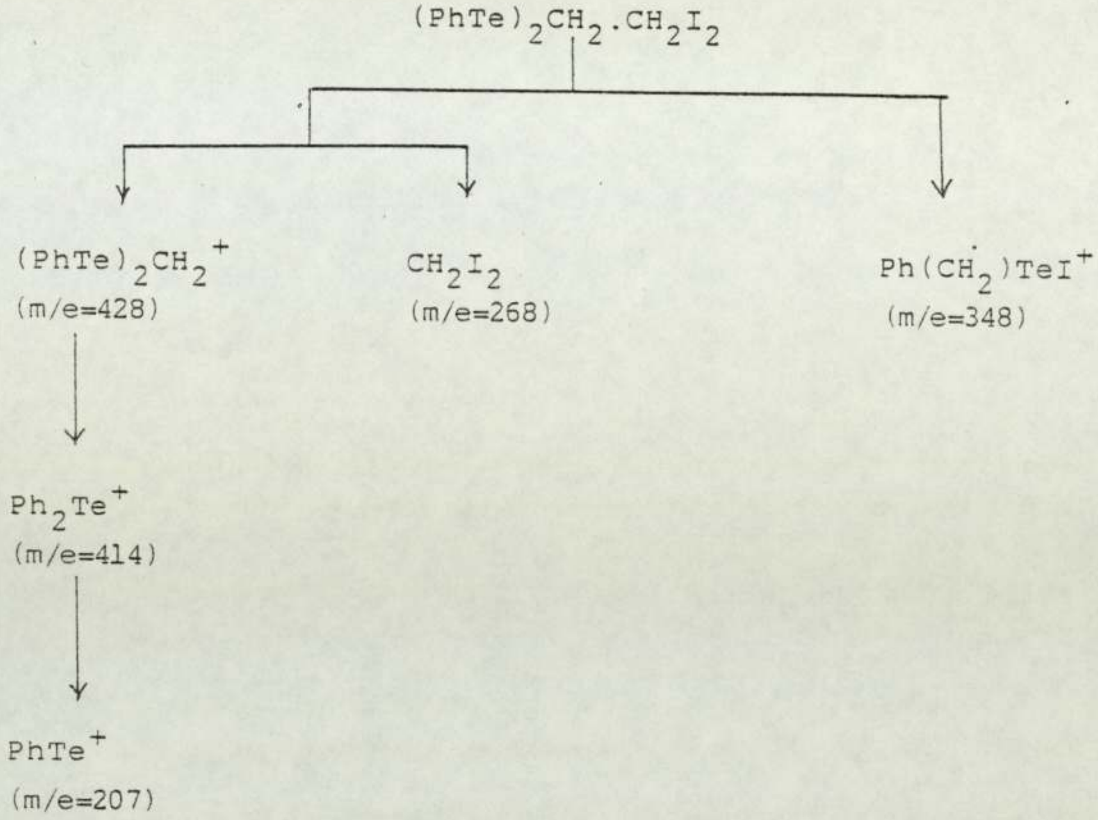
* data from ref(157) and (158)

<u>Table 5.5</u> ^{13}C and ^{125}Te NMR data for 1-telluracyclopentane derivatives in DMSO



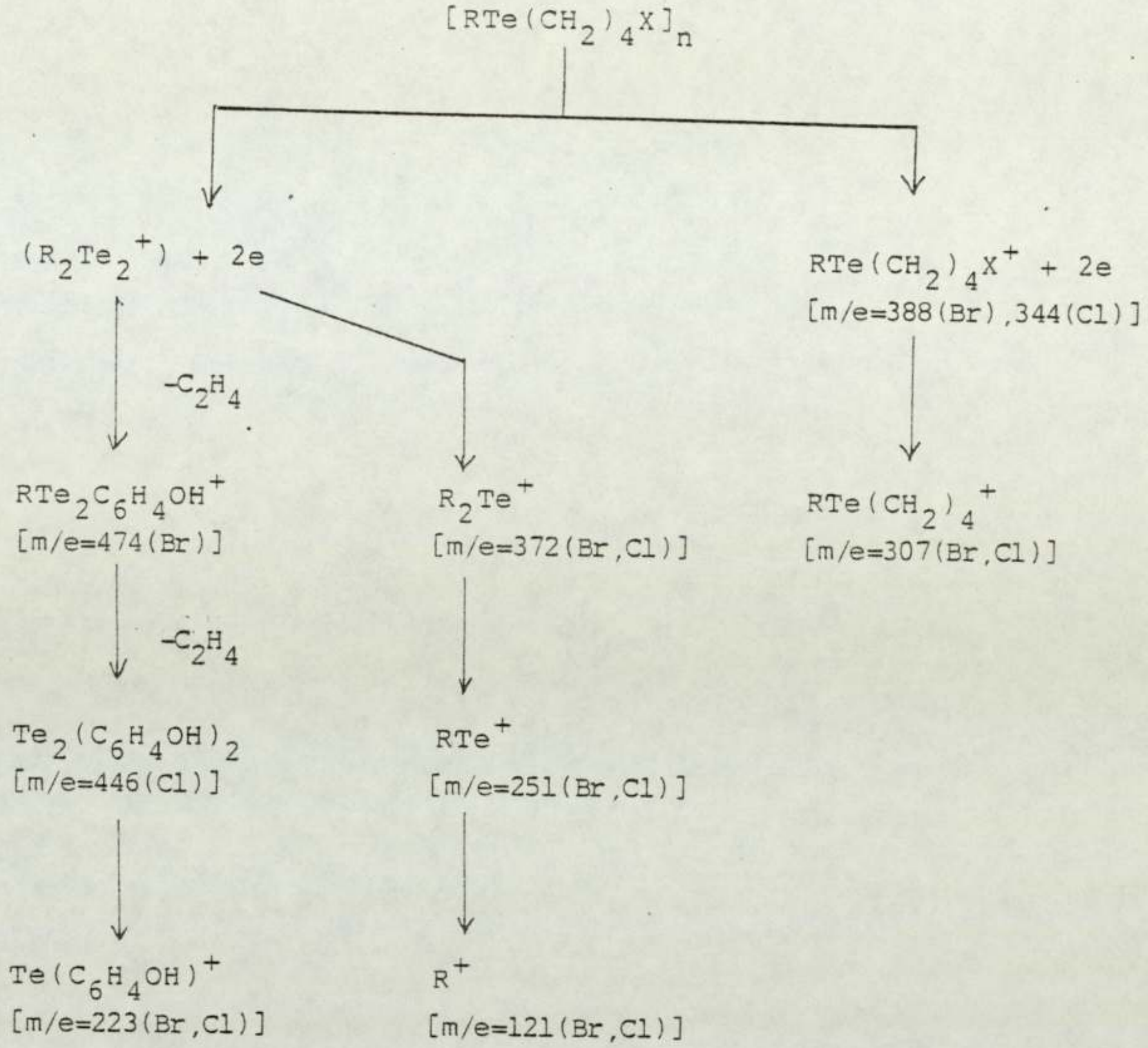
Quoted m/e values are referenced to ^{130}Te, ^{127}I, ^{12}C, ^{1}H and ^{16}O.

Figure 5.3 Major peaks in the mass spectrum of $[(pEtOC_6H_4)Te)_2CH_2.CH_2I_2$



Quoted m/e values are referenced to ^{130}Te, ^{127}I, ^{12}C and ^{1}H.

Figure 5.4 Major peaks in the mass spectrum of $(PhTe)_2CH_2$. CH_2I_2



Major peaks in the mass spectrum of $(pEtOC_6H_4)Te(CH_2)_4X$ (X=Cl or Br). Quoted m/e values(140) are referenced to ^{130}Te, ^{37}Cl, ^{81}Br, ^{12}C, ^{1}H and ^{16}O.

A round bracket around a fragment implies 'not observed' and (Br and/or Cl) implies 'observed for indicated X only'.

Figure 5.5

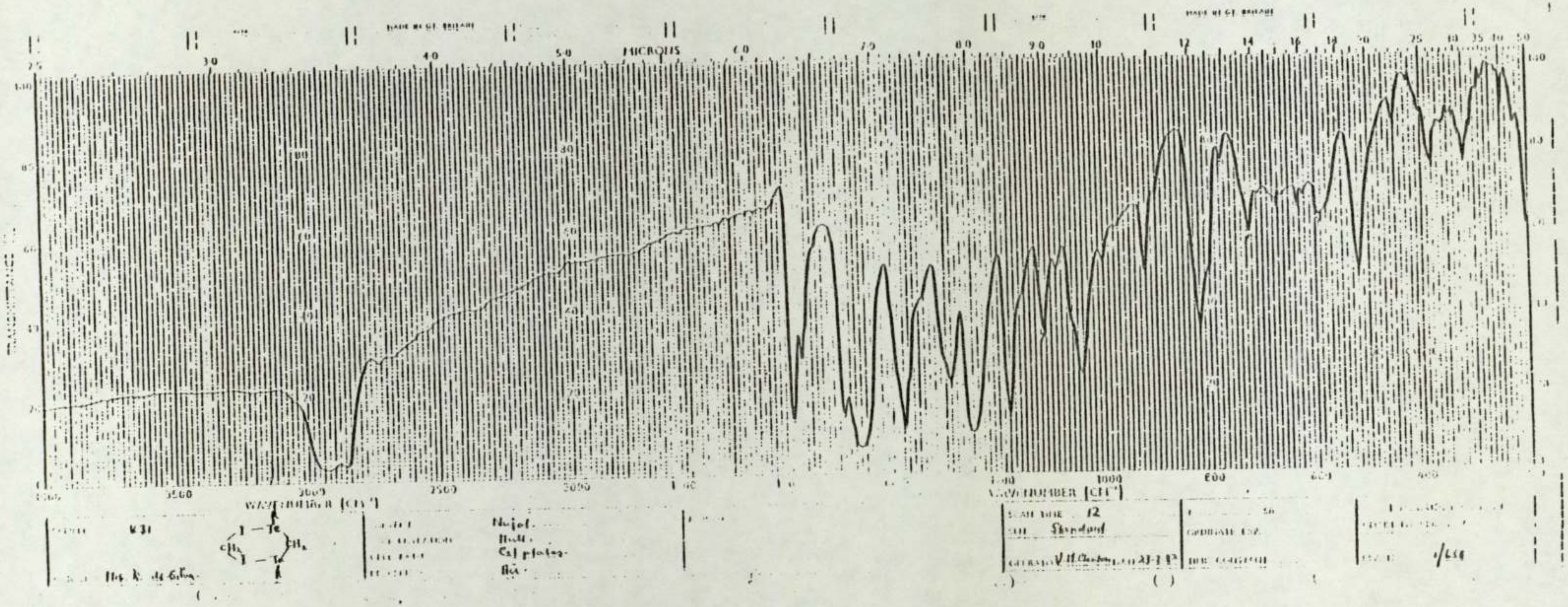

MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
3500
3000
2500
2000
1000
800
600
400
WAVENUMBER (CM⁻¹)
K31
Nujol.
Mull.
CsI plates.
Air.
SCAN TIME 12
SLIT Standard
ORDINATE EXP.

Figure 5.6

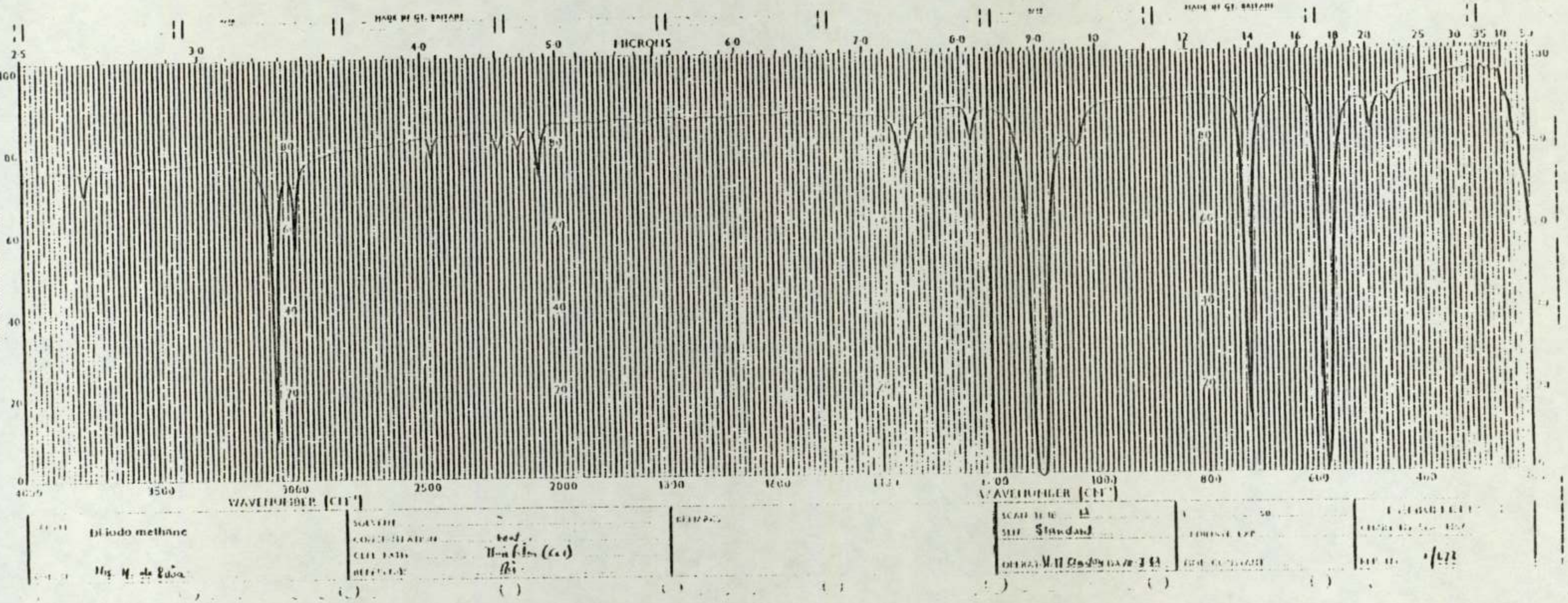

MICRONS
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)
Diiodo methane
neat
Thin film (cel)
Standard

Figure 5.7

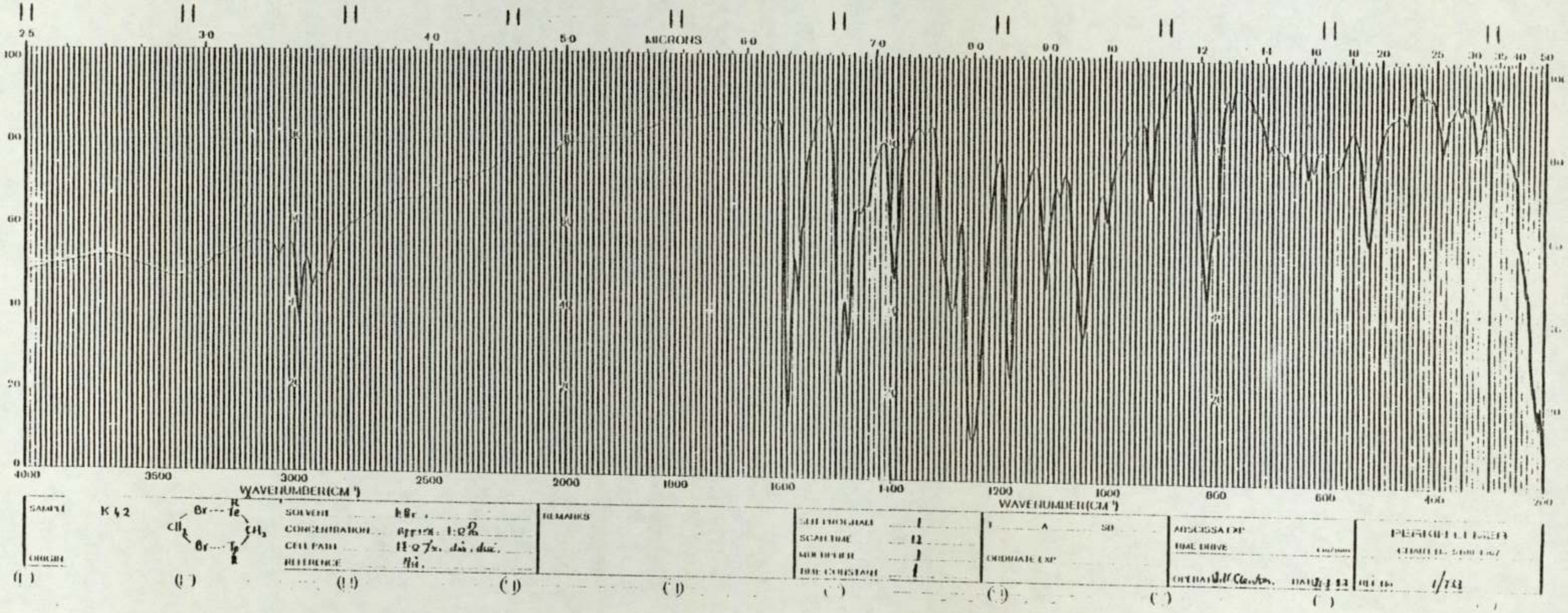

MICRONS
WAVENUMBER(CM⁻¹)
SAMPLE K42
SOLVENT KBr
REMARKS
PERKIN ELMER

Figure 5.8

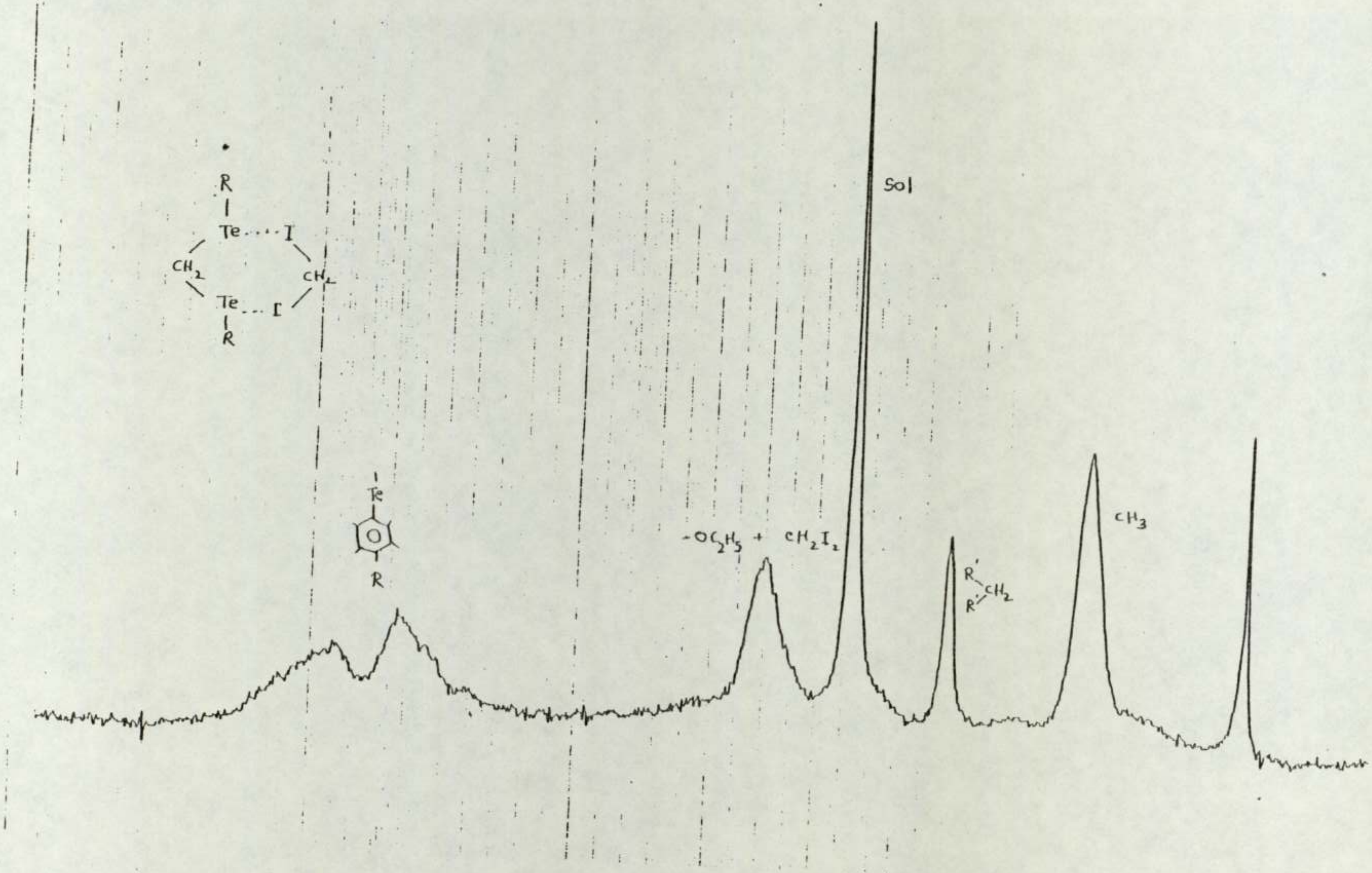


Figure 5.9 ^{1}H NMR spectra for $(pEtOC_6H_5Te)_2CH_2.CH_2I_2$ in DMSO

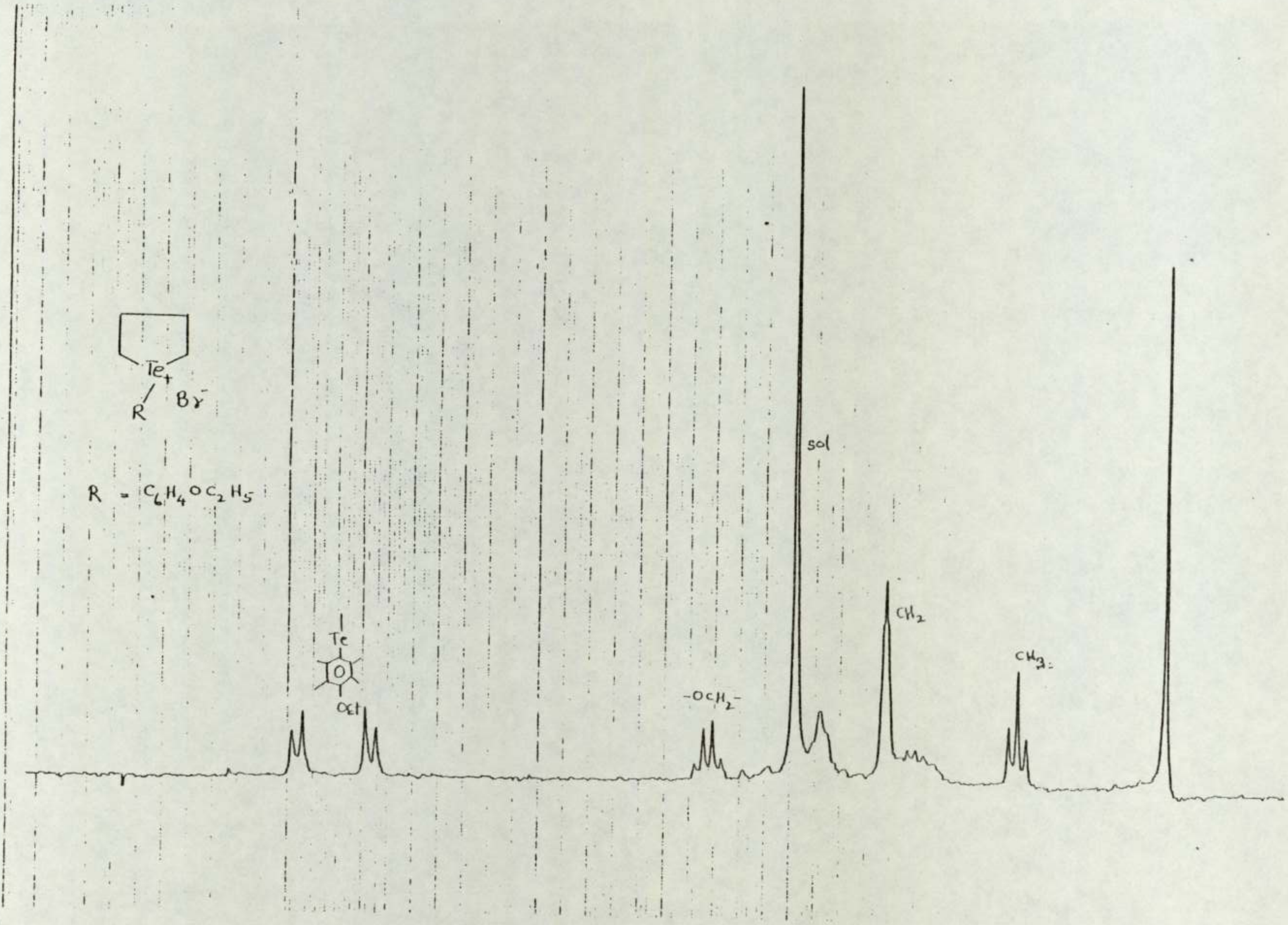


Figure 5.10 ^{1}H NMR spectra for p-EtO(CH$_2$)$_4$Br in DMSO

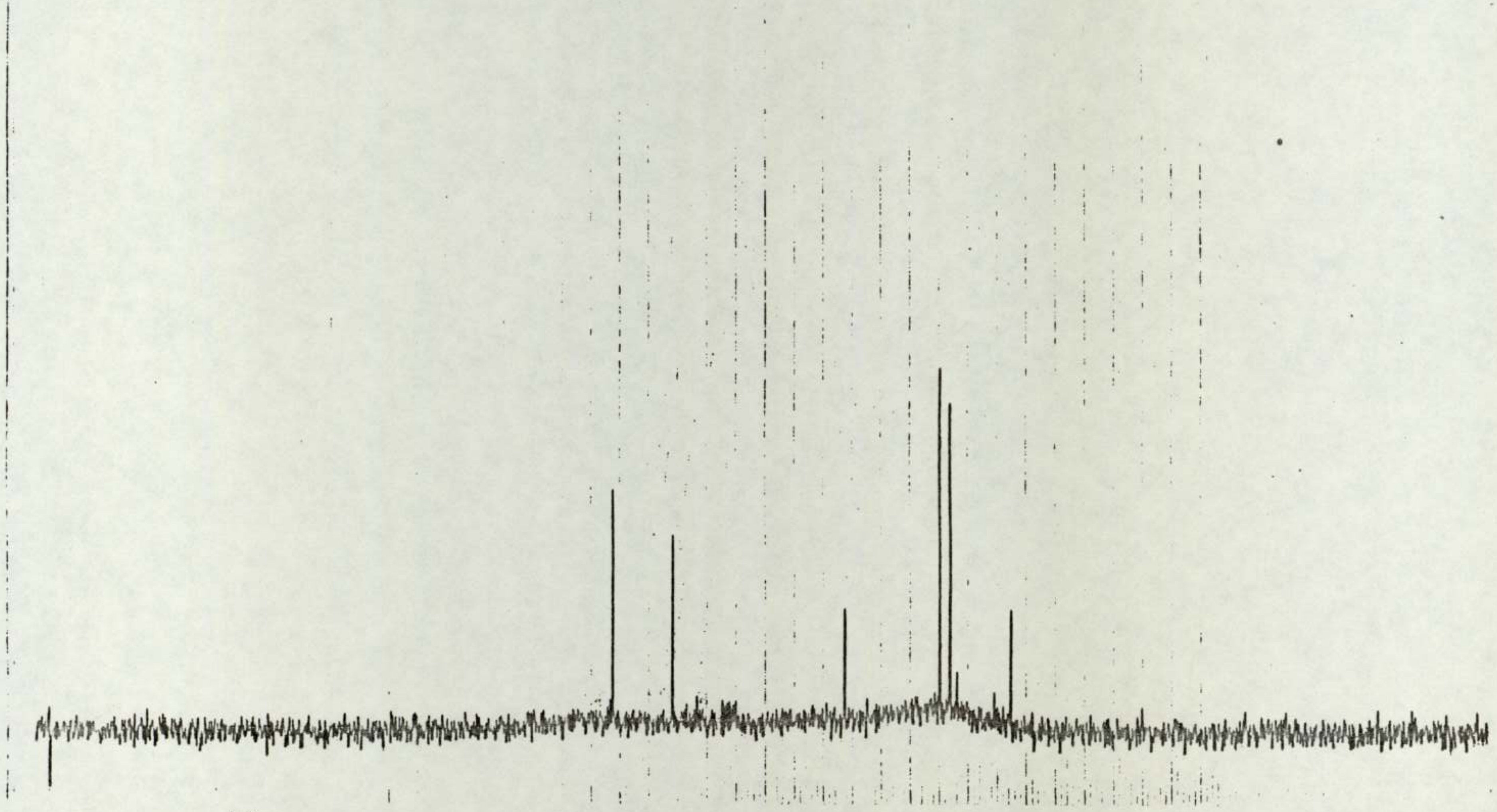


Figure 5.11 ^{13}C NMR for $(pEtOC_6H_4)Te(CH_2)_4Br$

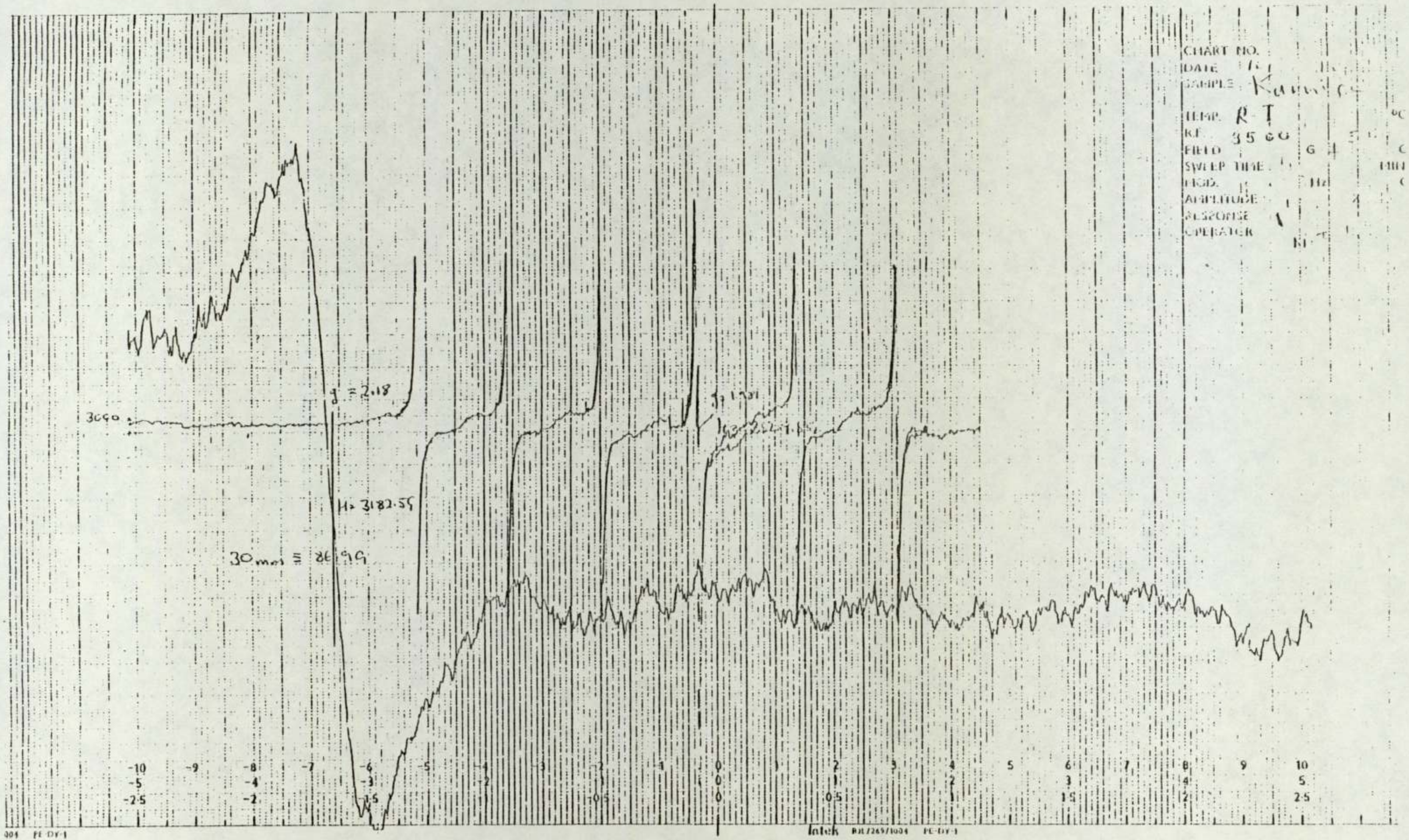


Figure 5.12 ESR spectrum for $(pEtOC_6H_4Te)_2CH_2.CH_2I_2$

ribed in Method A. The addition of alkaline sodium tetrahydroborate affords a solution with the chemical properties of NaTeR. Addition of $X(CH_2)_n)X$ (where X=Cl, Br, I and n=1, 3, 4) to NaTeR solutions gave compounds similar to those obtained using the phase transfer catalyst (Method B).

In both methods the same reaction products were obtained but the use of a phase transfer catalyst shows no obvious advantage in these systems.

From the analytical data (Table 5.1), the empirical formula of $(RTe)_2CH_2.CH_2X_2$ (where $R=pEtOC_6H_4$, Ph and X=Br, I) is obtained for the methylene compounds which is different from the empirical formula $(RTe)_2(CH_2)_nX$ obtained for 1,4 dibromobutane and 1,3 dibromopropane with n=4 and 3 respectively. This suggests that the reaction of NaTeR with dibromo-and diiodo-methane follows a different course.

In this instance, nucleophilic substitution of both halogen atoms proceeds but the products are isolated as pale yellow (CH_2Br_2) or deep yellow (CH_2I_2) solids containing 1 mol. of dihalogenomethane $(RTe)_2CH_2.CH_2X_2$ (X=Br or I).

The mass spectra (Tables 5.2 and 5.3) are in accord with this formulation.(Products from the reaction with CH_2Br_2 sometimes showed variable C analysis figures but this correlates with partial loss of dibromomethane. The broad features of the spectra may be related as in Figures 5.3 and 5.4. Preliminary experiments indicate that the materials behave as bis(telluride) ligands with 'soft' metal centres - vide infra)

Infra-red and ^1H NMR spectra support the formulation of the complexes. For example, strong features at 1114, 725 and 529 cm^{-1} in the spectrum of $[(pEtOC_6H_4)Te]_2CH_2.CH_2I_2$ (Figure 5.6) certainly arise from CH_2I_2 (Figure 5.7) and correlate with bands at 1100, 721 and 599 cm^{-1} in the free liquid. A rather dilute solution of $[(pEtOC_6H_4)Te]_2CH_2.CH_2I_2$ in $(CD_3)_2SO$ gave a ^1H NMR spectrum as shown in Figure 5.9, in which significant broadening of signals had occurred, doubtless due to the paramagnetism detected by ESR spectroscopy (see below); the spectrum integrates correctly but the broad lines mask coupling of the Te-CH_2-Te methylene protons to ^{125}Te (natural abundance 6.99%).

The Mössbauer spectrum has been obtained for $[(pEtOC_6H_4)Te]_2$-$CH_2.CH_2Br_2$ and it will be noted (Table 5.4) that the parameters are out of step with those of the telluronium salts discussed below. ^{125}Te Mössbauer data for $(pEtOC_6H_4)Te(CH_2)_4Br$ is typical of a telluronium (IV) compound and, in particular, Δ is within the expected range for a telluronium salt. The results obtained for methylene compounds are seen to be more consistent with a tellurium (II) species when comparing values obtained for other tellurium (II) compounds[87].

The chemical isomer shift is, within the errors, more positive than δ for the other two compounds, which implies a greater s electron density on tellurium in this compound. This may imply that some mechanism is operative which leads to withdrawal of 5p-electron density thus deshielding the 5s electron pair. This hypothesis gains more positive support from the value of Δ, which is significantly lower than that expected (ca. 10 mm s^{-1}) for a telluride(87). At the same time the value is too high for a telluronium salt. Thus the methylene species are considered to be of two possible formulations as illustrated in Figure 5.13.

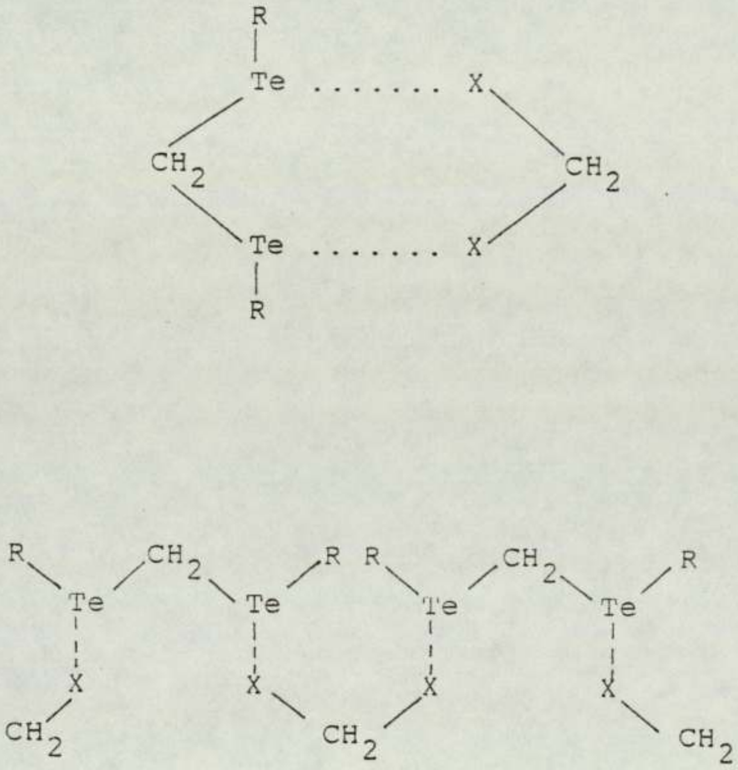


Figure 5.13

The compound $[(pEtOC_6H_4)Te]_2CH_2.CH_2I_2$ gives a broad ESR signal in solid state ($\Gamma_{\frac{1}{2}}$=75 G) centered on g=2.18, as shown in Figure 5.11. This suggestion that these materials are indeed charge-transfer complexes is the only one which offers a self-consistent interpretation of all the data. It is proposed that electron density is transferred from the spare-pair p-orbital on tellurium. This will decrease the p-orbital occupational imbalance and, accordingly, reduce Δ. Simultaneously, removal of p-electron density will increase δ. Similar effects have been noted for organotellurium complexes with 7,7,8,8-tetracyanoquinodimethane (TCNQ)(159) and the implication is that charge-transfer is considerable.

It has previously been suggested that a charge-transfer interaction may be the first step in the oxidative addition of methyl-iodide to diphenyl-telluride(149). These data support that hypothesis.

The formulations of the n=1 compounds i.e., the methylene compounds, have previously been suggested by Davis(141) to be as shown in Figure 5.14. These formulations were postulated although they were not supported by physical data.

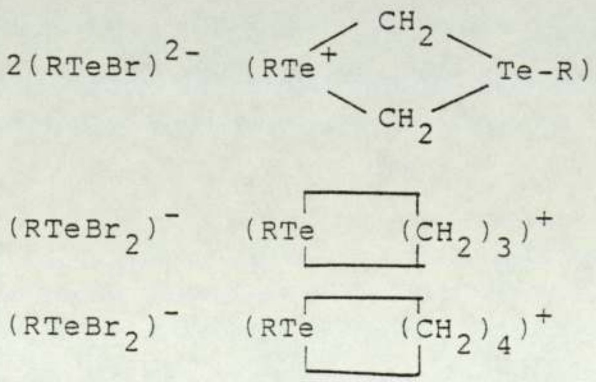


Figure 5.14

Davis also suggested that $(RTe)_2(CH_2)_nBr_2$ could possibly have a polymeric structure of the type shown in Figures 5.15 and 5.16.

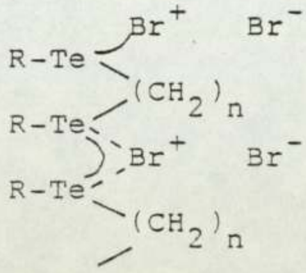


Figure 5.15

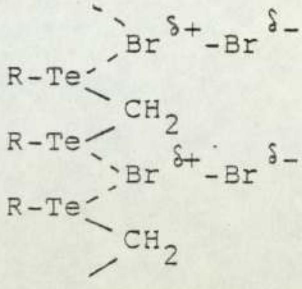


Figure 5.16

However, it would appear that Davis based his proposals on an incorrect stoicheometry.

The reaction of tetrahydroborate reduced ditellurides, R_2Te_2 with $(CH_2)_nX_2$(n=3 or 4) gives materials of stoicheometry $RTe(CH_2)_nX$. The compounds $RTe(CH_2)_4X$ (R=$pEtOC_6H_4$ or Ph; X=Cl or Br) are salt like and dissociate as 1:1 electrolytes in water. ^{125}Te Mossbauer data (Table 5.4) for $(pEtOC_6H_4)Te(CH_2)_4Br$ are typical of a tellurium (IV) compound and, in particular, Δ is within the expected range for a telluronium salt. Thus the most acceptable formulation of the product is as a telluronium salt derived from 1-tellurocyclopentane (Figure 5.17).

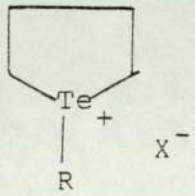


Figure 5.17

Nucleophilic attack on 1,4-dibromobutane by RTe^- has taken place, but quaternisation then proceeds more rapidly than attack at the second C-X bond by further RTe^-, as shown in Figure 5.18 (it seems likely that the telluronium salt may function as a phase-transfer catalyst once small quantities have been formed, thus helping to explain why no advantage accrues from the use of benzyl-tri-n-butylammonium bromide).

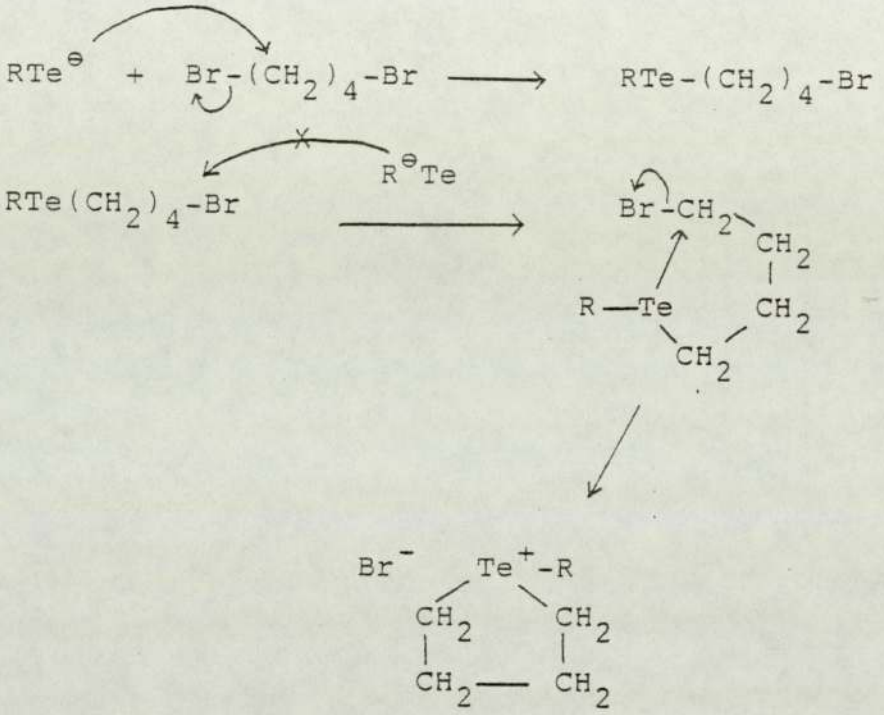


Figure 5.18

The mass spectra of $\overline{RTe(CH_2)_4}X$ (X=Cl or Br) support the formulation shown in Figure 5.17 and, in general respect, do not differ greatly from the spectra of a range of salts based on 1,3-dihydro-2-telluraindene(157). In particular, the observation of fragments containing two tellurium atoms may reflect a degree of association in the solid state.

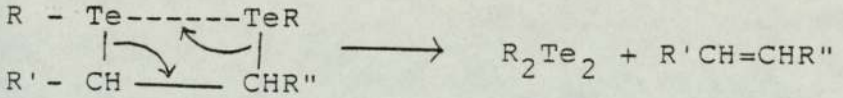
which is quite common for this variety of compound (158). The general features of the spectra may be related as in Figure 5.5.

Attempts were made to study the NMR spectra of the products from the reaction of 1,4-dichlorobutane with NaTe(C_6H_4OEt). The compound was not excessively soluble but a ^{13}C NMR spectrum was obtained (Table 5.5) in DMSO which was essentially the same as for a solution in D_2O, a solvent in which salt-like character has been demonstrated. Significant ion pairing occurs in DMSO as demonstrated by the Λ_m value which was 13.6 $ohm^{-1}cm^2mol^{-1}$ as compared with values in excess of 30 $ohm^{-1}cm^2mol^{-1}$ expected for strong electrolytes. The spectrum is certainly inconsistent with an open-chain structure RTe$(CH_2)_4$Cl for which extra carbon resonances would be expected. Also it contains features in common with data for salts derived from 1,3-dihydro-2-tellurindene (157,160). The ^{125}Te data are consistent with the telluronium salt formulation since the chemical shift is within the range of values for similar compounds. Thus, despite the limited solubility of the material, these NMR data (Table 5.5) provide good support for the proposed structure in Figure 5.17.

The product of the reaction of NaTe(C_6H_4OEt) with 1,3-dibromopropane is, from the Mössbauer data, also a telluronium salt.

It seems improbable that it should be formulated as a derivative of 1-telluracyclobutane since such a ring would be too strained. Thus, a polymeric formulation is more plausible and, indeed, the mass spectra of such compounds are very complex with many fragments of significantly higher m/e than $[RTe(CH_2)_3X]^+$.

Addition of <u>vic</u> dibromides, 2-methyl-2,3-dibromopentane and 2-methyl-2,3-dibromobutane to the colourless solution on NaTeR produced the familiar ditelluride colouration and, indeed, R_2Te_2 was recovered quantitatively. The other product was (when dibromides were used) an alkene which was generally identifiable by g.l.c. Thus it is possible that nucleophilic substitution does proceed and the ditelluride then eliminates in a concerted process (Equation 5.6). It is of interest that 2-iodo-2-methylbutane gave 2-methyl-2-butene under these conditions.



$$\begin{array}{ccc} R-Te & \cdots\cdots & TeR \\ | & & | \\ R'-CH & \text{---} & CHR'' \end{array} \longrightarrow R_2Te_2 + R'CH{=}CHR'' \qquad \text{Eq. 5.6}$$

It has recently been shown that sodium hydrogen telluride is a useful debrominating agent$^{(161)}$; it would appear that NaTeR is no less effective.

It is known$^{(162)}$ that the reaction of telluroester ($PhCOTeC_6H_4OEt$-p) with dichlorobis(benzonitrile)palladium(II), $Pd(PhCN)_2Cl_2$ results in an extremely insoluble red-brown product having an empirical formula Pd(RTe)$_2$ where R=pEtCC$_6$H$_4$. Diaryl-(163,164) and dialkyl-(163,165) tellurides are known to substitute for the labile benzonitrile ligand in dichlorobis(benzonitrile)palladium (II) to form four coordinated complex. Thus it was expected that the reaction between Pd(PhCN)$_2$Cl$_2$ and (RTe)$_2$CH$_2$.CH$_2$I$_2$ where R=pEtOC$_6$H$_4$ would give a complex.

The reaction is immediate upon the mixing of the two starting materials in the solvent, the product being isolated as a dark red-brown insoluble material with a melting point of 148°C. The structure is possibly dimeric, although this cannot be verified experimentally because the insolubility of the compound precluded molecular weight measurements in solution.

Figure 5.20 shows the infra-red spectrum of the complex Pd(PhCN)$_2$Cl$_2$. The infra-red spectrum of the palladium complex with (RTe)$_2$CH$_2$I$_2$ where R=EtOC$_6$H$_4$ (Figure 5.21) shows the disappearance of $\nu_{(C\equiv N)}$ at 2224 cm^{-1} and 2298 cm^{-1} and the absence of the broad $\nu_{(Te=O)}$ band around 600 cm^{-1} supporting the proposed structures (Figure 5.19). The elemental analysis is also in good agreement with the structures shown in Figure 5.19, having an empirical formula (RTe)$_2$CH$_2$.PdCl$_2$.

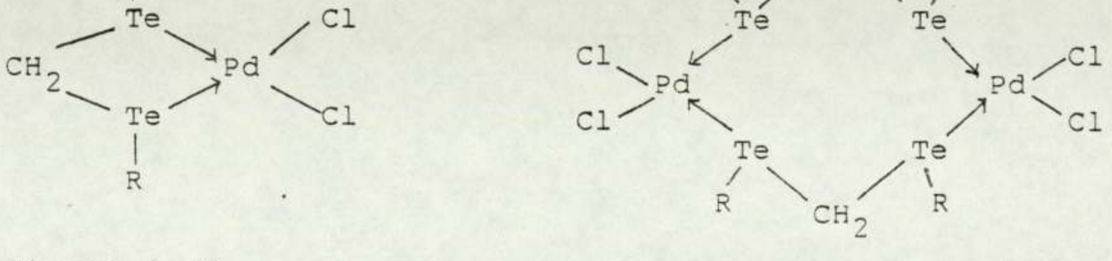
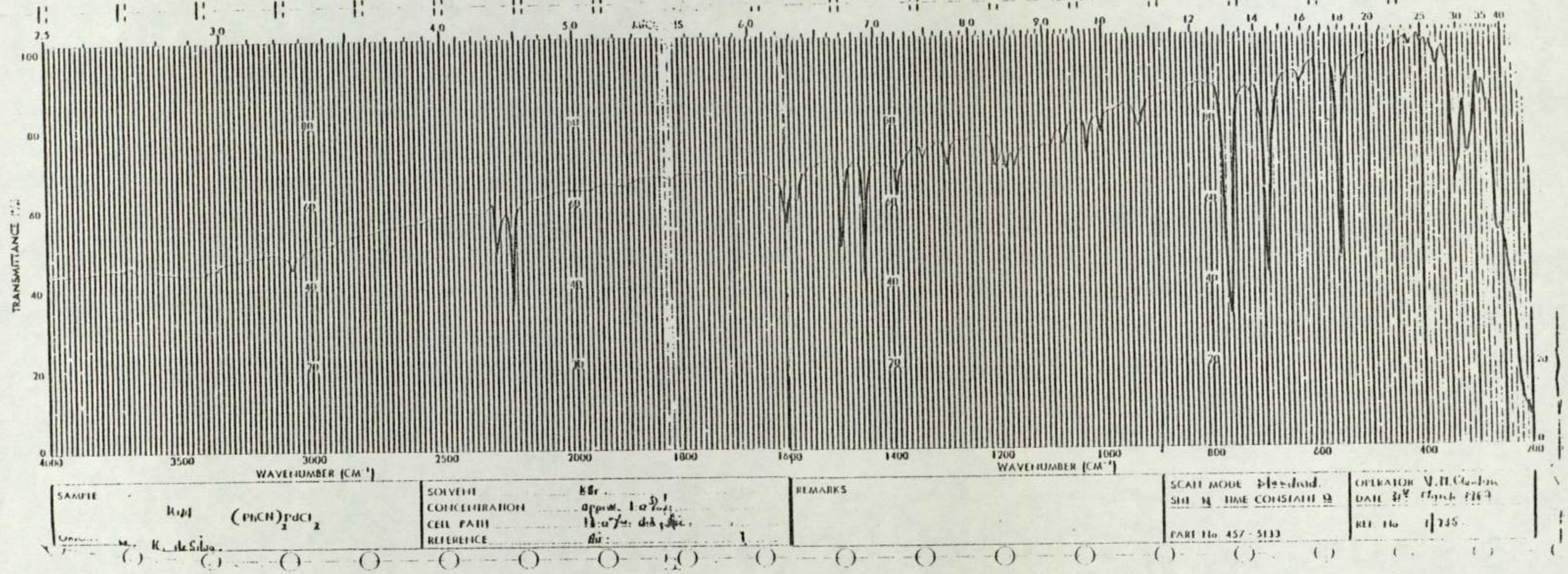


Figure 5.19



SAMPLE Ru(pl) (PhCN)$_2$PdCl$_2$

ORIGIN M. K. deSilva.

SOLVENT KBr.

CONCENTRATION approx. 1.0 ...

CELL PATH [illegible]

REFERENCE Air

REMARKS

SCAN MODE Standard.

SLIT N TIME CONSTANT Ω

PART No. 457 - 5133

OPERATOR V.H. Gordon

DATE 31st March 1969

REF No. 1/735.

Figure 5.20

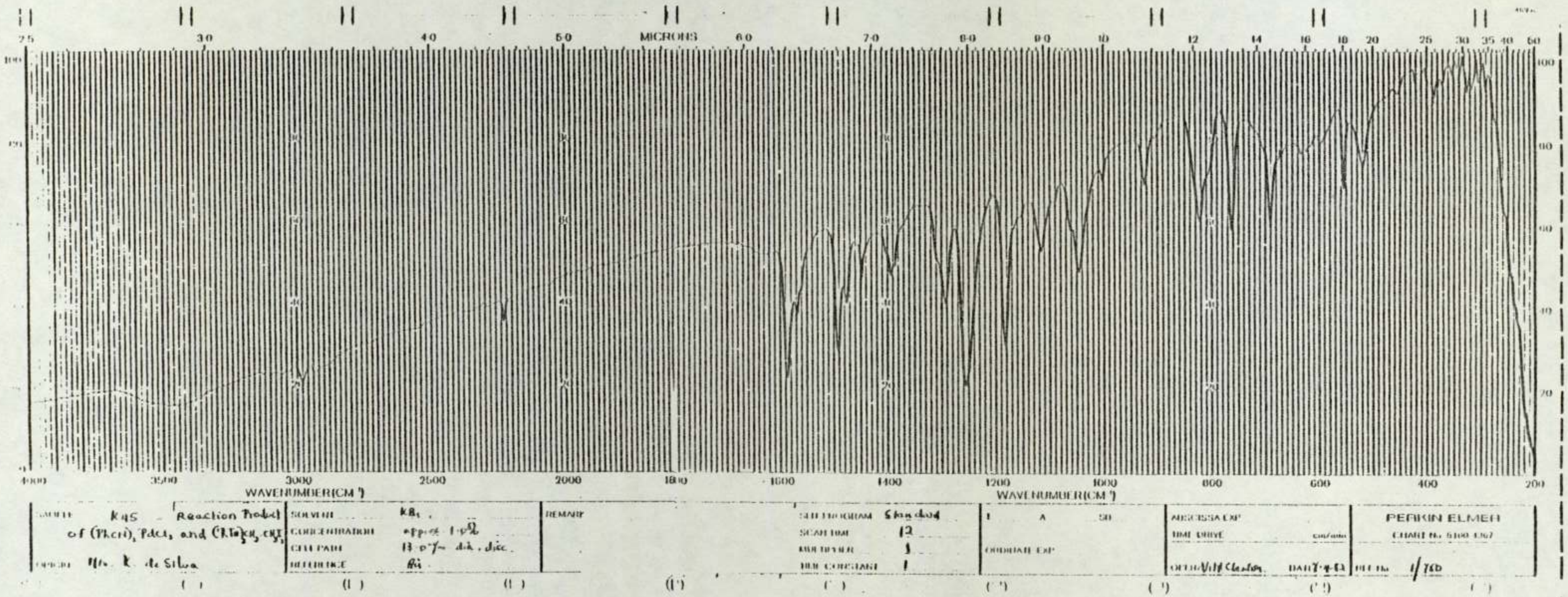
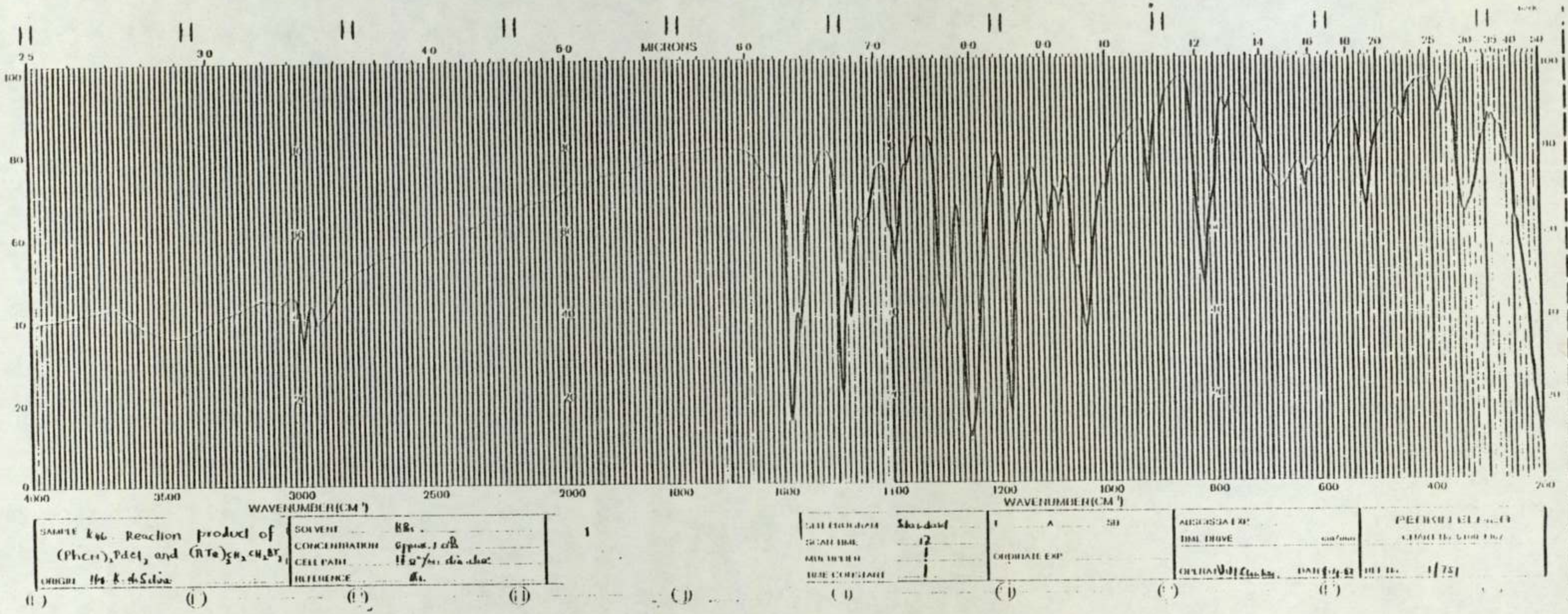

MICRONS
2.5
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
12
14
16
18
20
25
30
35
40
50
100
80
60
40
20
0
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER(CM⁻¹)
SAMPLE K45 – Reaction Product of (PhCN)$_2$PdCl$_2$ and (RTe)$_2$CH$_2$CH$_2$
ORIGIN Mr. K. de Silva
SOLVENT KBr
CONCENTRATION approx 1.0%
CELL PATH 13.0 mm dia. disc
REFERENCE Air
REMARK
SLIT PROGRAM Standard
SCAN TIME 12
MULTIPLIER 1
TIME CONSTANT 1
ABSCISSA EXP
TIME DRIVE cm/min
ORDINATE EXP
OPERATOR Clarke
DATE 7.4.83
PERKIN ELMER
CHART No. 5100 1367
REF No. 1/760

Figure 5.21



SAMPLE K46 Reaction product of (PhCN)$_2$PdCl$_2$ and (RTe)$_2$CH$_2$CH$_2$Br$_2$

ORIGIN Mr K. de Silva

SOLVENT KBr.

CONCENTRATION 6ppm. 1 cm

CELL PATH 13 mm dia disc

REFERENCE Air.

SLIT PROGRAM Standard

SCAN TIME 12

MIN ORDER 1

TIME CONSTANT 1

1 A 50

ORDINATE EXP

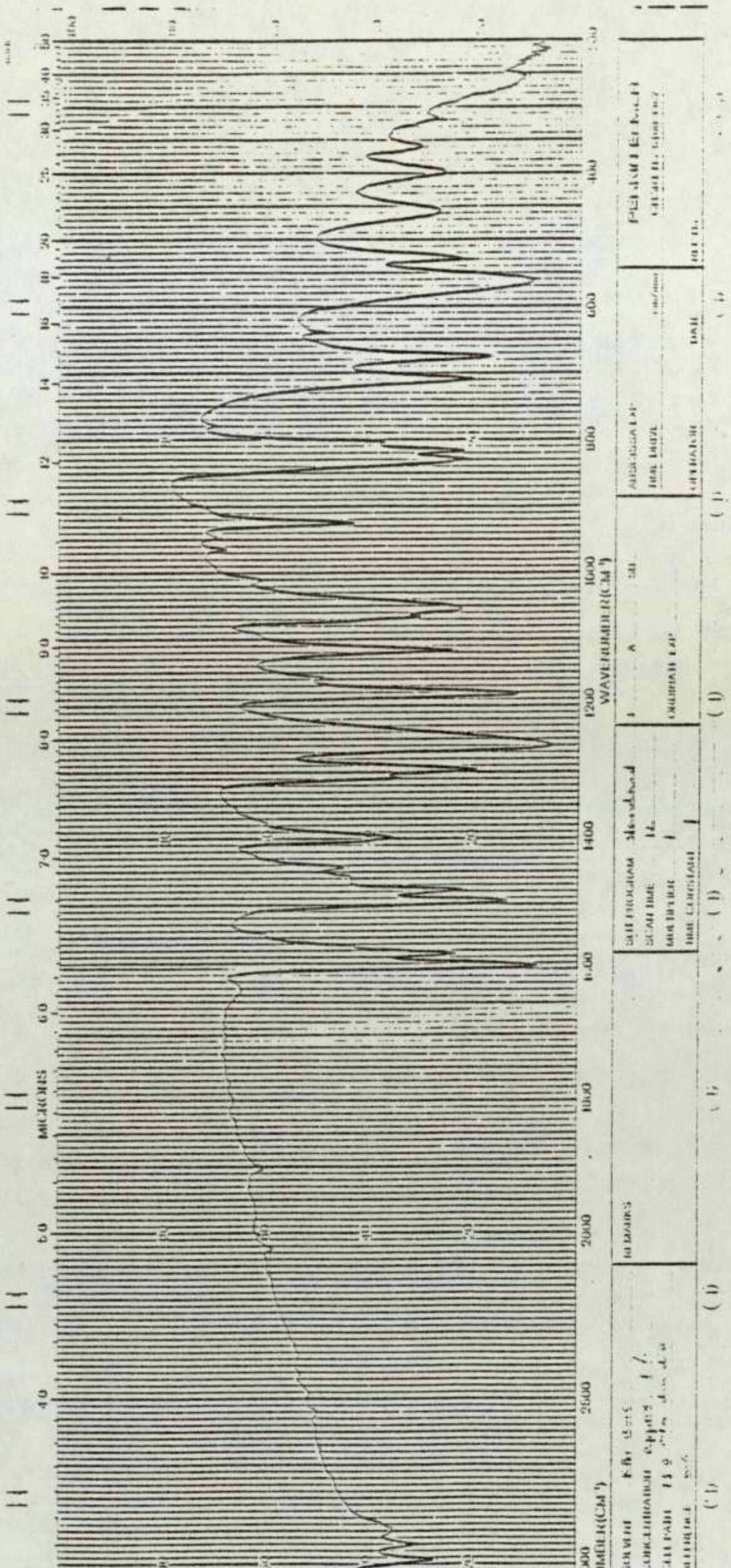
ABSCISSA EXP

TIME DRIVE

OPERATOR V.J. Clarke DATE 8.4.82

REF. No. 1/751

Figure 5.22



WAVENUMBER(CM⁻¹)
MICRONS
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
600
400
250
2.5
3
4
5
6
7
8
9
10
12
14
16
18
20
25
30
40
50
0
20
40
60
80
100
SAMPLE
$(KeO)_2O$
SOLVENT
CONCENTRATION
CELL PATH
REFERENCE
REMARKS
PERKIN-ELMER

Figure 5.23

However, the mass spectrum of the complex does not show fragments of higher m/e than the molecular ion $[(RTe)_2CH_2PdCl_2]^+$, ruling out the possibility of a dimeric structure in the gas phase.

With the dibromo-compound, $(RTe)_2CH_2.CH_2Br_2$, $Pd(PhCN)_2Cl_2$ forms a dark brown material with a melting point of 160°C. The infra-red spectrum of this compound (Figure 5.22) shows strong bands centered on 550 cm^{-1} which are very characteristic(129) of $\nu_{(Te=O)}$. Thus, the product almost certainly contains oxygen.

There is evidence that ditelluride may react with oxygen in solution to produce radical intermediates(160) and this could occur with oxygen present in the solvent. There is also evidence that the ditelluride may undergo an ethanol catalysed photochemically initiated reaction with oxygen(166) as in Equation 5.10.

$$R_2Te_2 \xrightarrow[h\nu]{O_2} RTe^{\bullet} \longrightarrow RTeO^{\bullet} \qquad \text{Eq. 5.10}$$

The complex $(RTe)_2CH_2.CH_2Br_2$ produced from the reaction between CH_2Br_2 and RTe^- sometimes showed variable carbon analysis figures as discussed earlier. This correlates with partial loss of dibromomethane. Having such a group present makes it reasonable to assume that the tellurium(II) in $(RTe)_2CH_2.CH_2Br_2$ could easily be oxidised to $(RTe{=}O)_2CH_2$

in solution before reacting with $(PhCN)_2PdCl_2$. Thus, the reaction product (Figure 5.24) could be different to that formed by the diiodomethane complex reaction with $Pd(PhCN)_2Cl_2$. However, complete structural analysis of these metal complexes are in progress(167).

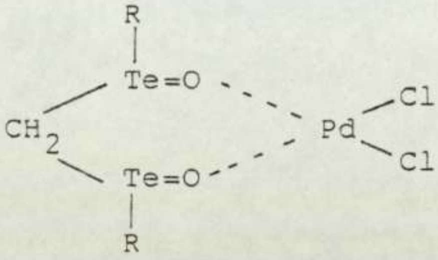
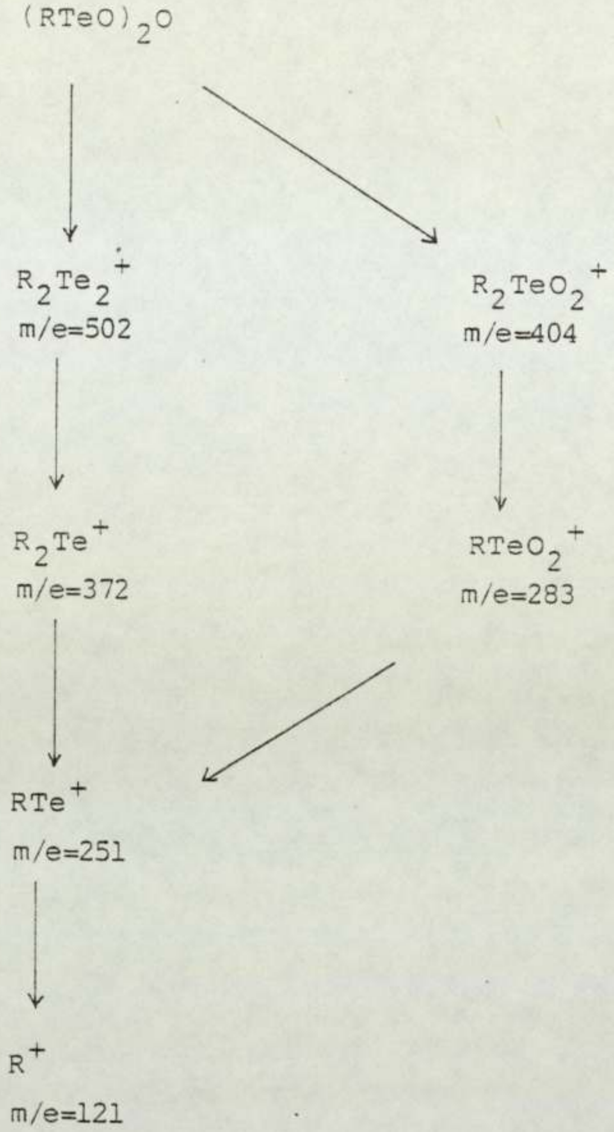


Figure 5.24

Summarising the above discussion of dibromo-alkane reactions with ditellurides, it can be noted that generally vic-dibromides eliminate the corresponding alkene together with ditelluride from the reaction, although the dibromomethane and diiodomethane resulted in charge-transfer complexes and 1,4-dibromobutane and 1,3-dibromopropane resulted in telluronium salts. Thus the reactions of brominated natural rubber with the RTe^- anion would follow the same mechanisms according to the model reactions described above. If these reactions were extended to brominated natural rubber, the attack of $RTe^\ominus$ at the adjacent bromine atoms would eliminate natural rubber and the attack of RTe^- at the bromine atoms separated by four carbon atoms would result in quaternization. It therefore appears that these reactions are not suitable



A relative to ^{1}H ^{12}C ^{130}Te ^{16}O

Figure 5.25 Major peaks in the mass spectrum of $(RTeO)_2O$ where $R=pEtOC_6H_4$

for study of tellurium-carbon crosslinks with brominated natural rubber molecules.

Another attempt was made to react the chlorine atoms in carbonated alkenes with RTe^-. The carbenation of natural rubber by the phase transfer technique has appeared in literature(168,169). It seemed that carbenated cyclohexene and 2-methyl-2-pentene would be suitable models for the above.

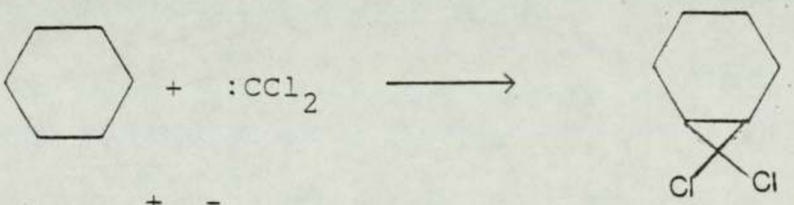
The reagent ($:CCl_2$) is prepared <u>in situ</u> by a two-phase system involving reaction of chloroform with concentrated aqueous sodium hydroxide solution in the presence of a quaternary ammonium salt as catalyst. In this instance, tributylbenzylammonium bromide was used as catalyst.

$$NaOH(aq) + QBr(org) \longrightarrow QOH(aq) + NaBr(aq)$$

$$QOH(aq) \longrightarrow QOH(org)$$

$$QOH(org) + CHCl_3(org) \longrightarrow H_2O + Q^+Cl_3C^-(org)$$

$$Q^+Cl_3C^- \longrightarrow QCl + :CCl_2$$



where Q^+Br^- = tributylbenzylammonium bromide

The reaction of bis(p-ethoxyphenyl)ditelluride with 7,7-dichloromonorcarane in the presence of the phase transfer catalyst afforded a white compound of melting point 256°C. Analytical data suggests an empirical formula of $(RTeO)_2O$. The infra-red spectrum of the white material (Figure 5.24) shows the presence of $\nu_{(Te=O)}$ at 600 cm^{-1}(129.170) and $\nu_{(Te-O)}$ at ~285 cm^{-1}(129.170). The mass spectrum of the compound (Figure 5.25) shows a base peak at m/e 502 $(R_2Te_2^{+})$ indicating the probable polymeric nature of the compound (Figure 5.26).

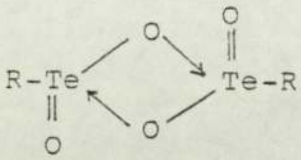
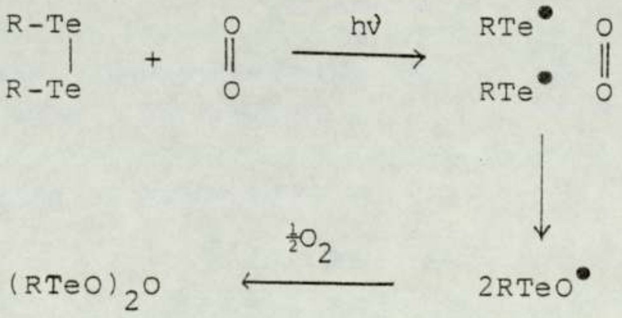


Figure 5.26

This suggests that the ditelluride is affected by atmospheric oxygen as discussed earlier in this section. Hence the following Equation 5.7 might indicate the method of production of $(RTeO)_2O$.



Eq. 5.7

It therefore appears that no reaction took place with the carbenated organic species and extension to the actual rubber network could not be followed further.

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The Reaction of Organic Dihalides with Organyltelluride (RTe^-) Anions: Telluronium Salts and Charge-transfer Complexes†

K. G. Karnika De Silva, Zahra Monsef-Mirzai, and William R. McWhinnie *
Department of Chemistry, University of Aston in Birmingham, Birmingham B4 7ET

The reaction of NaTeR (R = p-$EtOC_6H_4$ or Ph) with organic dihalides $(CH_2)_nX_2$ (n = 1—4) affords telluronium salts (n = 3 or 4; X = Cl or Br) the nature of which is discussed. For n = 1 (X = Br or I) the products are formulated as charge-transfer complexes of stoicheiometry $(RTe)_2CH_2{\cdot}CH_2X_2$. For n = 2, elimination of ditelluride occurs with formation of an alkene. The compound NaTeR is shown to be an effective dehalogenating agent for *vic*-dihalides. Some ^{125}Te Mössbauer data are discussed and it is suggested that the unusually low value of Δ (7.58 mm s^{-1}) for (p-$EtOC_6H_4Te)_2CH_2{\cdot}CH_2Br_2$ relates to removal of 5p-electron density from the spare-pair orbital *via* the charge-transfer interaction. The related di-iodomethane complex gives a solid-state e.s.r. signal. Mass spectroscopic data are discussed and these support the formulations proposed.

The reaction of a diorganyl ditelluride (R_2Te_2) with aqueous alkaline sodium tetrahydroborate affords a solution with the chemical properties of NaTeR.[1] Our work had its origin in a desire to synthesise a range of bis(tellurides), $RTe(CH_2)_nTeR$, and to study the ligand chemistry of these potentially bidentate materials. It seemed that nucleophilic attack by RTe^- on organic dihalides, $X(CH_2)_nX$ (X = halogen, normally Br), would be worth examining; hence we carried out two-phase reactions (both in the presence and absence of a phase-transfer catalyst) involving NaTeR and the dihalides. Here we report on the products obtained.

The literature[2] contains a report of the synthesis of $(RTe)_2CH_2$ (R = p-$MeOC_6H_4$ or p-$EtOC_6H_4$) from the reaction of diazomethane with a ditelluride.

Experimental

(*a*) *Synthesis.*—Two methods of preparation were used. These are illustrated for the reaction of di(p-ethoxyphenyl) ditelluride[3] with 1,4-dibromobutane.

1-*Bromo*-1-p-*ethoxyphenyltelluracyclopentane*. *Method A*. Di(p-ethoxyphenyl) ditelluride (6.2 mmol) in benzene (2.5 cm^3) and ethanol (7.5 cm^3) was heated to reflux. To this solution, sodium tetrahydroborate (10 mmol) in 1 mol dm^{-3} sodium hydroxide (8.5 cm^3) was added dropwise. The reaction mixture became colourless on completion of the addition. 1,4-Dibromobutane (1 mmol) in benzene (5 cm^3) was then added, and the warm mixture was stirred for 30 min. A fibrous white precipitate was obtained in 80% yield which was filtered off, washed with diethyl ether, and dried *in vacuo*. Recrystallisation from acetonitrile gave a white material, m.p. 280 °C.

Method B. Di(p-ethoxyphenyl) ditelluride (1 mmol) in benzene (50 cm^3) was treated with a solution of $NaBH_4$ (10 mmol) and benzyltri-n-butylammonium bromide (2 mmol) in 1 mol dm^{-3} sodium hydroxide (20 cm^3). The mixture was stirred for 2 h during which time the colour of the ditelluride was lost. 1,4-Dibromobutane (1 mmol) was added and stirring continued for 4 h at room temperature. On setting aside, a fibrous precipitate was obtained in 70% yield and was separated, washed with diethyl ether, and dried *in vacuo*. Recrystallisation from acetonitrile gave the compound described in method A.

It was found that 1,4-dichlorobutane was effective in the above preparations. Generally method A was used with the following organic dihalides: CH_2Br_2, CH_2I_2, and $(CH_2)_3Br_2$. Reactions with dichloromethane gave products of indefinite composition containing tellurium–oxygen bonds (i.r.). Some reactions were also carried out using diphenyl ditelluride.[4]

Reactions with dihalogenoethanes. When method A was used with dibromomethane and NaTeR, evolution of ethene occurred with regeneration of R_2Te_2. 2,3-Dibromobutane gave but-2-ene (g.l.c.) and ditelluride; 2,3-dibromo-2-methylpentane gave 2-methylpent-2-ene (g.l.c.). 1,2-Dibromocyclohexane afforded cyclohexene (g.l.c., i.r.), and, interestingly, 2-iodo-2-methylbutane gave 2-methylbut-2-ene (g.l.c.).

(*b*) *Physical Measurements.*—Infrared spectra (4 000—250 cm^{-1}) were measured using a Perkin-Elmer 457 instrument, mass spectra with an AEI MS9 instrument (70 eV). G.l.c. analyses were carried out with Pye-Unicam equipment. Elemental analyses for carbon and hydrogen were obtained from the Microanalytical Service, Department of Chemistry, University of Aston. Conductivities were measured over a concentration range for aqueous solutions using a standard bridge.

Some ^{125}Te Mössbauer data were obtained at Simon Fraser University, Burnaby, Canada, at 4 K using equipment previously described.[5]

^{13}C N.m.r. spectra for p-$EtOC_6H_4Te(CH_2)_4Br$ were obtained in dimethyl sulphoxide (dmso) and in water. A ^{125}Te n.m.r. spectrum for the same compound was obtained in dmso. The compound has only limited solubility and no ^{13}C–^{125}Te coupling was detectable in the ^{13}C spectrum. Proton n.m.r. spectra were measured in $(CD_3)_2SO$ using either a Perkin-Elmer R14 or JEOL FX 90Q instrument. The ^{13}C and ^{125}Te n.m.r. data were obtained at the Université de Rouen as previously described.[6]

Analytical data are given in Table 1 and Mössbauer data in Table 2. Data for 1-chloro-1-p-ethoxyphenyltelluracyclopentane are compared in Table 3 with data for some telluronium salts derived from 1,3-dihydro-2-telluraindene which have previously been published. Several of these salts have been characterised crystallographically. The main features of the mass spectra are summarised in Schemes 1 and 2.

Discussion

Reaction with Dihalogenobutanes and Propanes.—The use of conventional phase-transfer catalysis was of no obvious

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† *Non. S.I. units employed:* eV ≈ 1.60 × 10^{-19} J, G = 10^{-4} T.

Table 1. Analytical data for new organotellurium compounds

Compound	Analysis (%) Found C	H	Calculated C	H	Λ_M [a] (water)	M.p. (°C)
$[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2\cdot\text{CH}_2\text{Br}_2$ [b]	30.0	3.10	31.5	3.20	—	154
$[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2\cdot\text{CH}_2\text{I}_2$	27.2	2.90	27.8	2.80	—	118
$(p\text{-EtOC}_6\text{H}_4)\overline{\text{Te}(\text{CH}_2)_3}\text{Br}$	36.0	3.80	35.5	4.00	—	260—262
$(p\text{-EtOC}_6\text{H}_4)\overline{\text{Te}(\text{CH}_2)_4}\text{Br}$	37.2	4.40	37.4	4.40	176	258—260
$\text{Ph}\overline{\text{Te}(\text{CH}_2)_4}\text{Br}$	34.9	3.60	35.1	3.80	—	280
$(p\text{-EtOC}_6\text{H}_4)\overline{\text{Te}(\text{CH}_2)_4}\text{Cl}$	41.9	5.10	42.3	4.90	185	228—230
$\text{Ph}\overline{\text{Te}(\text{CH}_2)_4}\text{Cl}$	39.9	4.10	40.4	4.35	—	240

[a] In $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$; extrapolation to infinite dilution. [b] Te: found 37.7, calc. 37.2%, Br: found 24.1, calc. 23.4%.

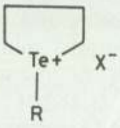
Table 2. ^{125}Te Mössbauer data (mm s^{-1}) for reaction products of $\text{NaTe}(\text{C}_6\text{H}_4\text{OEt-}p)$ with dibromoalkanes

Compound	δ [a]	Δ [b]	$\Gamma_{\frac{1}{2}}$
$[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2\cdot\text{CH}_2\text{Br}_2$	0.53	7.58	6.33
$(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)_3\text{Br}$	0.36	5.58	5.68
$(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)_4\text{Br}$	0.38	5.50	5.43

[a] $\pm 0.08\ \text{mm s}^{-1}$, *vs.* ^{125}Sb/Cu. [b] Quadrupole splitting ($\pm 0.1\ \text{mm s}^{-1}$).

advantage in reactions of 1,4-dichloro- or 1,4-dibromobutane with sodium organotellurates, NaTeR. However, we have previously shown that when the catalyst is supported on an expandable clay good yields of product may be obtained in a short time.[7]

The reaction of tetrahydroborate-reduced ditellurides, R_2Te_2, with $(\text{CH}_2)_n\text{X}_2$ (n = 3 or 4) gives materials of stoicheiometry $\text{RTe}(\text{CH}_2)_n\text{X}$. Our most extensive studies have been with the $n = 4$ compounds since these show potential for application to organic synthesis.[8] The compounds $\text{RTe}(\text{CH}_2)_4\text{X}$ (R = p-EtOC$_6$H$_4$ or Ph; X = Cl or Br) are salt like and dissociate as 1 : 1 electrolytes in water. ^{125}Te Mössbauer data for $(p\text{-EtOC}_6\text{H}_4)\text{Te}(\text{CH}_2)_4\text{Br}$ are typical of a tellurium(IV) compound and, in particular, Δ is in the expected range for a telluronium salt. Thus the most acceptable formulation of the product is as a telluronium salt derived from 1-telluracyclopentane (I). Nucleophilic attack on 1,4-dibromobutane by RTe^- has taken place, but quaternisation then proceeds more rapidly than attack at the second C–X bond by further RTe^-. (It seems likely that the telluronium salt may function as a phase-transfer catalyst once small quantities have been formed, thus helping to explain why no advantage accrues from the use of benzyltri-n-butylammonium bromide.)



(I)

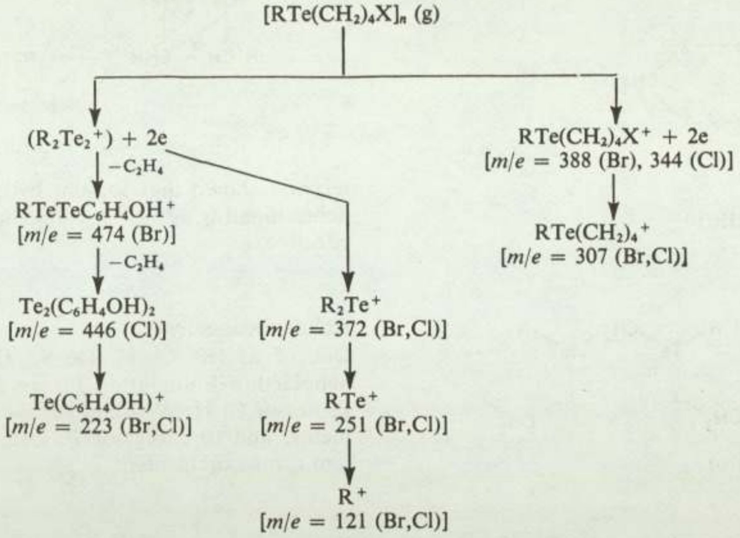
The mass spectra of $\text{R}\overline{\text{Te}(\text{CH}_2)_4}\text{X}$ (X = Cl or Br) support formulation (I) and, in general respects, do not differ greatly from the spectra of a range of salts based on 1,3-dihydro-2-telluraindene.[6] In particular, the observation of fragments containing two tellurium atoms may reflect a degree of association in the solid state which is quite normal for this variety of compound.[9] The broad features of the spectra may be related as in Scheme 1.

Attempts were made to study the n.m.r. spectra of the products from the reaction of 1,4-dichlorobutane with NaTe(C$_6$H$_4$OEt). The compound was not excessively soluble but a ^{13}C n.m.r. spectrum was obtained in dmso (Table 3) which was essentially the same as for a solution in D$_2$O, a solvent in which salt-like character has been demonstrated. Significant ion pairing occurs in dmso since Λ_M was 13.6 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ compared with values in excess of 30 $\text{ohm}^{-1}\ \text{cm}^2\ \text{mol}^{-1}$ expected for strong electrolytes. The spectrum is certainly inconsistent with an open-chain structure $\text{RTe}(\text{CH}_2)_4\text{Cl}$ for which extra carbon resonances would be expected, also it contains features in common with data for salts derived from 1,3-dihydro-2-telluraindene.[6,8] The ^{125}Te data are also consistent with the telluronium salt formulation since the chemical shift is within the range for similar compounds. We have previously demonstrated that $\delta(^{125}\text{Te})$ is sensitive both to the anion and the quaternising group R within a given solvent for a particular series of telluronium salts.[6] Thus despite the limited solubility of the material, these n.m.r. data provide good support for the proposed structure (I).

The product of the reaction of NaTe(C$_6$H$_4$OEt) with 1,3-dibromopropane is, from the Mössbauer data, also a telluronium salt. It seems improbable that it should be formulated as a derivative of 1-telluracyclobutane since such a ring would be too strained. Thus a polymeric formulation is more plausible and, indeed, the mass spectra of such compounds are very complex with many fragments of significantly higher m/e than $[\text{RTe}(\text{CH}_2)_3\text{X}]^+$.

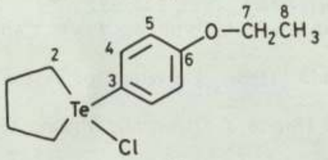
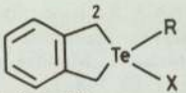
Reactions with Dihalogenomethanes.—The reaction of NaTeR with dibromo- or di-iodo-methane followed a different course. In this instance, nucleophilic substitution of both halogen atoms proceeds but the products are isolated as pale yellow (CH$_2$Br$_2$) or deep yellow (CH$_2$I$_2$) solids containing 1 mol of dihalogenomethane, $(\text{RTe})_2\text{CH}_2\cdot\text{CH}_2\text{X}_2$ (X = Br or I). The mass spectra (Scheme 2) are in accord with this formulation. [Products from the reaction with CH$_2$Br$_2$ sometimes showed variable C analysis figures but this correlates with partial loss of dibromomethane. Preliminary experiments indicate that the materials behave as bis(telluride) ligands with 'soft' metal centres.]

I.r. and ^{1}H n.m.r. spectra support the formulation of the complexes. For example strong features at 1 114, 725, and 592 cm^{-1} in the spectrum of $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2\cdot\text{CH}_2\text{I}_2$ certainly arise from CH$_2$I$_2$ and correlate with bands at 1 100, 721, and 599 cm^{-1} in the free liquid. A rather dilute solution of $[(p\text{-EtOC}_6\text{H}_4)\text{Te}]_2\text{CH}_2\cdot\text{CH}_2\text{I}_2$ in (CD$_3$)$_2$SO gave a ^{1}H n.m.r.



Scheme 1. Major peaks in the mass spectrum of $(p\text{-EtOC}_6H_4)\overline{Te(CH_2)_4}X$ (X = Cl or Br). Quoted *m/e* values are referenced to ^{130}Te, ^{37}Cl, ^{81}Br, ^{12}C, ^{1}H, and ^{16}O. A round bracket around a fragment implies not observed and (Br and/or Cl) implies observed for indicated X only

Table 3. Carbon-13 and ^{125}Te n.m.r. data for 1-telluracyclopentane derivatives in dmso

Compound	$\delta(^{13}C)$ *vs.* $SiMe_4$	$\delta(^{125}Te)$ *vs.* Me_2Te
	31.43 (C^1), 35.68 (C^2), ? (C^3), 134.66 (C^4), 115.73 (C^5), 160.11 (C^6), 63.21 (C^7), 14.33 (C^8)	761
	34.4 * (C^2) (R = Me, X = I) 34.3 * (C^2) (R = allyl, X = Br)	651 * (R = Me, X = I) 688.3 * (R = allyl, X = Br) 722 * (R = benzyl, X = Br)

* Data from refs. 6 and 9.

(*a*) $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$

$[(p\text{-EtOC}_6H_4)Te]_2CH_2^+$,	$(p\text{-EtOC}_6H_4)_2Te_2^+$,	$(p\text{-EtOC}_6H_4)_2Te^+$,	$CH_2I_2^+$,	$(p\text{-EtOC}_6H_4)Te(CH_2)^+$,	$(p\text{-EtOC}_6H_4)Te^+$,	$(p\text{-HOC}_6H_4)Te^+$
(*m/e* = 516)	(*m/e* = 502)	(*m/e* = 372)	(*m/e* = 268)	(*m/e* = 265)	(*m/e* = 251)	(*m/e* = 223)

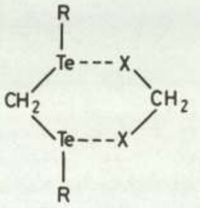
(*b*) $(PhTe)_2CH_2{\cdot}CH_2I_2$

$(PhTe)_2CH_2^+$,	$Ph_2Te_2^+$,	$Ph(CH_2)TeI^+$,	Ph_2Te^+,	$CH_2I_2^+$,	$PhTe^+$
(*m/e* = 428)	(*m/e* = 414)	(*m/e* = 348)	(*m/e* = 348)	(*m/e* = 268)	(*m/e* = 207)

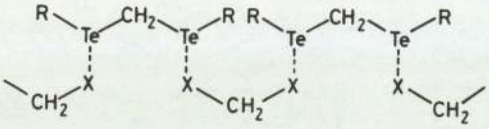
Scheme 2. Tellurium-containing fragments in mass spectra of charge-transfer complexes of $RTe(CH_2)TeR$ with di-iodomethane. Quoted *m/e* values are relative to ^{130}Te, ^{12}C, ^{1}H, ^{16}O and ^{127}I

spectrum in which significant broadening of signals had occurred, doubtless due to the paramagnetism detected by e.s.r. spectroscopy (see below); the spectrum integrates correctly but the broad lines mask coupling of the $Te{-}CH_2{-}Te$ methylene protons to ^{125}Te (natural abundance 6.99%).

A Mössbauer spectrum has been obtained for $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2Br_2$ and it will be noted (Table 2) that the parameters are out of step with those of the telluronium salts discussed above. The chemical isomer shift is, within the errors, more positive than is δ for the other two compounds which implies a greater *s*-electron density at tellurium in this compound. This may imply that some mechanism is operative which leads to withdrawal of 5*p*-electron density thus deshielding the 5*s* pair. This hypothesis gains more positive support from the value of Δ which is significantly lower than that expected (*ca.* 10 mm s^{-1}) for a telluride.[5] At the same time the value is too high for a telluronium salt. We suggest that the material is a charge-transfer complex and two possible formulations are the illustrated (IIa) and (IIb). The compound $[(p\text{-EtOC}_6H_4)Te]_2CH_2{\cdot}CH_2I_2$ gives a broad e.s.r. signal in the solid state ($\Gamma_{\frac{1}{2}} \simeq 75$ G) centred on $g = 2.18$. The suggestion that these materials are indeed charge-transfer complexes is the only one which offers a self-consistent interpretation of all the data. It is proposed that electron density is transferred from the spare-pair *p* orbital on tellurium. This will decrease the *p*-orbital occupational im-



(IIa)



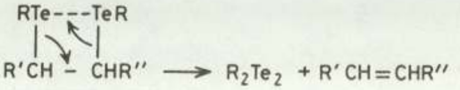
(IIb)

balance and, accordingly, reduce Δ. Simultaneously removal of *p*-electron density will increase δ. Similar effects have been noted for organotellurium complexes with 7,7,8,8-tetracyanoquinodimethane (tcnq)[10] and the implication is that the charge transfer is considerable.

We have previously suggested that a charge-transfer interaction may be the first step in the oxidative addition of methyl iodide to diphenyl telluride.[11] These data support that hypothesis.

Very recently, Engman and Cava[12] reported that the reaction of LiTeR with dichloromethane affords $RTeCH_2TeR$ (*e.g.* R = benzo[*b*]thien-2-yl).

Reactions with Dibromoethanes and other vic-*Dibromides*.—Only brief comment is necessary. Addition of these dibromides to the colourless solution of NaTeR produced the familiar ditelluride colouration and, indeed, R_2Te_2 was recovered quantitatively. The other product was (when dibromides were used) an alkene which was generally identified by g.l.c. Thus it is possible that the nucleophilic substitution proceeds and that ditelluride then eliminates in a concerted process (Scheme 3). It is of interest that 2-iodo-2-methylbutane gave 2-methylbut-2-ene under these conditions. We have not checked the generality of this reaction. It was recently shown that sodium hydrogentelluride was a useful debrominating agent,[13] it would appear that NaTeR is no less effective.



Scheme 3.

Acknowledgements

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