TO MY PARENTS

AND

TO THE MEMORY OF MY BROTHER

KILLED AT WAR 1981

AN EVALUATION OF TELLURIUM COMPOUNDS AS POLYMER STABILISERS

BY

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Submitted for the degree of

Doctor of Philosophy

of the University of Aston in Birmingham

August 1983

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by

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A thesis submitted to the
University of Aston in Birmingham
for the degree of
Doctor of Philosophy-1983

SUMMARY

Some new organotellurium compounds were synthesised and their ability to act as stabilisers for poly(vinylchloride) (PVC) and polypropylene (PP) assessed. Molecular weight measurements and mass spectra data indicate that diphenyltellurium maleate and diaryltellurium β-mercaptopropionate exist as dimers, whilst in the case of dicetyltellurium maleate there was shown to be an equilibrium between monomer and dimer. The dimer was shown by IR to contain an ester-like bridge which would allow ready dissociation to monomer species.

The organotellurium compounds have been shown to neutralise hydrogen chloride, replace chlorine atoms of chlorohydrocarbons with carboxylate groups and also have the ability to stoichiometrically decompose peroxides.

The effect of organotellurium compounds on PVC during processing, thermal ageing and UV irradiation was examined by measuring unsaturation, colour and carbonyl formation. These compounds were found to be effective stabilisers during processing and thermal oxidation but they do not lead to good UV stability during photo-oxidation. When used in combination with 4-octyloxy-2-hydroxybenzophenone (HOBP) or when analogues of HOBP were incorporated into the organotellurium molecule the UV stability was dramatically improved.

Tetrakis(diethyldithiocarbamato) tellurium (IV), $Te(dtc)_4$, and bis(diethyldithiocarbamato)tellurium (II), $Te(dtc)_2$, were found to be efficient melt stabilisers for PP and was also effective during thermal and photo-oxidation. Increasing the processing time for PP containing $Te(dtc)_4$ led to an increase in the life-time for the PP but showed an initial pro-oxidant effect during photo-oxidation. This is due to the formation of tetraethylthiuram disulphide, TETD, by the decomposition of $Te(dtc)_4$ into $Te(dtc)_2$ and TETD. During the thermal oxidation $Te(dtc)_4$ was a better stabiliser than $Te(dtc)_2$, this is due to decomposition of $Te(dtc)_4$ into $Te(dtc)_2$ and TETD. By analogy with other metal dithiocarbamates, it seems likely that $Te(dtc)_4$ and $Te(dtc)_2$ act as a stabiliser for PP by destroying hydroperoxides into non radical products.

Key Words
Tellurium Compounds
Stabiliser
Poly(vinylchloride)
Polypropylene

ACKNOWLEDGEMENTS

I would like to express my sincere thanks to Professor W. R. McWhinnie and Professor G. Scott for their invaluable supervision, guidance, encouragement and support throughout this project.

I would also like to thank Mr. D. Gregory and Dr. K. B. Chakraborty for their helpful suggestions.

My thanks also to the technical staff of the Chemistry Department for obtaining physical measurements.

Special thanks are due to my parents for their moral and financial support and for their encouragement throughout my studies. My special thanks also to Miss S. J. Coulson for her invaluable help in preparing and typing this thesis.

Declaration

The work described in this thesis was carried out between 1979 and 1983 at the University of Aston in Birmingham. It has been done independently and has not been submitted for any other degree.

Sera

S. S. ABED-ALI

CONTENTS

Chapter One	INTRODUCTION	1
1-1	Degradation of Polymers	1
1-1-2	Auto-oxidation of Polymers	1
1-2	Degradation of PVC	3
1-2-1	Photodegradation of PVC	5
1-2-2	Mechanism of Thermal Dehydrochlorination	7
1-3	Stabilisation of PVC	12
1-4	Antioxidant Mechanisms	19
1-4-2	Preventive Antioxidants	20
1-5	The Chemistry and Technology of Tellurium	23
Chapter Two	EXPERIMENTAL	34
2-1	Chemicals	34
2-2	Elemental Analysis	35
2-3	Physical Measurements	35
2-3-1	Melting Points	35
2-3-2	Mass Spectra	35
2-3-3	Nuclear Magnetic Resonance Spectra	35
2-3-4	Infra-red Spectra	36
2-3-5	UV Spectroscopy	36
2-3-6	Cryoscopic Method	36
2-3-7	Chromatography	36
2-3-8	Gas Liquid Chromatography Analysis	37
2-4	Processing of the Polymer	37
2-5	Preparation of Films	38

2-6 Melt Flow Index 39
2-7 Determination of Unsaturation 40
2-8 Measurement of Thermal-Oxidative Stability 40
2-9 Measurement of UV Stability 42
2-10 Estimation of Degradation 42
2-10-1 Total Colour Difference 42
2-10-2 Infra-red Spectroscopy 43
2-10-3 Tear Strength Test 45

Chapter Three INVESTIGATION OF THE FEASIBILITY OF ORGANOTELLURIUM COMPOUNDS AS STABILISERS FOR PVC 46
3-1 Organotellurium Compounds 46
3-2 Reaction between Organotellurium Compounds and Hydrogen Chloride 46
3-3 Reaction of Organotellurium Compounds with Model Compounds of PVC 48
3-4 Reaction of Organotellurium Compounds with Peroxides 49
3-5 Results and Discussion 53
3-5-1 Results 53
3-5-2 Discussion 58

Chapter Four SYNTHESIS OF NEW ORGANOTELLURIUM COMPOUNDS 69
4-1 Experimental 69

4-2 Results 79

4-3 Discussion 108

Chapter Five A STABILISATION OF PVC 131

5A-1 Experimental 131

5A-2 Results and Discussion 131

5A-2-1 Effect of Organotellurium Compounds during Processing 131

5A-2-2 Effect of Organotellurium Compounds during Thermal Oxidation 140

5A-2-3 Effect of Organotellurium Compounds during UV Exposure 142

Chapter Five B STABILISATION OF PP 165

5B-1 Experimental 165

5B-2 Results and Discussion 166

Suggestions for Further Work 195

References 197 to 207

LIST OF TABLES

PAGE

3-1 54

3-2 55

3-3 56

3-4 57

4-1 81

4-2 84

4-3 85

4-4 86

4-5 87

4-6 88

4-7 89

4-8 93

5-1 132

5-2 175

LIST OF FIGURES

Fig No	Page	Fig No	Page
2.1	41	5.12	156
4.1(a)	96	5.13	157
4.1(b)	97	5.14	158
4.1(c)	98	5.15	159
4.2(a)	99	5.16	160
4.2(b)	100	5.17	161
4.3(a)	101	5.18	162
4.3(b)	102	5.19	163
4.4(a)	103	5.20	164
4.4(b)	104	5.21	176
4.5	105	5.22	177
4.6	106	5.23	178
4.7	107	5.24	179
5.1	147	5.25	180
5.2	147	5.26	181
5.3	148	5.27	182
5.4	148	5.28	183
5.5	149	5.29	184
5.6	150	5.30	185
5.7	151	5.31	186
5.8	152	5.32	187
5.9	153	5.33	188
5.10	154	5.34	189
5.11	155	5.35	190

5.36 191
5.37 192
5.38 193
5.39 194

CHAPTER ONE

1-1 Degradation of Polymers

Natural and synthetic polymers are susceptible to deterioration by dioxygen (triplet ground state) on exposure to environmental conditions. Scott(1) has concluded that the most important accelerating environmental influences apart from dioxygen are heat, light, ozone, contamination by metal ions and mechanical deformation. Deterioration of polymers leads to undesirable changes in the physical, mechanical and electrical properties. The discolouration of poly(vinylchloride), yellowing of cotton fabrics, embrittlement of plastics and the cracking of rubber are typical examples of polymer degradation.

Deterioration takes place during two principal stages(2); the first occurs as the polymer is fabricated into the form in which it is to be used. This period is characterized by exposure to relatively high temperatures and mechanical shear. The second is concerned with long-term ageing during which the polymer is exposed to conditions of actual use.

1-1-2 Auto-oxidation of Polymers

Deterioration of polymers takes place through auto-oxidation:

which is defined(3) as the reaction of dioxygen with organic materials by a free radical process. The mechanism of the polymer auto-oxidation process is based on the free radical sequence originally postulated by Bolland et al(4-6) and subsequently extended to most hydrocarbon polymers(3). The basic auto-oxidation processes may be outlined as follows.

The polymer molecules (R-R) undergo shear induced macroalkyl radical formation leading to peroxidation, under most commercial processing conditions

$$R - R \xrightarrow{\text{Shear}} 2R^{\cdot}$$

Macroalkyl radicals $R^{\cdot}$, react rapidly with dioxygen to form alkylperoxyl radicals

$$R^{\cdot} + O_2 \longrightarrow ROO^{\cdot} \qquad (1)$$

The alkylperoxyl radicals may either abstract a hydrogen atom from another polymer molecule (2) or add to polymer unsaturation (3)

$$ROO^{\cdot} + RH \longrightarrow ROOH + R^{\cdot} \qquad (2)$$

$$ROO^{\cdot} + -\overset{|}{C}=\overset{|}{C}- \longrightarrow ROO\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^{\cdot} \qquad (3)$$

When no unsaturation is present in the substrate, reaction (2) is the only propagating step but both (2) and (3) may be involved in the auto-oxidation of unsaturated substrates. For most polymers, reaction (2) determines the overall rate of auto-oxidation and hence under a normal oxygen atmosphere the radical present in highest concentration in the system is the alkylperoxyl radical $(ROO^{\cdot})^{(7)}$. Consequently, termination occurs predominantly by reaction of this species (4), where as, when dioxygen is deficient in the system, the alkyl radical concentration will be higher$^{(8,3)}$ and the termination steps (5) become dominant.

$$2ROO^{\cdot} \longrightarrow \text{Inert products} \qquad (4)$$

$$\left.\begin{array}{l} ROO^{\cdot} + R^{\cdot} \\ 2R^{\cdot} \end{array}\right] \longrightarrow \text{Inactive products} \qquad (5)$$

Scott et al $^{(3,2)}$ have shown that macroalkyl hydroperoxides are the main initiators for the process of oxidative degradation of the polymer both during thermal and photo-oxidative degradation.

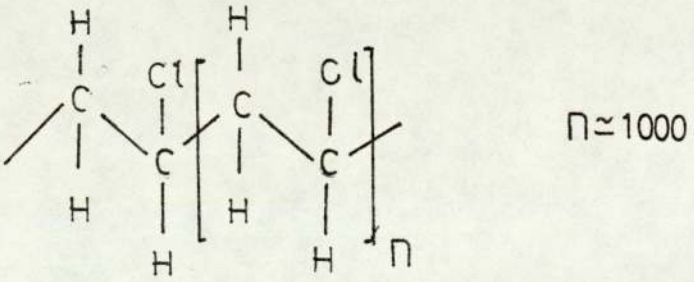
It has been stated that the hydroperoxide decomposition into radicals is accelerated mainly by transition metal ions (e.g. Co^{2+}, Co^{3+})

$$ROOH + M^{n+} \xrightarrow[\text{or light}]{\text{heat}} RO^{\cdot} + M^{(n+1)} + OH^{-}$$

$$ROOH + M^{n+1} \longrightarrow ROO^{\cdot} + M^{n+} + H^{+}$$

1-2 Degradation of poly(vinylchloride) (PVC)

Poly(vinylchloride) is a polymer which has been shown to have an essentially head-to-tail structure by X-ray diffraction studies$^{(9)}$



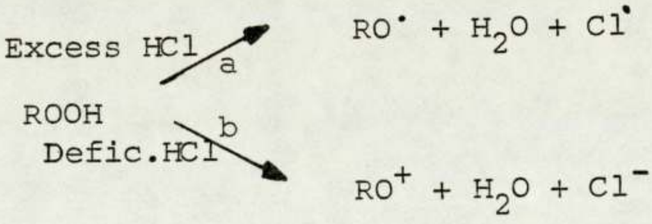
PVC usually has low crystallinity (10) but this can be greater in polymers prepared at low temperatures. This is due to a higher degree of syndiotacticity and to a lower extent of branching.

The main disadvantage of PVC is its low thermal stability. Thus, when PVC is heated above 100°C it degrades (11) with evolution of hydrogen chloride leading to discolouration. This also occurs under the influence of ultra-violet light. Dehydrochlorination rapidly propogates through the whole molecule in a 'zipper' reaction by the allyl activation of adjacent C-Cl bonds with concomitant formation of unsaturation in the polymer chain. The dehydrochlorination is accompanied by cross-linking, chain-scission and changes in the mechanical properties are also observed.

The relatively low thermal stability of PVC, as compared to low molecular weight analogues of PVC, is generally attributed to abnormal structures in the polymer chain (11,12,13). This includes chain end with initiator residues or unsaturated end groups, head-to-head units, oxidation structures, extraneous impurities, branching sites, tertiary chlorine atoms and random unsaturation with allylic chlorine atoms. The tertiary and allylic chloride structures are often (14) initial sites for dehydrochlorination under thermal conditions.

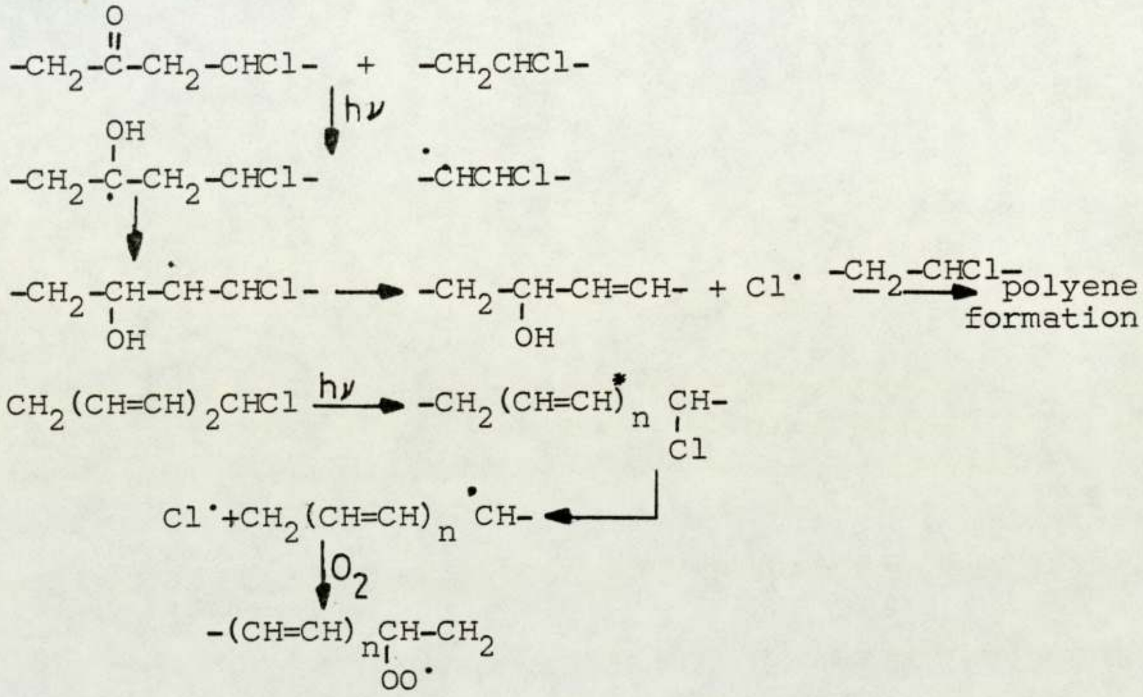
The effect of hydrogen chloride on the thermal degradation of PVC has been reported by many workers, some workers have stated that hydrogen chloride is an accelerater during thermal degradation by ionic catalysis(12,101,102). Other workers have reported that hydrogen chloride has no effect on dehydrochlorination in the absence of dioxygen(15,16).

Recently Scott(17) has shown that a redox reaction occurs involving anhydrous hydrogen chloride and hydroperoxides which are both formed during processing. In the presence of a molar deficiency of hydroperoxide, hydrogen chloride has been found to be an effective pro-oxidant as a result of HCl induced destruction of peroxides to give free radicals. However, when the molar ratio [ROOH]/[HCl] is greater than unity, hydroperoxide is decomposed into ionic products and inhibition of auto-oxidation results.

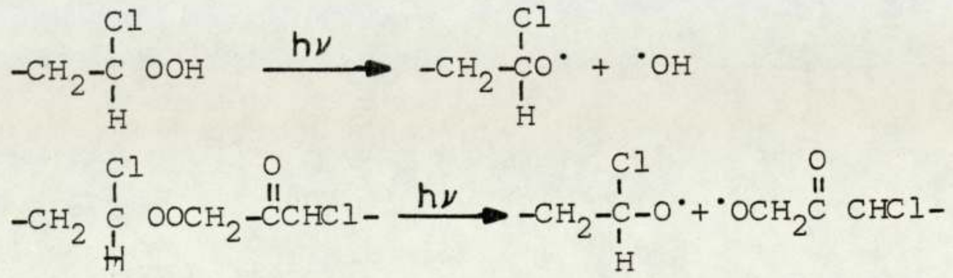


1-2-1 Photodegradation of PVC

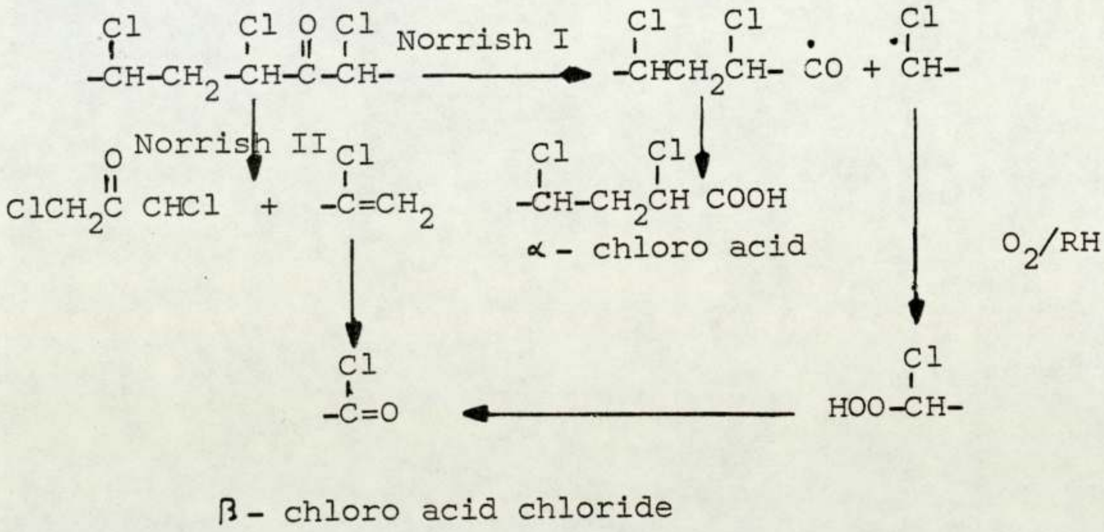
Dehydrochlorination has been shown(18) to proceed effectively in irradiated PVC with a concomitant discolouration of the polymer due to polyene formation and subsequent chain rupture and crosslinking. The mechanism originally assumed(19) is given in the following scheme with the main light absorbing species being the carbonyl group and the carbon-to-carbon double bond in the PVC chain:



Scott(17) has shown that the formation of both unsaturation and peroxides during processing has a dominating influence on the subsequent light ageing behaviour, as well as during environmental exposure.



He also demonstrated that the embrittlement of PVC, during the later stages of UV exposure, is due to two possible alternative modes of photolysis of the intermediate chloroketones(20) formed as a result of peroxide breakdown.



1-2-2 Mechanism of Thermal Dehydrochlorination

For the thermal dehydrochlorination of PVC, three distinct mechanisms have been assumed,(11,13,21) radical, ionic and unimolecular elimination. Because of the use of different experimental conditions and different polymer samples with varied history, a clear decision in favour of any one mechanism is not yet possible. However, under more controlled conditions in the presence of dioxygen, it is most probable that the reaction follows a radical mechanism(22,12,13,3).

Free Radical Mechanisms

The presence of free radicals in thermally degraded PVC has been demonstrated by electron spin resonance(23) measurements.

The steps of this radical mechanism(24) are:

A - Initiation to produce halogen atoms.

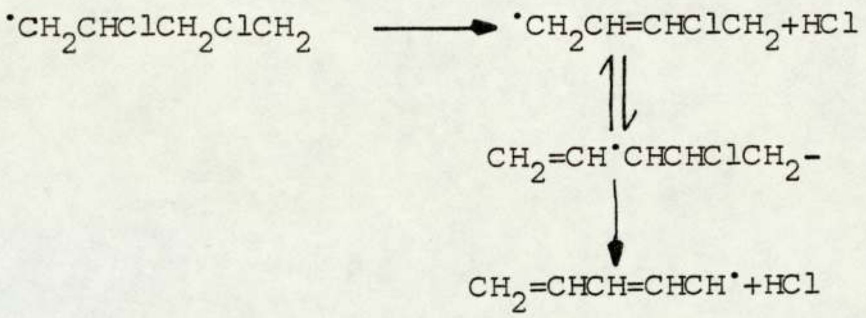
B - Abstraction of a hydrogen atom from the alkyl halide, and,

C - Re-arrangement of the ensuing radical to an alkene and another halogen atom which can then continue the chain.

$$CH_2ClCH_2Cl \xrightarrow{\dot{Cl}} CH_2Cl\dot{C}HCl+HCl$$

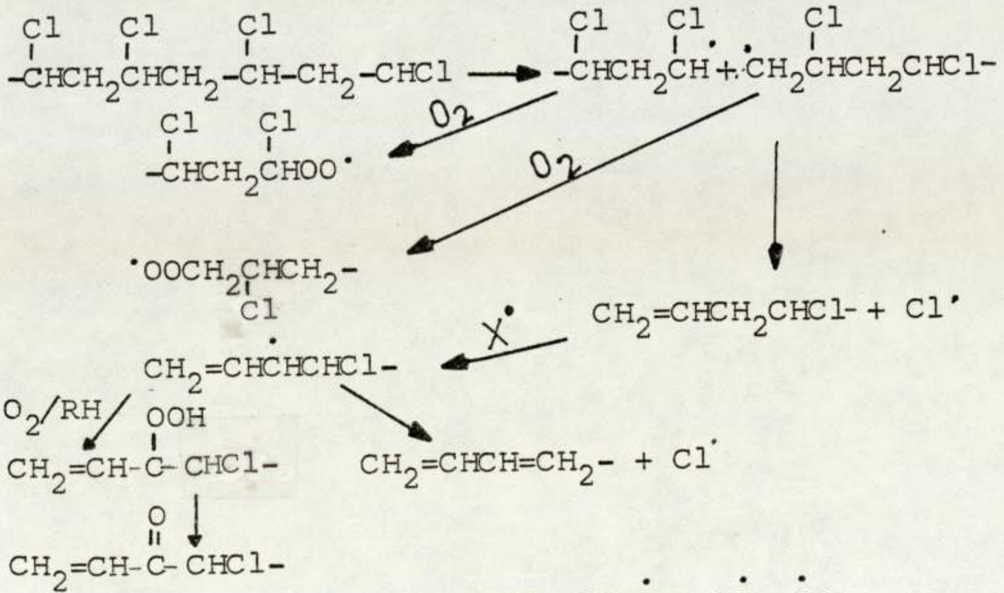
$$CH_2Cl\dot{C}HCl \longrightarrow CH_2{=}CHCl+\dot{Cl}$$

The first such mechanism postulated by Arlman(15) is based on the evidence that free radical initiators increase the rate of dehydrochlorination. The failure of normal free radical scavengers to disrupt dehydrochlorination was explained as being due to very stable free radical intermediates. Arlman's mechanism involves the liberation of hydrogen chloride from the repeat unit adjacent to the radical.



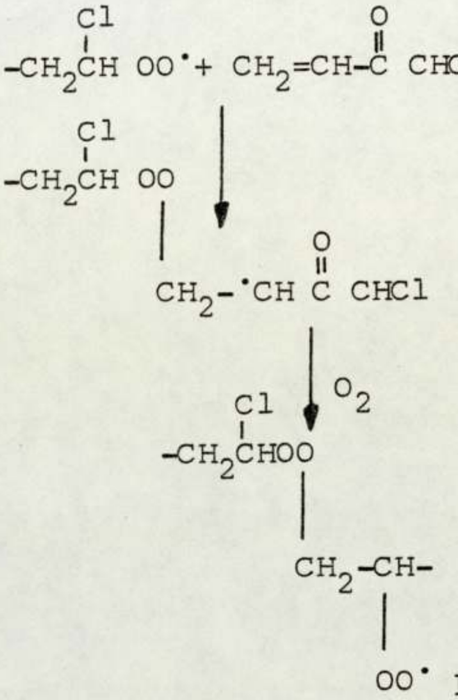
The unsaturated free radical then rearranges, giving a structure which is capable of another activated elimination of hydrogen chloride followed by successive re-arrangements and eliminations until long polyene chains are built up.

Scott(21,25) has shown that the primary formed radicals can either react with available dioxygen to give alkyl peroxyl radicals, or they can form the site for dehydrochlorination by the loss of a chlorine atom. The chlorine atom may itself initiate a 'zipper' reaction leading to conjugated unsaturation or radicals formed from the peroxide species may perform the same funtion.



where X·=Cl·, ȮH, ȮR, ȮOR

Crosslinking is a well established feature of thermal degradation and is believed to occur by the combination of two polymeric radicals or by addition of polymeric radicals to the conjugated unsaturation(25), and these peroxyl cross links are thermally unstable.

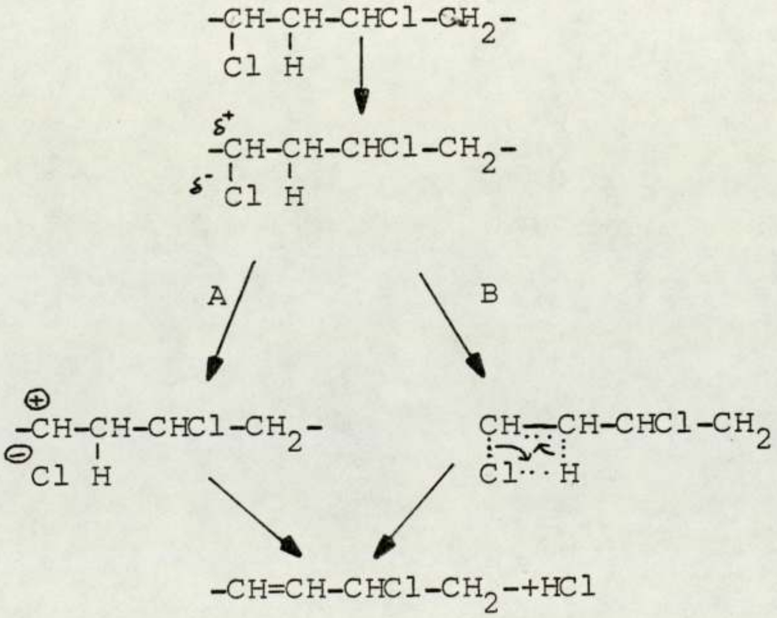


peroxyl crosslinking

Scott(17) pointed out that the conditions to which PVC is subjected during processing differ from those involved during thermal degradation in two respects. The first concerns the mechanochemical chain scission of the polymer under the influence of sheer in the mixing process, giving rise to free radicals which initiate the loss of hydrogen chloride. The second is the presence of a small amount of dioxygen, which can also react with the mechanochemically formed radicals to give hydroperoxide. The three species, hydrogen chloride, unsaturation and hydroperoxides are known to be formed very rapidly in unstabilised PVC during the first minutes of a typical processing operation(21,26).

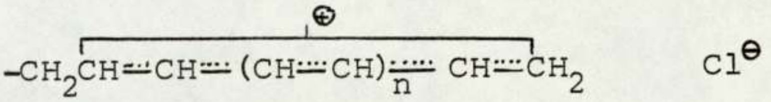
An Ionic Mechanism

Marks (27) has concluded that thermal dehydrochlorination of PVC takes place by the following reaction



The stabilisation of the polar transition state can be either internal, due to a delocalisation of the positive charge of the carbonium ion within the given molecule, or external, due to an interaction with the surrounding medium(28).

Dehydrochlorination takes place along the repeating units with formation of a system of conjugated double bonds, thus providing an increasingly better stabilisation of the transition state by delocalisation of the positive charge over the whole polyene system.



$$-CH_2\overset{\oplus}{\overbrace{CH\overset{...}{=}CH\overset{...}{=}(CH\overset{...}{=}CH)_n\overset{...}{=}CH\overset{...}{=}CH_2}}\qquad Cl^{\ominus}$$

Unimolecular Elimination Mechanism

Unimolecular elimination of hydrogen chloride has been treated as compatible with a 'zipper' mechanism by assuming allylic activation(29,30,31-34). After the loss of the first molecule of hydrogen chloride the residual structure, $-CH=CHCHClCH_2-$, is considered to have reactive chlorines in the allylic position so that the second molecule of hydrogen chloride is lost more easily.

1-3 Stabilisation of PVC

The complexity of the degradation process makes it inevitable that the stabilisation be equally complex. Scott(3) first adequately summarised the situation and identified at least six possible roles for a complete PVC stabiliser system. Subsequent work has clarified some points and brought a change in emphasis but it still recognises the following five prominent features desirable in an effective stabilising system(12,35)

A - Binding (scavenging) of hydrogen chloride liberated by degrading polymer.

B - Replacement of labile chlorine atoms with entities of greater thermal stability.

C - Interruption of conjugated polyene sequence, thus improving the colour of the polymer.

D - Decomposition of peroxides.

E - Rendering prodegradant substance (including products of the stabilisation process) innocuous.

The main PVC stabilisers used could be arranged into groups as follows:

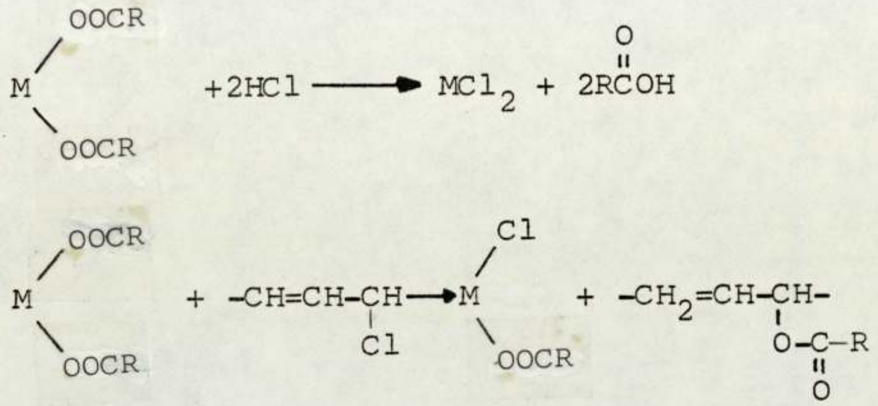
1 - Basic lead salts.
2 - Metal soaps.
3 - Organotin compounds.
4 - Organic synergists.

1 - Basic lead salts

Lead salts are used principally in stabilising plasticised PVC, electrical wire insulation and gramophone record compositions. The lead stabilisers include basic lead carbonate, dibasic lead phthalate and dibasic lead phosphite. Basic lead salts have been shown to neutralise HCl, replace reactive chlorine atoms and to form complexes with the partly degraded polymer(172).

2- Metal soaps and organic compounds

Both metal (Zn, Cd, Ba, Ca) carboxylates and organic compounds (epoxides, phosphite, α-phenylindole, β - aminocrotonate, β - diketones and polyols) were considered to be primary hydrogen chloride acceptors(36). It has been shown by Frye and Horst(37) with the use of infra-red spectroscopic measurement and radioactivity that metal carboxylate replaces the labile chlorine to give an ester.



$$M(OOCR)_2 + 2HCl \longrightarrow MCl_2 + 2R\overset{O}{\overset{\|}{C}}OH$$

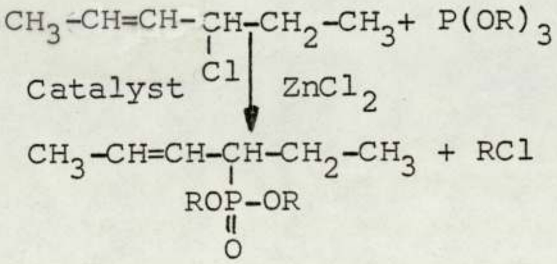
$$M(OOCR)_2 + -CH{=}CH-\underset{Cl}{\underset{|}{CH}}- \longrightarrow Cl-M-OOCR + -CH_2{=}CH-\underset{O-\underset{\underset{O}{\|}}{C}-R}{\underset{|}{CH}}-$$

Metal chlorides are formed by the reaction of hydrogen chloride with metal carboxylates and by ester exchange, the subsequent metal chlorides may then accelerate the dehydrochlorination(38,39) of PVC. Zinc chloride is the most active in that connection followed by $CdCl_2$; $BaCl_2$ and $CaCl_2$ on the other hand are not active. The elimination of metal chlorides (Lewis acid) effect is based on either an exchange reaction or on the moderation of their catalytic activity through complexation. The former, for the exchange reaction Klemchuck(40) and Onozuka(41) showed the zinc or cadmium carboxylates were able to cause the esterification at relatively low temperatures while barium or calcium did not. They suggested that the synergistic effect was caused by an exchange reaction between metal chlorides and metal carboxylates(11).

$$ZnCl_2 + Ca(OOCR)_2 \longrightarrow CaCl_2 + Zn(OOCR)_2$$

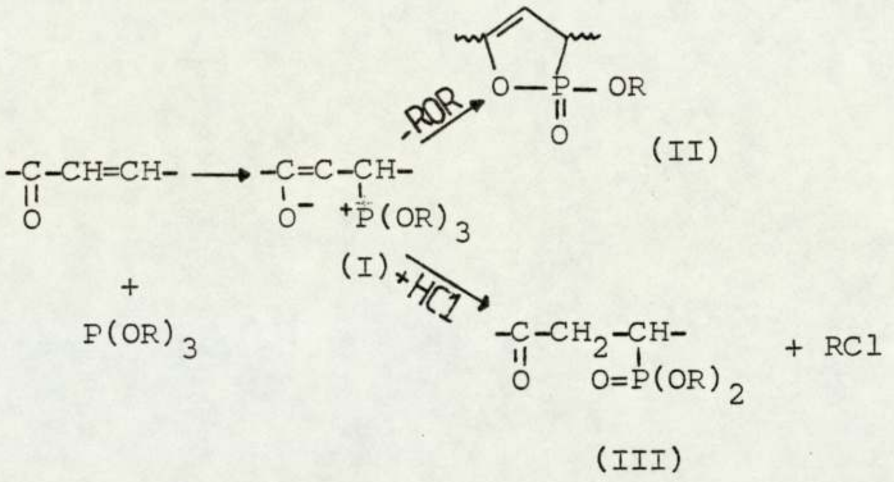
Thus the inactive calcium stearate reacts with prodegradant $ZnCl_2$ to give calcium chloride, which is neutral in dehydrochlorination and zinc stearate which is active in stabilisation.

Model compound studies show that aliphatic phosphites react with labile chlorine atoms(42) , the reaction is catalysed by $ZnCl_2$.



$$CH_3{-}CH{=}CH{-}\underset{\displaystyle Cl}{\underset{|}{CH}}{-}CH_2{-}CH_3 + P(OR)_3 \xrightarrow[\text{Catalyst}]{ZnCl_2} CH_3{-}CH{=}CH{-}\underset{\displaystyle \underset{\displaystyle \overset{\|}{O}}{ROP{-}OR}}{\underset{|}{CH}}{-}CH_2{-}CH_3 + RCl$$

Other workers(166) have shown that t-butyl phosphite reacts with model compounds to give an intermediate ion (I) of the type shown in the figure below, which is then transformed either into cyclic oxaphospholene (II) or in the presence of proton donors (HCl, etc..) into the stable ketophosphonate (III). It is well known that phosphites are peroxide decomposers (PD-S) and also react with HCl.



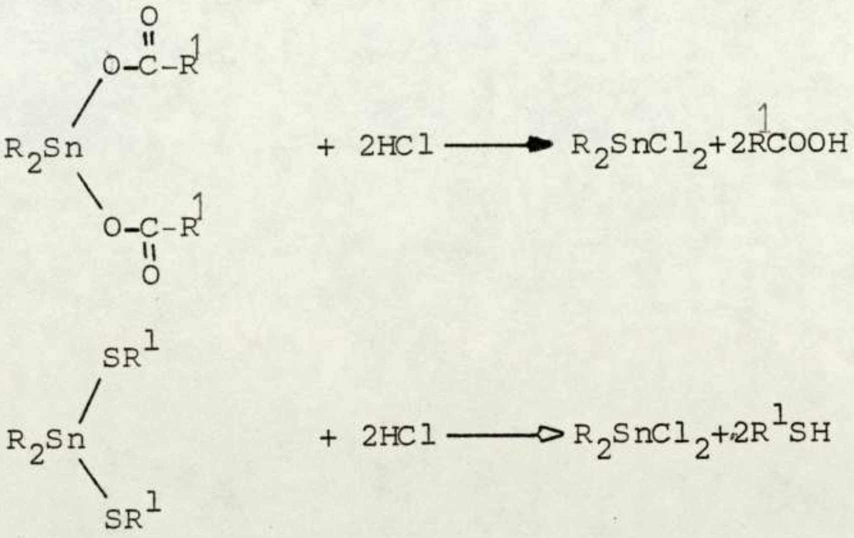
Hindered phenols, mercaptans, mono and disulphides, 2-hydroxybenzophenone, salicylate, 3,5-ditertiarybutyl-4-hydroxybenzylmercaptan(BHBM), 4-ethyloxymercapto-acetato-2-hydroxybenzophenone(EBHPT) and waxes are rarely used as primary stabilisers but find extensive use in a secondary role.

3 - Organotin compounds

Organotin compounds used as PVC stabilisers have the general formula $R_nSn(Y)_{(4-n)}$ ($R=CH_3$, C_2H_5, C_4H_9 or C_8H_{17}) and Y includes a wide variety of saturated or unsaturated carboxylates, mercaptides or mercaptide esters such as mercapto-acetates or mercapto-propionates(138). The efficiency of a given family of stabilisers depends on the number of alkyl groups attached to tin as follows:

$$R_2SnY_2 \gg RSnY_3 > R_3SnY$$

A - Removal of hydrogen chloride. Dialkyltin carboxylates and mercaptides are known to react with hydrogen chloride by a rapid stoichiometric process and the resultant dialkyltin dichloride has been shown to be ineffective in catalysing dehydrochlorination(42,35).

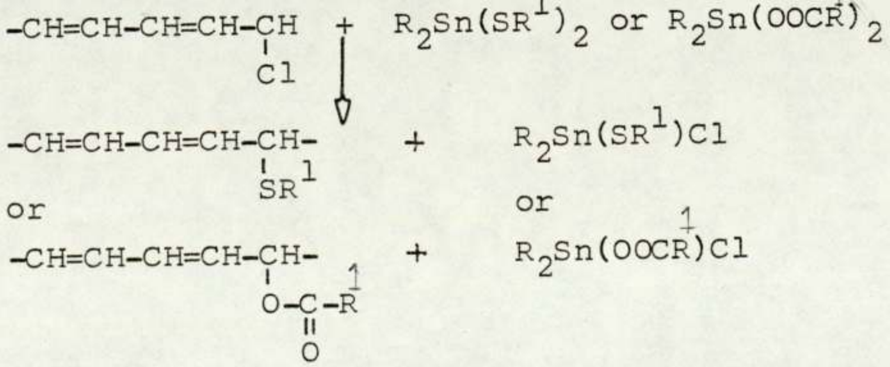


$$R_2Sn(OCOR^1)_2 + 2HCl \rightarrow R_2SnCl_2 + 2R^1COOH$$

$$R_2Sn(SR^1)_2 + 2HCl \rightarrow R_2SnCl_2 + 2R^1SH$$

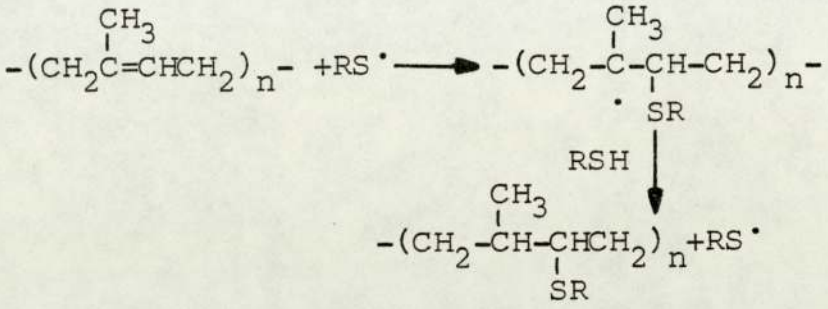
It is not unlikely that Sn-O and Sn-S bond cleavage is preceded by accomodation of hydrogen chloride in an expanded ligand co-ordination.(171)

B - Replacement of Allylic chlorine. Dialkyltin carboxylate(12,21) and dialkyltin dimercaptide(43) are also involved in the replacement of labile chlorine (tertiary and allylic) along the polymer chain by thermodynamically more stable ester moieties from the tin compound, there by, increasing the thermal stability of the polymer.

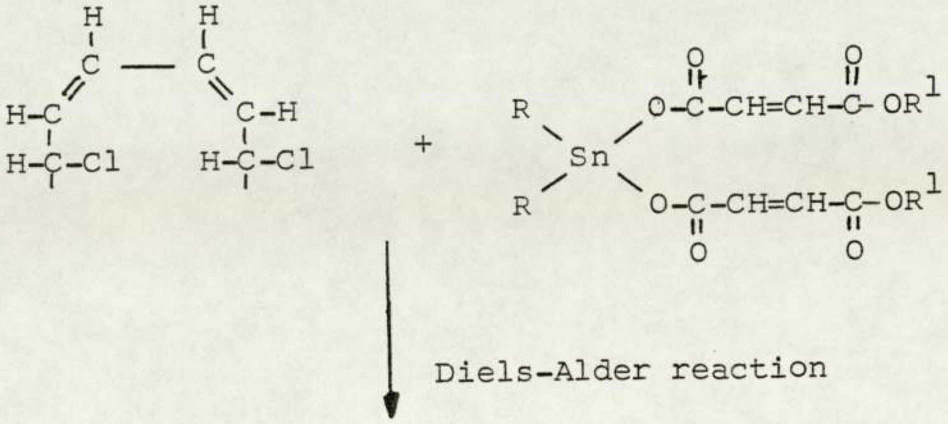


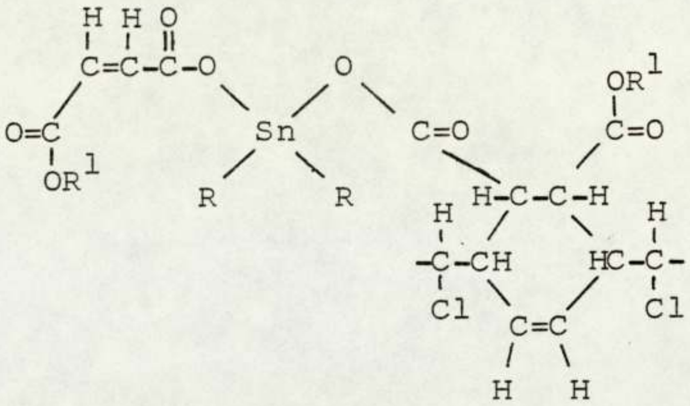
$$\text{-CH=CH-CH=CH-CH(Cl)} + R_2Sn(SR^1)_2 \text{ or } R_2Sn(OOCR^1)_2 \rightarrow \text{-CH=CH-CH=CH-CH(SR}^1\text{)-} + R_2Sn(SR^1)Cl \text{ or } \text{-CH=CH-CH=CH-CH(OCOR}^1\text{)-} + R_2Sn(OOCR^1)Cl$$

C - Reaction with unsaturation. The dialkyltin maleate and dialkyltin mercaptide react with unsaturation. The addition of thiols to unsaturation in polymers has been shown to be a radical catalysed process (44) involving the conversion of free thiol to thioyl radicals which subsequently show anti-Markownikoff addition to unsaturation.



It has been proved that dialkyltin maleates react with conjugated unsaturation produced in the polymer (21,45) but maleic acid or alkyl hydrogen maleate derived from hydrogen chloride neutralisation of the stabiliser is reported to undergo the Diels-Alder reaction more readily than the stabiliser itself (46).





D - Hydroperoxide Decomposition. Many organotin sulphur compounds have the ability to decompose peroxides. It was concluded(26,47) that dioctyltin bis(isooctylthioglycollate)(DOTG) reduces hydroperoxides to alcohols by a rapid molecular stoichiometric process (PD-S), oxidation products of DOTG undergo alcoholysis to yield peroxidalytic Lewis acid species characteristic of the sulphur antioxidant (PD-C) after an initial pro-oxidant stage. The processing and thermal oxidative stability of PVC formulated with DOTG is attributable in part to both PD-S and PD-C antioxidant effects.

1-4 Antioxidant Mechanisms

1-4-1 Chain Breaking (CB) antioxidants(48)

Alkyl radicals formed during hydrocarbon oxidation are readily oxidised to alkyl peroxyl radicals under atmospheric conditions. The ratio of these two radicals in an auto-oxidising system depends on the concentration of dioxygen. Ambient oxygen pressure (air) favours alkylperoxyl radical ($ROO^{\cdot}$) formation (e.g. processing in an opened mixer) where as dioxygen-deficient conditions (processing in a closed mixer) favours alkyl radicals ($R^{\cdot}$). In practise, therefore, the ratio ($ROO^{\cdot}$):($R^{\cdot}$) determines the choice of a particular antioxidant.

Electron donor chain breaking (CB-D) antioxidants, e.g. hindered phenols and aromatic amines, are effective at high ($ROO^{\cdot}$):($R^{\cdot}$) ratios , where as electron acceptor (CB-A) antioxidants e.g. quinones, nitro compounds, nitrones and phenoxyl and nitroxyl radicals, are effective at lower ($ROO^{\cdot}$:$R^{\cdot}$) ratios. It is probable that except at very low oxygen concentrations $ROO^{\cdot}$ is always in excess(164). Thus reducing agents (CB-D antioxidants) interfere with $ROO^{\cdot}$ while oxidising agents (CB-A antioxidants) intercept $R^{\cdot}$ much more efficiently.

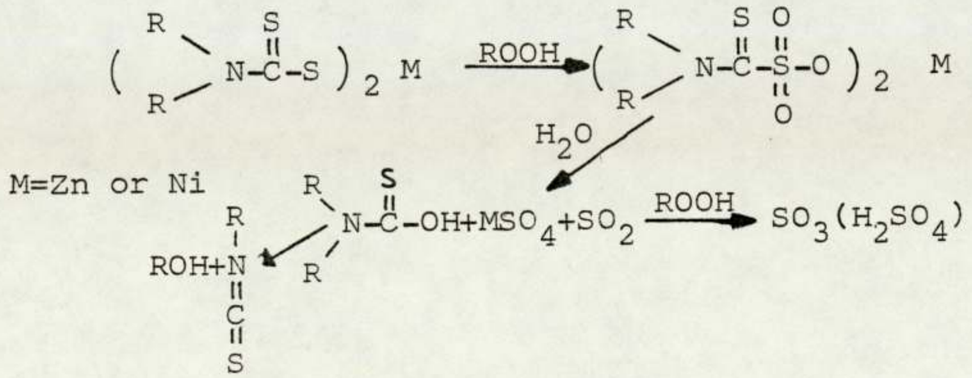
1-4-2 Preventive Antioxidants

These act to reduce the rate of chain initiation. Their function is, therefore, to suppress the degradation rate by a physical process (absorbing, quenching, screening) or by chemical reactions (decomposing peroxides).

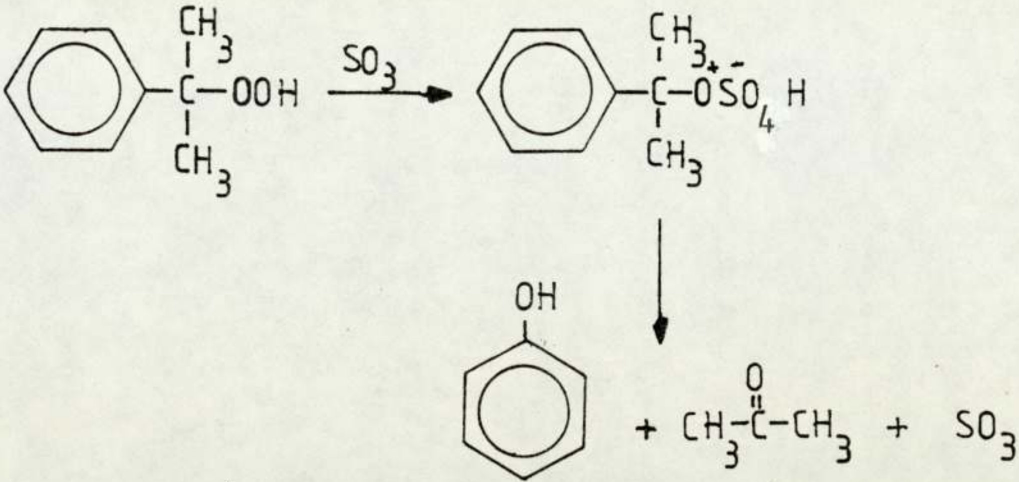
A - Peroxide Decomposition

The main function of this type of antioxidant is decomposition of hydroperoxides by a non-free radical process. Catalytic peroxide decomposers (PD-C) are exemplified by sulphur-containing compounds. The active species(49) (SO_2 and SO_3 or H_2SO_4) formed from these compounds are the antioxidants responsible for the removal of hydroperoxide in a non radical generating process. Examples within this class include dialkyl mono and disulphides, metal dialkyldithiophosphates and metal dithiocarbamates (52-53). Phosphite esters, on the other hand, have been shown(48) to behave primarily as stoichiometric peroxide decomposers (PD-S).

Scott(50,54,55,56,150) has shown the mechanism of action of sulphur containing antioxidants (in the case of metal dithiocarbamates).



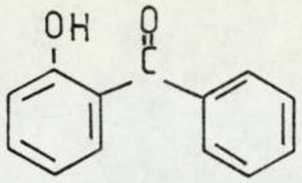
Peroxide may be decomposed via an ionic reaction generally involving Lewis acid such as SO_3 or H_2SO_4 (50,150)



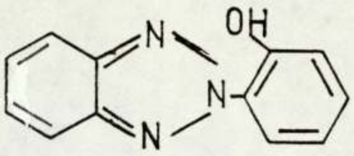
B - Photo-stabilisation

Compounds such as orthohydroxybenzophenones (I) e.g. UV 531 (4-octyloxy-2-hydroxy-benzophonone 'HOBP'), orthohydroxybenzotriazoles (II) and salicylates (III) have been shown (57,58) to be UV absorbers. All these compounds have a common structural feature, the intramolecular hydrogen bond (permits energy transfer, energy dissipation mechanisms) UV 531 has the effect of screening and has been shown to be involved in the removal of radicals from a photo oxidising medium (59,60) (CB-D). Other compounds such as Irganox 1076 (CB-D), phosphite esters (PD-S), bis(diethyldithiocarbamato)nickel(II) (PD-C, screening) bis(diethyldithiocarbamato)zinc (II) (PD-C) and Tin UV in 770 are UV stabilisers. The order of activity of these compounds as UV stabilisers is (61)

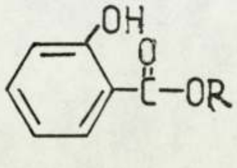
NiDEC(PD-C) $>$ UV531(UV absorber) $>$ 1076(CB-D) $>$ ZnDEC(PD-C)



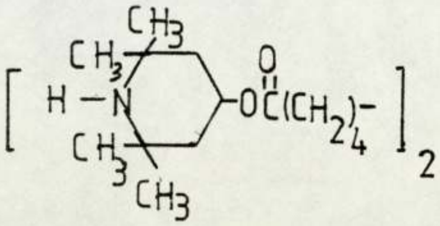
(I)



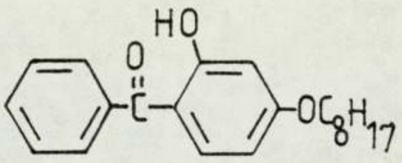
(II)



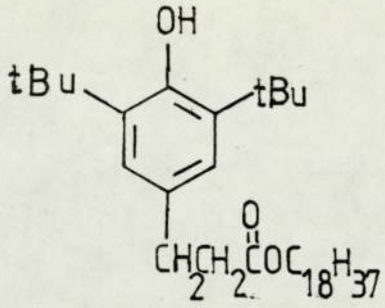
(III)



Tin UV in 770



UV531



Irganox (1076)

1-5 The Chemistry and Technology of Tellurium

Organotin compounds R_2SnY_2 have been successfully used for the stabilisation of PVC. There is evidence from the previous discussion that Y groups play an important role in stabilisation. Organotellurium compounds tend to show marked similarities to analogous organotin compounds, e.g. in both cases the most common oxidation states are M(II) and M(IV), in the case of tellurium interchange between oxidation state Te(II) and Te(IV) is easier than the corresponding two electron change in tin. Tellurium can also exhibit oxidation states M(-II), (I) and (VI).

A hundred years ago tellurium was a laboratory curiosity. Today it is an important material with a wide variety of uses in science and industry. The estimated break-down for tellurium consumption in 1971 was as follows: metallurgy 79% ; chemical, rubber, plastic and allied industries 18% and the thermoelectric and electrical use 3% (62-64).

Tellurium and some of its compounds such as tetrakis-(dialkyldithiocarbamato) tellurium (IV) have been shown to play a useful rôle as rubber-curing accelerators which significantly improve the resistance of rubber compositions to ageing(65,66). Tellurium rubber is noted for its resistance to heat and abrasion, because of this, it is used as jacketing in portable cables for dredging and mining, welding and other equipment, and also in special conveyor belts.

Numerous patents(67,68) have been issued, in which some organic tellurium compounds have been claimed as antioxidants and additives in lubricating oils and grease, especially in extreme pressure lubricating and hydraulic fluids. Some refactory metal tellurides have excellent lubricating properties combined with good stability in a high vacuum at elevated temperatures. They are useful in electronics, instrumentation, aerospace and military fields.

Organotellurium compounds have a history dating back to 1840 when Wöhler (69) prepared some dialkyltellurides by the reaction of potassium telluride with ethylsulphate. The aromatic derivatives are more stable to oxidation by air and are much easier to handle than the lower molecular weight aliphatic members which, in addition to their sensitivity towards dioxygen, posses an obnoxious, persistent odour. The major theme of the present work is to synthesise new classes of organotellurium compounds and to investigate their uses in polymers. A brief review of the chemistry of organotellurium compounds is appropriate in this context.

Diorganotellurides

There are many methods used to prepare tellurides, some of which are discussed below.

1 - Dialkyltellurides are prepared most conveniently by the alkylation of sodium telluride, which can be prepared either by the method of Tschugaff and Chlopin(70) or by reacting one mole of tellurium with two moles of sodium in liquid ammonia(71), or in N,N-dimethylformamide.(168)

$$2RX + Na_2Te \longrightarrow R_2Te + 2NaX$$

2 - McWhinnie (72) prepared diphenyl, dibenzyl and bis(pentafluorophenyl)telluride by reaction of tellurium tetrachloride with an appropriate Grignard reagent. No free elemental tellurium was observed with this modified procedure (it was reported to be a side-product by Rheinbolt)(74).

$$4RMgX + TeCl_4 \longrightarrow R_2Te + R_2 + 4MgXCl$$

3 - The reaction between aryltellurium trichlorides with arylmercuric chloride in boiling dioxane resulted in unsymmetrical diaryltellurium dichloride(73), which was reduced with sodium sulphide monohydrate at 100°C.

$$ArTeCl_3 + \grave{A}rHgCl \longrightarrow HgCl_2 + Ar\grave{A}rTeCl_2 \xrightarrow[100^{\circ}C]{Na_2S.9H_2O} Ar\grave{A}rTe$$

4 - Diorganotellurides are prepared by reducing diorganotellurium dichloride using agents such as hydrazine(75).

$$2R_2TeX_2 + N_2H_4 \longrightarrow 2R_2Te + N_2 + 4HX$$

The structures of several diorganotellurides(76) have been determined from X-ray crystallographic studies, in all tellurides examined the C-Te-C bond angle is about 90°-100°. Along with studies involving ^{125}Te Mössbauer quadrupole splitting(100); X-ray crystallographic studies have shown that in diorganotelluride compounds the Te-C bonds are predominatly p in character, with a small amount of s contribution.

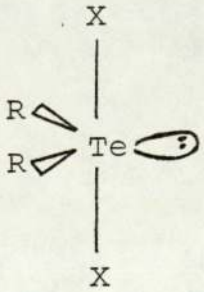
Organotellurium (IV) compounds

This is one of the most stable oxidation states of tellurium with respect to hydrolysis and oxidation. These compounds include R_2TeX_2, $RTeX_3$, R_3TeX and R_4Te, where X(F, Cl, Br, I) and R can be dialkyl, alkyl, aryl or diaryl.

1 - Derivatives of the type R_2TeX_2. The reaction of diorganotelluride with elemental halogens, which is a widely used method for the synthesis of diorganotellurium dichloride, was used to prepare a number of new derivatives(77).

$$R_2Te + X_2 \longrightarrow R_2TeX_2$$

It is known that diorganotellurium dihalides have a ψ-trigonal bipyramidal structure(78,79); available evidence suggests that diorganotellurium dicarboxylates have the same type of structure(80). In all cases the axial positions are occupied by halide or carboxylate and the equatorial position are occupied by two remaining organic groups and the non-bonding electron pair.



Structure of R_2TeX_2

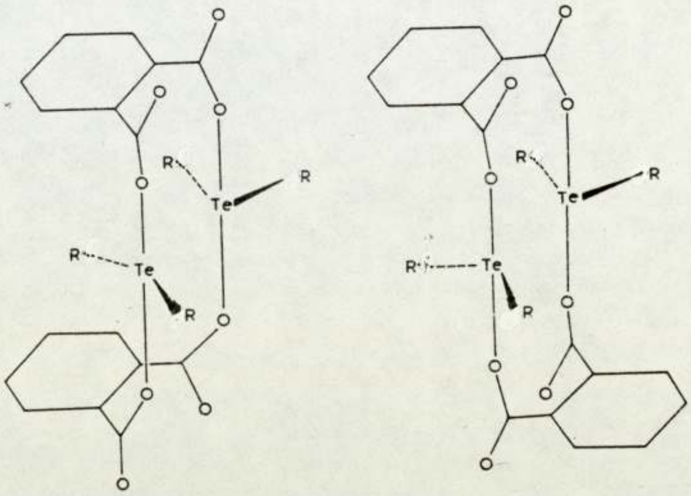
The axial bonds have been elongated and weakened compared to the equatorial bonds and the two equatorial Te-C bonds have been assumed to have a high degree of p character , in all the compounds the C-Te-C bond angles are about 90°, hence, a high s character for the spare pair. The character of the axial and equatorial Te-C bonds would be expected to be different, and cleavage of the longer, weaker axial bond would be expected to take place more readily than cleavage of the equatorial Te-C bonds found in the normal R_2TeX_2 structure.

The organotellurium carboxylates have recently become of interest in organotellurium chemistry. Carboxylate groups may interact in a number of ways with metal centres, they may act as unidentate ligands, symmetrical (or unsymmetrical) bidentate ligands, and they may be bridging groups or even be present as free ions. Diaryltellurium dicarboxylates have been prepared either by the reaction of diaryltellurium dichloride with metal carboxylates or via the lead-tetraacetate oxidation of tellurides(81,82).

$$Ar_2TeCl_2 + 2AgCOOR \longrightarrow Ar_2Te(OCOR)_2 + AgCl$$

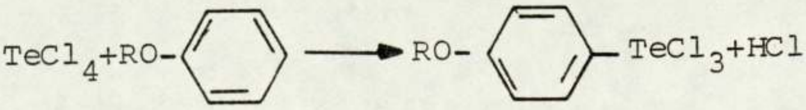
$$Ar_2Te + Pb(OCOR)_4 \longrightarrow Ar_2Te(OCOR)_2 + Pb(OCOR)_2$$

McWhinnie et al (129) have pointed out that the sodium salt of orthophthalic acid react with diaryltellurium dichloride to give dimers and suggested the structure to be

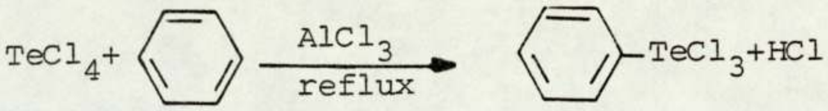


Tamagaki (84) has prepared a series of diphenyltellurium dicarboxylates by the reaction of diphenyltelluroxide with carboxylic acid in chloroform and he has reported the synthesis of monomeric diphenyltellurium phthalate by described method. Quite recently, McWhinnie (85) has reported that phenyl methyl tellurium ortho phthalate is monomeric in a chloroform solution.

2 - Derivatives type $RTeX_3$. These have been prepared by the condensation of tellurium tetrachloride with aromatic compounds containing activating substituent groups such as alkoxy groups(86)



Günther (87) has prepared phenyl tellurium trichloride by the reaction of tellurium tetrachloride with aluminium chloride in benzene.



Tellurium tetrachloride can react with aryl mercury chlorides to give aryl tellurium trichloride(88)

$$RHgCl+TeCl_4 \xrightarrow[\text{reflux}]{\text{dioxane}} RTeCl_3+HgCl_2$$

Diorgano ditellurides were converted to aryl tellurium trichloride by halogen e.g.

$$R_2Te_2+X_2 \longrightarrow RTeX_3$$

3 - Derivative type R_3TeX. Triorganotellurium salts have been known for nearly one hundred years. The examples of trialkyl, triaryl and mixed alkyl-aryl derivates containing many different anions are plentiful.

The synthesis of these compounds is mainly by the combination of diaryl tellurides with alkyl halides, the reaction of tellurium tetrachloride with a Grignard reagent, or the reaction of diorganotellurium dichloride with Grignard reagents.

$$R_2Te+R^1X \longrightarrow R_2R^1TeX$$

$$TeCl_4+3RMgX \longrightarrow R_3TeCl+3MgClX$$

$$R_2TeCl_2+R^1MgX \longrightarrow R_2R^1TeCl+MgClX$$

McWhinnie (89) et al demonstrated the preparation of tellurium salts (R_2TeR^1X) by reaction of R_2Te with alkyl halids via radical pathways by using E.S.R., and the recently developed spin trapping techniques. A mechanism was proposed for oxidative addition which involves the preformation of charge transfer complexes RX(alkyl halides) and diphenyl telluride. From this evidence, it can be concluded that R_2Te acts as a halogen atom acceptor.

4-Derivatives of the type R_4Te, were reported by Wittig and Fritz (90), who prepared it by the reaction of tellurium tetrachloride, diphenyltellurium dichloride or triphenyltellurium chloride with phenyl lithium.

Little has been reported on the ability of organotellurium compounds to decompose peroxide. Telluride combined with benzoyl peroxide to give diorganyltellurium dibenzoate (91) and it has been recently reported that t-butyl hydroperoxide oxidises several tellurides in benzene to give telluroxide (92,93).

There are few studies of the reaction of hydrogen chloride with organotellurium compounds. According to Lederer (94), diphenyl telluride and hydrogen chloride combine to form a compound of the formula $Ar_2Te \cdot HCl$. Perhaps this substance should be designated as a tellurium salt $(Ar_2TeH)^+Cl^-$, although experimental evidence appears to be lacking. Other workers (95) have confirmed that tellurides can be easily transformed into the corresponding dichloride by the action of hydrogen chloride. In the absence of oxygen the telluride was recovered unchanged. Hydrogen chloride can react with R_2TeO (96), $R_2Te(NO_3)_2$ (97), $R_2Te(OH)Cl$ to give the corresponding dichloride.

As was mentioned previously, metal chlorides(Lewis acid characteristics) function as accelerators for the dehydrochlorination of PVC. The Lewis acidity of organotellurium compounds depends on the number of halogen atoms, as the number of chlorine atoms increases, the Lewis acidity also increases. The acidity of organotellurium compounds is represented as follows:

$$RTeCl_3 \gg R_2TeCl_2 > R_3TeCl$$

When the Lewis acidity of organotellurium compounds is compared with that of the corresponding organotin compounds, it is found that the tellurium compounds have the lower acidity. Probably the main factor affecting this behaviour is the presence of a lone pair of electrons in tellurium while the corresponding tin has none. This means that incoming nucleophiles are repulsed, hence, tellurium behaves as weaker Lewis acid.

As was mentioned before, tetrakis(dialkyldithiocarbamato) tellurium (IV) was used as an accelerator for rubber. Scheele $^{(99)}$ et al reported that tetrakis(diethyldithiocarbamato)tellurium (IV) is a rather unstable compound under certain conditions. For example; on warming the canary yellow coloured solution of tetrakis(diethyldithiocarbamato) tellurium (IV) the solution turns brick-red in colour which corresponds to tetraethylthiuram disulphide and bis(diethyldithiocarbamato) tellurium (II). When tetrakis(diethyldithiocarbonato) tellurium (IV) is dissolved in various organic solvents, it undergoes reduction to give equimolar of bis(diethyldithiocarbamato)tellurium (II) and tetraethylthiuram disulphide.

From the above discussion,it is clear that there are many good reasons to examine organotellurium or tellurium compounds which are analogous to tin compounds as stabilisers (antioxidants) in polymers.

CHAPTER TWO

EXPERIMENTAL

2-1 Chemicals

All chemicals were obtained from commercial sources and where necessary, melting points and other physical data such as infra-red and 'H n.m.r. spectra were used to assess the purity of the compounds. Tellurium tetrachloride and tellurium powder, the starting materials for many reactions, were supplied by British Drug House (BDH). Dibutyltin maleate was obtained as Irgastab DBTM from Ciba Geigy Limited. 2-Hydroxy-4-octyloxybenzophenone was obtained as Cyasorb UV531 from Cynamid Corporation. Tetrakis(diethyldithiocarbamato)tellurium (IV) was obtained as ethyl tellurac from the Vanderbilt Company.

The polymer was Breon poly(vinylchloride) M90/50 homopolymer supplied by British Petroleum and polypropylene [D 714(5)] supplied by I.C.I. The polymers were obtained as the unstabilised powders and normally stored in the dark inside a deep freezer.

The common solvents as supplied by the Chemistry Department Stores were purified according to literature(103).

2-2 Elemental Analysis

Microanalysis for carbon, hydrogen, nitrogen, sulphur and halogen were obtained from analytical services of the Chemistry Department of Aston University. Tellurium analysis was carried out by the method of Suttle(104).

2-3 Physical Measurements

2-3-1 Melting Points

These were determined using a Gallenkamp electrically heated melting point apparatus.

2-3-2 Mass Spectra

Mass spectra were obtained on the AEI-MS9 spectrometer at ionising potentials of 70 eV or 15 eV.

2-3-4 Nuclear Magnetic Resonance Spectra

All proton magnetic resonance spectra at 60 MHZ were recorded on a Perkin-Elmer R14 spectrometer. Appropriate solvents were chosen for each sample and TMS (tetramethylsilane) was used as internal reference.

2-3-4 Infra-red Spectra

Spectra in the range 4000-200cm^{-1} were recorded on a Perkin-Elmer (599) spectrophotometer. Solid state samples were examined as Nujol mulls supported between KBr plates or polyethylene films. Some samples were also examined as solid discs, prepared by pressing a mixture of sample and powdered KBr or CsI.

2-3-5 UV Spectroscopy

UV spectroscopy of the additive containing polymer and solutions were carried out using the Unicam sp800 spectrophotometer. For the former, a processed additive-free polymer film of identical thickness was used (as a compensator) in the reference beam. In the case of the solution, the spectra were recorded using quartz cells of 10.0mm path length with the pure solvent being used in the reference beam.

2-3-6 Cryoscopic Methods

All molecular weight measurements were carried out in appropriate solvents by using a Beckman thermometer.

2-3-7 Chromatography.

Thin layer chromatography (TLC) was carried out by using silica gel plates to identify the product or to separate the species. Chromatograms were developed with iodine. Column chromatography was used to purify the viscous oily compounds in appropriate solvents by using silica gel (80-200 mesh).

2-3-8 Gas Liquid Chromatography Analysis

The product of some reactions were analysed qualitatively by using APYE Unicam GCD chromatograph. The column was packed with 25% silicone grease on phase prep A or 5% silic fluid 96-2000 on chromosorb w/length 7 x ¼. The temperature was either fixed or a temperature program was used. Flow rate was 30ml/min.

2-4 Processing of the Polymer.

Poly(vinylchloride) and polypropylene were processed in a prototype RAPRA torque rheometer(105), which is essentially a small mixing chamber (cavity volume 39cc), with mixing screws contra-rotating at two different speeds; the high speed (60 r.p.m.) was used for processing.

The mixing chamber was operated either open to the atmosphere (open mixer) or sealed by pneumatically-operated ram to ensure processing under dioxygen deficient conditions (closed mixer). 46gm of poly(vinylchloride) and 35gm of polypropylene were used for processing in a closed mixer calculated weights of additives were mixed with the polymer charge to obtain the percentage or concentration required in the final polymer test film.

2-5 Preparation of films

The processed poly(vinylchloride),(above), was powdered by gentle abrasion and the polymer was uniformly dispersed on a special grade cellophane paper which was used to prevent the film sticking to the plates and then pressed. Processed polypropylene (6g) was wrapped in a layer of cellophane and flattened on a cold press (at room temperature) for 30 seconds at 25 ton Inh^{-2} and then the resulting disc was placed between cellophane sheets. The polymers were compression moulded between stainless steel glazing plates which were inserted in to an electric press whose plates were maintained at 170 ± 2°C and 180 ± 2°C for poly(vinylchloride) and polypropylene respectively. The polymer was pre-heated for 1.5 minutes (at zero pressure) to allow for the material to flow and then pressed for 1.5 minutes at full pressure (30 ton Inh^{-2}).

Immediately thereafter, the plattens were cooled to Ca 40°C by running cold water while maintaining full pressure. Sections of uniform thickness (0.0025 Inh PVC and 0.008 Inh PP) were selected as a test film for ageing and UV-exposure. The remaining sections were stored in the dark inside a deep freezer.

For selected experiments, polymer films were cast from 5% dichloromethane solution on a mercury surface. The solvent was evaporated completely under vacuum and the cast films of uniform thickness (0.0025 Inh) selected for examination.

2-6 Melt Flow Index (MFI)

Thermal-oxidative stability of unstabilised polyolefins during processing is markedly affected by the use of suitable melt stabilisers. MFI is inversly proportional to the molecular weight of the polymer. By comparison with the value of the unstabilised polymer (control) a constant MFI value suggests good melt stabilisation.

The MFI represents the weight in grams of polymers extruded in 10 minutes. Polypropylene (4.0gm) was extruded on a Davenport melt indexer (serial number 985)(106) at 230°C under a load of 2.16 Kg through a die 0.0465" diameter. The polymer was allowed to extrude for one minute before samples were collected. Samples extruded in 30 seconds were collected and weighed when cold, The average weight of five consecutive samples was obtained.

The melt flow index was calculated from the following relation:

$$\text{MFI} = \frac{600 \text{ x average weight of cut off in grams.}}{\text{Interval time in seconds.}}$$

2-7 Determination of Unsaturation

The mercuric acetate catalysed addition of iodine to unsaturation was adapted from Gallo,Weise and Nelson(107). 0.5gm of processed powdered polymer was swollen in 75cm^3 of chloroform for 12 hours in a conical flask fitted with a rubber seal. 5 cm^{3}of 20% trichloroacetic acid in chloroform was added, followed by 25cm^{3}of 0.1N iodine solution in chloroform and 25cm^{3}of mercuric acetate in glacial acetic acid. The mixture was gently agitated for one hour(167) in the dark and 75cm^{3}of 7.5% potassium iodide was added. Excess iodine in the aqueous phase was titrated with 0.1N sodium thiosulphate and by using the starch end point in the aqueous phase.

2-8 Measurement of UV stability

UV irradiation was carried out in a sun lamp/black lamp (S/B) cabinet which consisted of a cylindrical casing containing an inner cylindrical rotating drum. Samples were placed on this drum 15cm from the fluorescent tubes. The outer cylinder (diameter 1.1m) houses 32 fluorescent tubes: 24 type C Philips actinic blue lamps (0.5) and 8 type A_2

Westinghouse sun lamps (FS20) symmetrically distributed so that three blue lamps alternated with one sun lamp. The spectral output of this combination of fluorescent tubes is shown in Fig 2.1 . The combined light envelope approximates to the 280-340 nm region(108). To maintain a long-term uniform spectral distribution inside the UV-cabinet, fluorescent tubes are replaced sequentially every 200 hours of operation. Exposure times are indicated on a counter clock to the nearest 3.6 seconds. Temperature inside the cabinet is about 30°C.

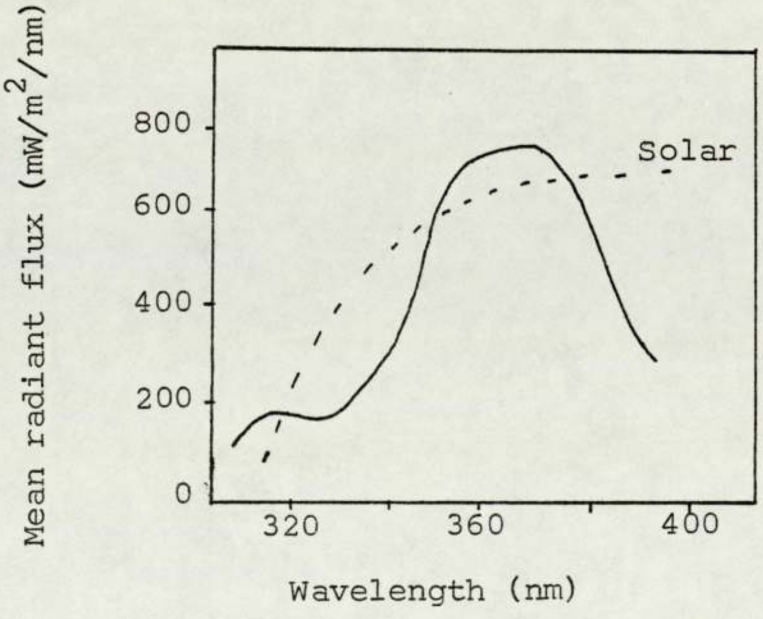


Fig 2.1 Spectral distribution of 8 'sunlamps' with 24 'Actinic' lamps arranged symmetrically [—] and solar radiation, maximum mid-summer clear sky (U.K) radiation [----]

2-9 Measurement of Thermal-Oxidative stability

Compression moulded polymer films of uniform thickness were subjected to thermal oxidative ageing in a Wallace oven at 140 ± 2^0C. Each sample was suspended in a separate cell to prevent the cross-contamination of the additives by volatilisation and was subjected to an air flow of 3.0 cu ft/h .

2-10 Estimation of Degradation

2-10-1 Total Colour Difference

In practise discolouration is normally the first manifestation of the degradation of poly(vinylchloride). Colour formation in poly(vinylchloride) films of uniform thickness was expressed as the total colour difference relative to the calibrated reference films cast from 5% dichloromethane solution of unprocessed polymer. The measurement was carried out using the MEECO Colormaster model V in transmission. Readings were obtained using red, green and blue filters and the total colour difference ΔT was calculated using the formula:

$$\Delta T = (\Delta R^2 + \Delta G^2 + \Delta B^2)^{\frac{1}{2}}$$

Where ΔR, ΔG and ΔB are the differences between the instrument reading of the test sample and the reference sample (unprocessed cast poly(vinylchloride) film without additives or film containing coloured additives) using the red, green and blue filters respectively.

The method was found to be sufficiently sensitive as to detect transparency changes in the films prior to visible colour formation.

2-10-2 Infra-red spectroscopy

Infra-red absorption spectra were obtained by using the Perkin-Elmer (model 599). The spectra from 4000-200cm^{-1} were recorded at medium scan speed. Spectra were obtained for each sample prior to and after heat-ageing and UV irradiation at regular intervals of time.

In all quantitative analyses, the following combined form of the Beer-Lambert equation was used(109)

$$A = \log_{10} {}^{I_o}/I = ECL$$

where A = absorbance of optical density.

I_o = intensity of radiation effectively entering the sample.

I = Intensity of radiation emerging from the sample

E = extinction coefficient expressed in litres mol^{-1} cm^{-1}

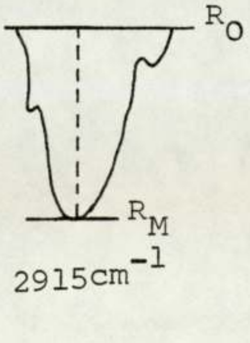
C = concentration of absorbing group present in mole/litre

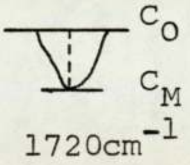
L = path length of radiation of the sample in cm.

to minimise errors due to variation in film thickness, as well as errors due to the instrument, and internal standard, a characteristic absorption peak was used as reference. The growth and decay of observed absorption peaks (for funtional groups) were expressed as indices which were defined as the ratio of the absorbance of functional group peaks to that of the reference peak.

$$\text{Index} = \frac{\text{Absorbance of functional group.}}{\text{Absorbance of a standard peak.}}$$

The concentration of carbonyl modifications in poly(vinylchloride) films was expressed as an index relative to the polymer reference peak at 2915 cm^{-1} which is due to carbon-to-hydrogen bond stretching. The carbonyl index was calculated from the carbonyl absorption at $1720cm^{-1}$ in the following manners.





where Rm = absorbance at reference peak maximum

Ro = absorbance at reference peak baseline

Cm = absorbance at carbonyl peak maximum

Co = absorbance at carbonyl peak baseline

so the carbonyl index

$$= \frac{\log \frac{Co}{Cm}}{\log \frac{Ro}{Rm}}$$

The carbonyl index for polypropylene was calculated in the same way except that the carbonyl absorption was at $1710cm^{-1}$ and the reference peak at $2715cm^{-1}$.

2-10-3 Tear Strength Test

Embrittlement times (EMT) were estimated by exposing the film to UV irradiation until it is fractured when flexed once through 180^o by hand. Each determination was carried out in duplicate. This test can serve as a qualitative guide for the durability of the films.

CHAPTER THREE

INVESTIGATION OF THE FEASIBILITY OF ORGANOTELLURIUM COMPOUNDS AS STABILISERS FOR POLY(VINYLCHLORIDE)

3-1 Organotellurium compounds

A - Diphenyltelluride was prepared by the method of McWhinnie et al(72) and was ultimately purified by distillation (b.p. 119-120°C, 0.3mm Hg).

B - Di-p-ethoxyphenylditelluride was prepared by the literature method(110), m.p.103-105°C (lit.107-108°C).

C - Di-p-ethoxyphenyltelluride was prepared by the literature method(111), m.p. 63°C (lit.64°C).

D - Diphenyltellurium diacetate was prepared by the literature method (81,82),m.p. 139-140°C (lit.139-141°C).

3-2 Reaction between organotellurium compounds and hydrogen chloride

Diphenyltellurium diacetate (1.0g) was dissolved in o-dichlorobenzene ($10cm^3$) and the solution was introduced into a small three necked round bottomed flask fitted with a gas inlet and a reflux condenser. A slow stream of dry hydrogen chloride was passed in to the solution, which was heated to reflux in an oil bath at 180°C. The solution was refluxed with the passage of hydrogen chloride for one hour. The hydrogen chloride stream was then replaced by dinitrogen for 15 minutes and heating was discontinued. The solution was left overnight, when a white solid was obtained. The solid was filtered and dried to give m.p. 157°C (diphenyltellurium dichloride,m.p. 158°C)(112). The filtrate was identified as an o-dichlorobenzene solution of acetic acid by GLC using 25% silicon grease on a phase prep A column, at a temperature of 240°C.

The following reactions between organotellurium compounds and hydrogen chloride were carried out as above.

A - Diphenyltelluride, the product was diphenyltellurium dichloride,m.p. 157°C.

B - Diphenyltellurium maleate, the product was diphenyltellurium dichloride and maleic acid. The maleic acid was isolated as the sodium salt by shaking the solution with aqueous sodium hydroxide after the separation of diphenyltellurium dichloride.

C - Diphenyltellurium β - mercaptopropionate , the product was diphenyltellurium dichloride and β - mercaptopropionic acid. The β- mercaptopropionic acid was isolated in the same way as maleic acid.

D - Di-p-ethoxyphenyltelluride. The reaction was also carried out in chloroform at room temperature. The product was tellurium and phenetole. The phenetole was analysed by GLC using 25% silicon grease on phase prep A column, at temperature 50-250°C.

E - Di-p-ethoxyphenyltellurium β- mercaptopropionate, the product was phenetole, tellurium and β-mercaptopropionic acid.

3-3 Reaction of organotellurium compounds with model compounds of poly(vinylchloride)

In the general procedure(117) the organotellurium compound (0.005 mole) and chlorohydrocarbon (0.05 mole) were frozen, in liquid nitrogen, in thick-walled pyrex glass tubes which were sealed. The tubes were heated to 180°C in an oil bath for various periods of time. After removal from the oil bath, the tubes were cooled to room temperature, then frozen in liquid nitrogen, the pyrex tube was then opened and the contents were analysed.

A - Diphenyltellurium diacetate with t-butyl chloride (reaction period 60 mins), the product was diphenyltellurium dichloride, m.p. 157°C, and t-butyl acetate. The latter was identified by transferring the contents to a small distillation apparatus. Careful distillation was carried out to give unreacted t-butyl chloride b.p. 51°C followed by t-butyl acetate b.p. 96°C. In the case of 3-chlorobut-1-ene (reaction period 90 mins), the product was diphenyltellurium dichloride and 3-acetoxybut-1-ene. The latter was analysed by GLC using a column of 5% silic fluid 96-2000 on chromosorb W, at a temperature of 50-250°C.

B - Diphenyltelluride with t-butyl chloride and 3-chlorobut-1-ene (reaction periods are 60 mins and 75 mins respectively), the product was diphenyltellurium dichloride.

Preparation of 3-acetoxybut-1-ene (113, 117). But-1-ene-3-ol (4.9g) acetic anhydride (7.15g), and pyridine ($12cm^3$) were mixed and allowed to stand in a stoppered flask for 3 hours at room temperature. Water ($30cm^3$) and pentane ($25cm^3$) were then added and the mixture was shaken vigorously. The pentane layer was separated, washed successively with water, diluted hydrochloric acid (0.5%) and water again, and then dried and distilled pure 3-acetoxybut-1-ene had b.p. 110°C.

3-4 Reactions of organotellurium compounds with peroxides

3-4-1 Reaction of diphenyltelluride with di(3-butoxycarbonyl-2-propenoyl) peroxide

Preparation of di(3-butoxycarbonyl-2-propenoyl) peroxide. (114) Firstly 3-butoxycarbonyl-2-propenoic acid was prepared by the reaction of maleic anhydride with an equimolar amount of dry butyl alcohol at 80°C, using a water bath for 90 minutes.

Secondly, 3-butoxycarbonyl-2-propenoyl chloride was prepared from 3-butoxycarbonyl-2-propenoic acid (o.5 mole) in a flask, heated on a water bath and (0.6 mole) redistilled thionyl chloride (0.6 mole) was added to it gradually for a period of 45 minutes. Stirring was maintained and the mixture was refluxed for 30 minutes. The apparatus was rearranged and the remaining thionyl chloride was then removed under vacuum distillation.

Finally, di(3-butoxycarbonyl-2-propenoyl) peroxide was prepared by immersing a beaker containing hydrogen-peroxide (0.185 mole 50% w/w) in an ice bath. Two separate dropping funnels, containing 30cm^3 of 4M sodium hydroxide solution and 3-butoxycarbonyl-2-propenoyl chloride (0.214 mole) were placed inside the beaker. The two reagents were added alternately, a few drops at a time, making sure that the temperature would not rise above 5-8°C and the solution was maintained faintly alkaline throughout. After all the reagents had been added the solution was stirred for a further half an hour. At this time the odour of 3-butoxycarbonyl-2-propenoyl chloride had disappeared. Di(3-butoxycarbonyl-2-propenoyl) peroxide was then extracted from the solution by diethylether and finally dried.

The diphenyltelluride (0.01 mole) was added slowly to a dry diethylether solution of di(3-butoxycarbonyl-2-propenoyl) peroxide (0.014 mole) which was continuously stirred under dinitrogen. The mixture was refluxed for one hour. After the diethylether had been removed the crude material was purified by preparative thin layer chromatography and column chromatography to give pure diphenyltellurium bis(monobutyl maleate). Chloroform was used as the solvent.

3-4-2 Reaction of diphenyltelluride with benzoyl-peroxide

Diphenyltelluride (0.01 mole) was added slowly to a solution of benzoyl peroxide (0.01 mole), dissolved in 50cm^3 of fresh dry dioxane, which was continuously stirred under dinitrogen. The mixture was heated at 80°C for one hour. The dioxane was then removed from the mixture by rotary evaporation and the crude material was obtained, which was recrystallised from a mixture of benzene and hexane to give pure diphenyltellurium dibenzoate, m.p. 159-160°C (lit. 159-161°C)(83)

3-4-3 Reaction of di-p-ethoxyphenylditelluride with benzoyl peroxide

Benzoyl peroxide (0.03 mole) was dissolved in 50cm^3 of dioxane and di-p-ethoxyphenylditelluride (0.01 mole), was added slowly. The reaction was carried out in the same way as diphenyltelluride with benzoyl peroxide.

Elemental analysis of the white solid suggests the following empirical formula : $(RTeO)_2O$, m.p. 195°C.

3-4-4 Reaction of diphenyltelluride with cumene hydroperoxide

Reaction of cumene hydroperoxide (0.01 mole) (purified by the Kharasch method)(115), and diphenyltelluride (0.01 mole) was carried out in the same way 3-4-2. When the reaction was complete (1 hour), the solution was left for 24 hours so that a white solid precipitate was formed. The whole mixture was filtered and the solid recrystallised from water to give diphenyltelluroxide, m.p. 188-189°C, (lit. 191°C)(123). The filtrate was identified as a dioxane solution of α,α-dimethylbenzyl alcohol by GLC using 25% silicon grease on a phase prep A, at a temperature 50-250°C.

The same experiment was repeated with excess of cumene hydroperoxide and after the filtration, the filtrate was treated with 25cm^3 and 10% acetic acid in isopropanol followed by 15cm^3 of 20% sodium iodide in isopropanol The mixture was refluxed for 5 minutes and allowed to cool for 3 minutes. 10cm^3 of distilled water was then added and the liberated iodine was titrated against 0.01N sodium thiosulphate to determine the unreacted cumene hydroperoxide, as shown below:-

$$ROOH + 2\ I^- + 2H^+ \longrightarrow ROH + H_2O + I_2$$

$$2S_2\bar{O}_3^- + I_2 \longrightarrow 2\ I^- + S_4\bar{O}_6^-$$

3-5 Results and discussion

3-5-1 Results

Elemental analyses of diphenyltellurium dichloride , diphenyltelluroxide, p-ethoxyphenyltellurium anhydride, diphenyltellurium bis(monobutyl maleate) and diphenyltellurium dibenzoate are presented in Table 3-1. The infra-red and 'H n.m.r. spectroscopic data of the above mentioned compounds are listed in Table 3-2. The GLC analysis of the solvent and the references are presented in Table 3-3.

The results of the reaction of some organotellurium compounds with hydrogen chloride, chlorohydrocarbons and cumene hydroperoxide are tabulated in Table 3-4. Table 3-4 also includes data relating to product identification.

Table3-1. Analytical data for some organotellurium compounds.

Compound.	Found.			Calculated.		
	C%	H%	Cl%	C%	H%	Cl%
Diphenyltellurium dichloride	41.2	3.00	19.4	41.0	2.84	19.9
Diphenyltelluroxide	48.0	3.50	-	48.5	3.36	-
P-ethoxyphenyltellurium anhydride	35.6	3.00	-	35.3	3.30	-
Diphenyltellurium bis(monobutyl maleate)	52.4	5.00	-	53.9	5.13	-
Diphenyltellurium dibenzoate	59.7	3.90	-	59.7	3.82	-

Table 3-2. Spectral data for some organotellurium compounds,

Compound	IR(cm^{-1}) (ν)	NMR chemical shifts δ ppm VS.TMS
Diphenyltellurium dichloride	268(m) [Te-Cl]	
P-ethoxyphenyltellurium anhydride	710 680 555 [Te-O] modes	
Diphenyltelluroxide	broad peak at 770-480 [Te-O]	
Diphenyltellurium bis(monobutyl maleate)	1660 1615 (s) as [COO] 1215 1170 (s) s [COO] 1730 (s) [C=O] ester	0.9 (t) 1.5 (m) 3.95(t) 3.55(m) Aliphatic protons 5.8-6.0 (d) 6.1-6.3 (d) Alkene protons 7.3-7.8 (m) Aromatic protons
Diphenyltellurium dibenzoate	1320 1300 (s) s [COO] 1645 1630 (s) as [COO]	7.5-7.95 (m) Aromatic protons

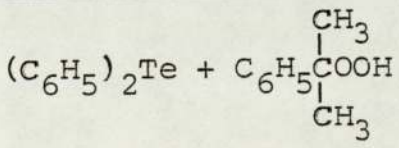
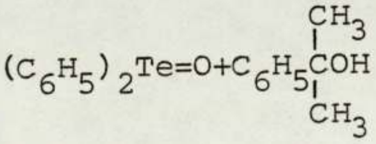
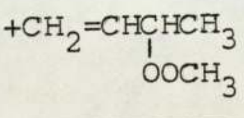
Table 3-3.

The retention distance for the reference and solvent relative to the reaction.

Compound	Retention distance	Temp.
o-Dichlorobenzene	2.4cm	240°C
Acetic acid	1.4cm	240°C
Chloroform	3.4cm	50-250°C
Phenetole	8.5cm	50-250°C
Dioxane	3.3cm	70-250°C
α-methyl styrene	6.8cm	70-250°C
α,α'-dimethylbenzyl alcohol	7.9cm	70-250°C
3-Chlorobut-1-ene	2.0cm	60°C
1-Chlorobut-2-ene	2.6cm	60°C
3-Acetoxybut-1-ene	12.5cm	50-250°C

Table 3-4.

Reaction of organotellurium compounds with hydrogen chloride, chlorohydrocarbons and cumene hydroperoxide.

Reaction	Product and Retention distance
$(C_6H_5)_2\ Te + HCl$	$(C_6H_5)_2Te\ Cl_2 + H_2$
$(C_6H_5)_2\ Te(OOCCH_3)_2 + HCl$	$(C_6H_5)_2TeCl_2 + 2CH_3COOH$ 1.4cm
$(C_2H_5OC_6H_4)_2\ Te + HCl$	$C_2H_5OC_6H_5 + Te$ 8.5cm
$(C_6H_5)_2Te\ C_4H_2O_4 + HCl$	$(C_6H_5)_2TeCl_2 + HOOCCH{:}CHCOOH$
$(C_6H_5)_2Te\ C_3H_4O_2S + HCl$	$(C_6H_5)_2Te\ Cl_2 + HSCH_2CH_2COOH$
$(C_2H_5OC_6H_4)_2\ TeC_3H_4O_2S + HCl$	$C_2H_5OC_6H_5 + Te + HSCH_2CH_2COOH$
 $(C_6H_5)_2Te + C_6H_5\overset{CH_3}{\underset{CH_3}{C}}OOH$	 $(C_6H_5)_2Te{=}O + C_6H_5\overset{CH_3}{\underset{CH_3}{C}}OH$ 7.9cm
$(C_6H_5)_2Te(OOCCH_3)_2 + (CH_3)_3CCl$	$(C_6H_5)_2Te\ Cl_2 + (CH_3)_3COOCCH_3$
$(C_6H_5)_2Te(OOCCH_3)_2+$ $CH_2{=}CHCHClCH_3$	$(C_6H_5)_2TeCl_2 + CH_3CH{=}CHCH_2Cl$  $+CH_2{=}CH\underset{OOCH_3}{C}HCH_3$ 12.5cm 2.6cm
$(C_6H_5)_2Te + (CH_3)_3CCl$ $(C_6H_5)_2Te + CH_2{=}CHCHClCH_3$	$(C_6H_5)_2Te\ Cl_2$

3-5-2 Discussion

Organotin compounds are amongst the main PVC stabilisers and they can function in a variety of ways.

1 - They have the ability to neutralise hydrogen chloride.

2 - They can replace chlorine atoms.

3 - They react with unsaturation.

4 - They decompose peroxides.

5 - The product of the reaction between hydrogen chloride and the organotin compounds is not a pro-degredant.

Organotellurium compounds sometimes show similarities to analgous organotin compounds, as explained in chapter one. In order to test the feasibility of organotellurium compounds to act as stabilisers for PVC the following reactions have been performed to obtain additional data.

3-5-2-1 Reaction of organotellurium compounds with hydrogen chloride

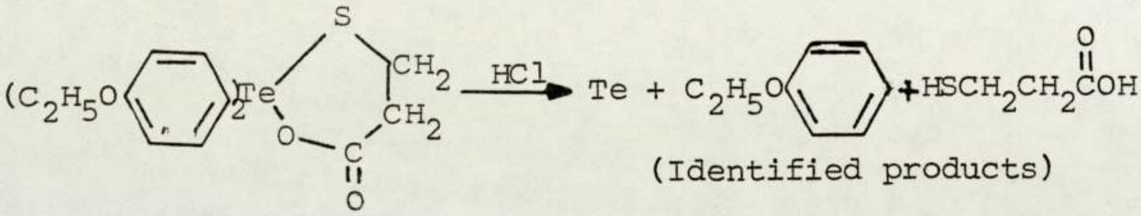
The organotellurium compounds were reacted with hydrogen chloride in a chlorinated hydrocarbon solvent at a temperature used in the commercial processing of stabilised PVC.

The results in Table 3-4 show that diphenyltelluride, diphenyltellurium diacetate, diphenyltellurium β-mercaptopropionate and diphenyltellurium maleate reacted with hydrogen chloride to produce diphenytellurium dichloride, which was identified by infra-red spectroscopy, m.p. and elemental analysis. The infra-red spectra, Table 3-2, show the tellurium-chlorine bond stretching frequencies at 268cm^{-1} (72).

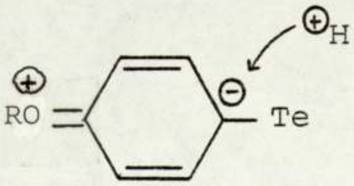
The reaction of these organotellurium compounds with hydrogen chloride gave two products, diphenyltellurium dichloride and a second product depending on the nature of the organotellurium compound. Diphenyltellurium diacetate gave a product which was identified by GLC (see Table 3-4) to be acetic acid. Diphenyltellurium maleate and diphenyltellurium β-mercaptopropionate gave maleic acid and β-mercaptopropionic acid respectively. The products were separated as the sodium salt and identified by infra-red spectroscopy.

From the above results it seems likely that the cleavage of both Te-O and Te-S bonds in these compounds took place when organotellurium compounds were treated in o-dichlorobenzene in the presence of hydrogen chloride.

Di-p-ethoxyphenyltelluride and di-p-ethoxyphenyltellurium β - mercaptopropionate react with hydrogen chloride by different pathways to give a black material; which is not soluble in o-dichlorobenzene or chloroform. It does not melt below 360°C and dissolved in H_2SO_4 to give a violet solution . Therefore, it is probably metallic tellurium. The reaction of these compounds with hydrogen chloride gave phenetole, tellurium and β-mercaptopropionic acid. The phenetole was identified by GLC (see Table 3-4) and β - mercaptopropionic acid was separated as the sodium salt. In this case, hydrogen chloride was able to cleave the Te-S, Te-O and Te-C bonds at the same time.



Cleavage of Te-C bond appears to be dependant on the nature of the organic groups attached to the tellurium atom. The cleavage occurs at the C-Te bond more readily when the phenyl group has substituent groups. This is due to the electron donating ability of -OEt to give higher electron density (more electro-negative) at the aromatic C-Te bond. Hence the C-Te bond becomes more polarized in the case of the substituted phenyl group than unsubstituted. This cleavage behaviour is also exhibited by tin compounds i.e. P-$MeOC_6H_4$-SnR_3 > Ph-SnR_3 (116). The suggested reaction mechanism involves a proton attack on the carbon atom of the C-Te bond e.g.



It is clear that the cleavage at C-Te bond gives tellurium powder, hence a black colour, which would lead to discolouration of the polymer. This cleavage is produced by hydrogen chloride which as a result, produces chlorine atoms which, in turn, may promote the dehydrochlorination reaction (as was discussed in chapter one). Thus, the most effective organotellurium compounds, as stabilisers, will be those in which Te-S or Te-O bond cleavage occurs; while cleavage at a C-Te bond would be expected to lead to reduced effectiveness as a stabiliser.

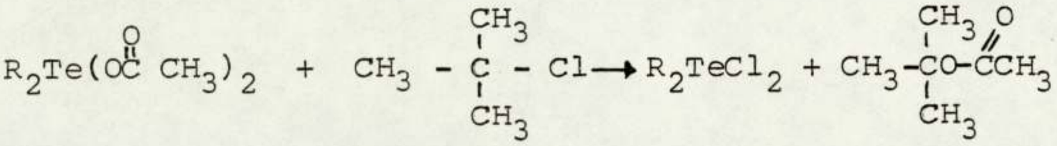
It is clear that organotellurium compounds may act as acceptors of hydrogen chloride according to the following reactions:

$$R_2TeY_2 + 2HCl \longrightarrow R_2TeCl_2 + 2HY$$

$$R_2Te + 2HCl \longrightarrow R_2TeCl_2 + H_2$$

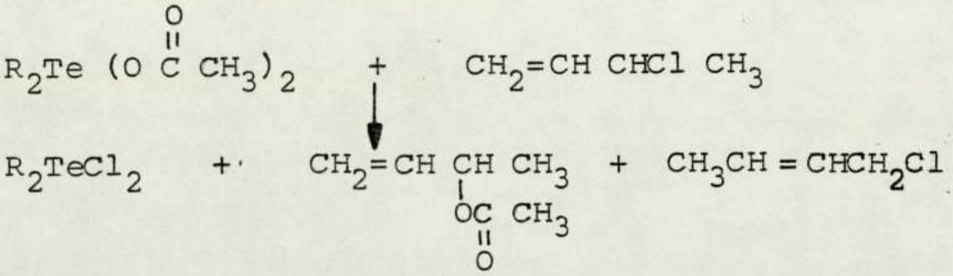
3-5-2-2 Reaction of organotellurium compounds with model compounds

Diphenyltelluride and diphenyltellurium diacetate were heated with excess of chlorohydrocarbon (t-butyl chloride and 3-chloro-1-butene) in sealed pyrex tubes at 180°C. The results presented in Table 3-4 show that the reaction between diphenyltellurium diacetate with t-butyl chloride gave diphenyltellurium dichloride and t-butyl acetate. t-Butyl acetate was identified from its boiling point (b.p. 96°C).



$$R_2Te(O\overset{O}{\overset{\|}{C}}CH_3)_2 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Cl \rightarrow R_2TeCl_2 + CH_3-\underset{CH_3}{\overset{CH_3}{C}}O-\overset{O}{\overset{\|}{C}}CH_3$$

The reaction of diphenyltellurium diacetate with 3-chlorobut-1-ene gave diphenyltellurium dichloride, 3-acetoxybut-1-ene and 1-chlorobut-2-ene. The latter two were identified by GLC (see Table 3-4). The reaction giving 1-chlorobut-2-ene could be explained by allylic rearrangement as follows:-



$$R_2Te(O\overset{O}{\overset{\|}{C}}CH_3)_2 + CH_2{=}CH\,CHCl\,CH_3 \rightarrow R_2TeCl_2 + CH_2{=}CH\,\underset{O\overset{\|}{\underset{O}{C}}CH_3}{CH}\,CH_3 + CH_3CH{=}CHCH_2Cl$$

Poller(117) studied the reaction of 3-chlorobut-1-ene with organotin compounds and also found products formed via allylic rearrangement of both the products and of the reactant unsubstituted chlorobutene giving four components in the reaction mixture.

The products formed by replacement of the chlorine atoms of t-butyl chloride and 3-chlorobut-1-ene with carboxylate groups are thermally stable under the reaction condition. This is regarded as strong supporting evidence for the reaction of reactive chlorine atoms in poly(vinylchloride) suggested by Fry et al(37).

In the reaction of diphenyltelluride with t-butyl chloride or 3-chlorobut-1-ene for one hour and 75 minutes respectively, diphenyltellurium dichloride was obtained. McWhinnie et al(89) gave positive evidence for radical pathways in oxidative addition of alkylhalidesto diphenyltelluride and they showed that the products depended on the stability of the alkyl radicals; thus 1,4-dibromo-2-butene which generates an allylic radical gave entirely diphenyltellurium dibromide. Thus, since radicals obtained from t-butyl chloride and chlorobutene are relatively stable, the formation of diphenyltellurium dichloride may be understood.

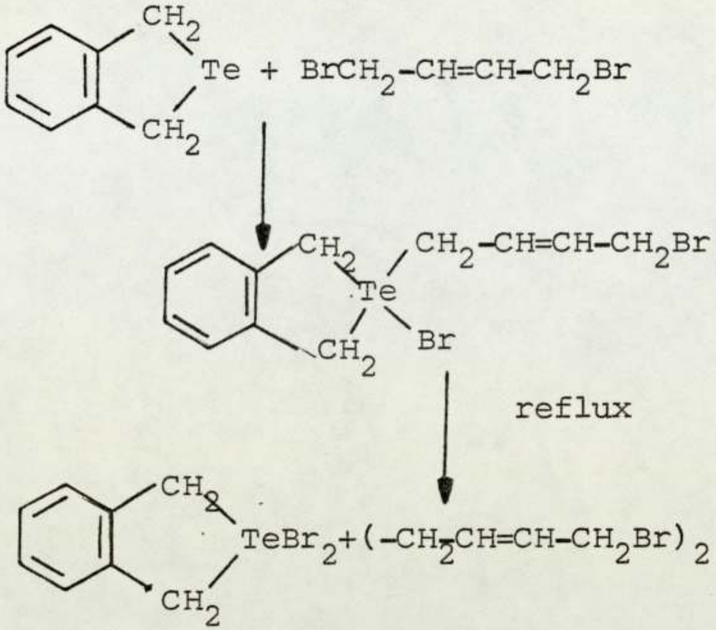
Petragnani(118) has studied the reaction of diphenyltelluride with 1,2-dibromoethane to obtain ethenes:

$$Ph_2Te \ + \ RCHBr\ CHBr\ R' \longrightarrow Ph_2TeBr_2 + RCH = CHR'$$

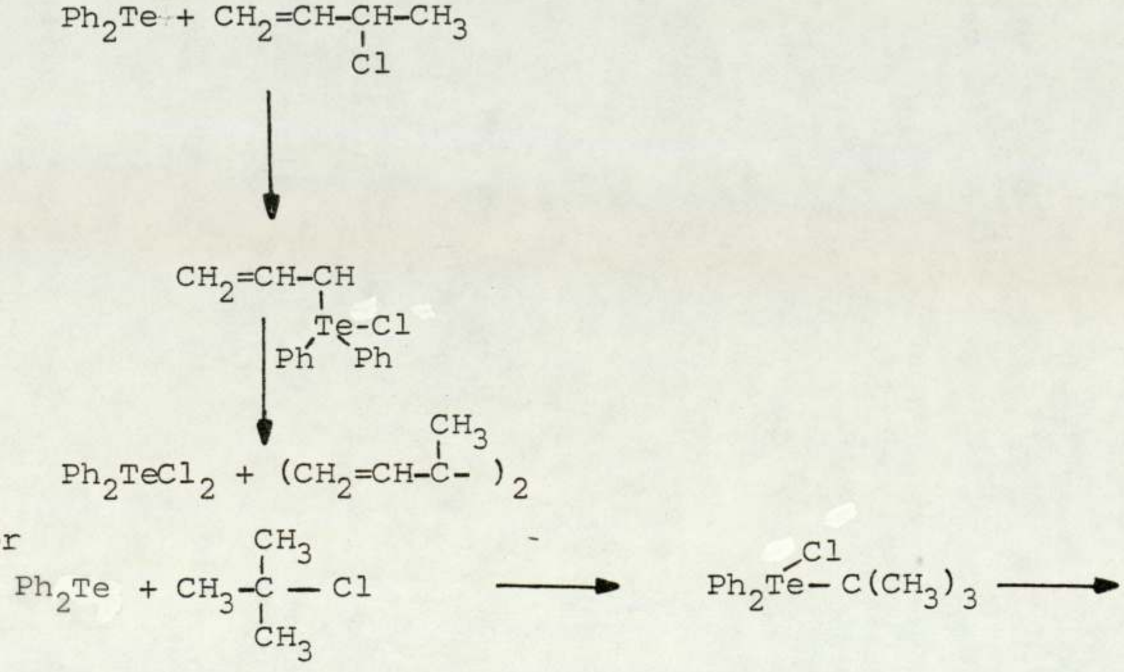
and he found that when a solution of diphenyltelluride in allylbromide was heated at 180°C in a sealed tube for three hours it gave rise to diphenyltellurium dibromide and probably dialkyl:

$$Ph_2Te \ + \ 2CH_2 = CHCH_2Br \longrightarrow \begin{array}{c} Ph_2TeBr_2 \\ + \\ (CH_2 = CH - CH_2)_2 \end{array}$$

It was observed(165) that, the reaction of benzo-1-telluracyclopentane with 1,4-dibromo-2-butene gave a tellurium salt at room temperature and upon refluxing, diaryltellurium dibromide and possibly butadiene or $(\text{-}CH_2CH{=}CHCH_2Br)_2$ were formed.



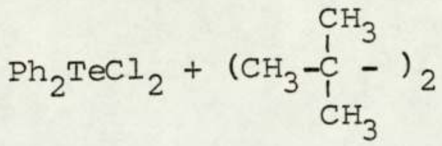
It seems likely, therefore, in the reaction of diphenyltelluride with 3-chlorobut-1-ene or t-butyl chloride, that telluronium species were initially formed and upon heating, diphenyltellurium dichloride and possibly [butadiene or $(CH_2\text{-}CH\text{-}\overset{CH_3}{C}H\text{-})_2$] or [2-methylpropene or $(CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-})_2$] were formed respectively.



$$Ph_2Te + CH_2{=}CH\text{-}\underset{Cl}{CH}\text{-}CH_3 \longrightarrow CH_2{=}CH\text{-}\underset{Ph\quad Ph}{\underset{|}{\overset{|}{CH}}\,Te\text{-}Cl} \longrightarrow Ph_2TeCl_2 + (CH_2{=}CH\text{-}\overset{CH_3}{C}\text{-}\ )_2$$

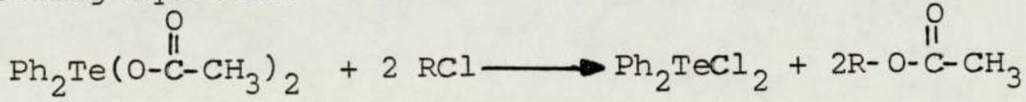
or

$$Ph_2Te + CH_3\text{-}\overset{CH_3}{\underset{CH_3}{C}} - Cl \longrightarrow Ph_2\overset{Cl}{Te}\text{-}C(CH_3)_3 \longrightarrow$$



$$Ph_2TeCl_2 + (CH_3\text{-}\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{C}}\text{ - })_2$$

From the above discussion, it can be concluded that diphenyltellurium diacetate has the ability to exchange carboxylate groups with chlorine atoms in the poly(vinylchloride) and thereby inhibit the initiation of the dehydrochlorination reaction. A mechanism is proposed for the stabilisation of poly(vinylchloride) which involves replacement of reactive chlorine atoms on the polymer chains by carboxylate groups to give structures with enhanced thermal stability by the following equation:



$$Ph_2Te(O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3)_2 + 2\ RCl \longrightarrow Ph_2TeCl_2 + 2R\text{-}O\text{-}\overset{\displaystyle O}{\overset{\|}{C}}\text{-}CH_3$$

3-5-2-3 Reaction of organotellurium compounds with peroxide

As was mentioned before (chapter one) the hydroperoxides are the key initiators for the process of degradation of polymers during processing, thermal oxidation and photo-oxidation. Therefore, as a part of this investigation it is necessary to study the reaction of organotellurium compounds with peroxides.

The reaction of diphenyltelluride with benzoyl peroxide gave diphenyltellurium dibenzoate. The infra-red spectrum of this compound shows, Table 3-2, a doubling of the $\nu_{as}[COO]$, $1645cm^{-1}$; $1630cm^{-1}$ and $\nu_s[COO]$ $1320cm^{-1}$; $1300cm^{-1}$ vibrations. McWhinnie(83) explained that the complex spectra arise from coupling vibrations of different carboxylate groups in the same molecule. Another possibility is that a slightly different environment for the two carboxylate groups is implied. Thus, it is conceivable that the "non-bonded" oxygen atom of one group is closer to the central tellurium atom than the corresponding oxygen atom of the other group.

The peaks at δ7.5 ppm and 7.95 ppm in the 'H n.m.r. spectrum, Table 3-2, of the compound due to the aromatic protons. The above data are identical to the data from the I.R. and n.m.r. spectroscopy which were obtained from the product of the reaction of diphenyltellurium dichloride with silver benzoate(81).

The reaction of diphenyltelluride with di(3-butoxycarbonyl-2-propenoyl) peroxide gave diphenyltellurium bis(monobutyl maleate). The I.R. and 'H N.m.r. data (Table 3-2) for diphenyltellurium bis(monobutyl maleate) are identical with thoses from the reaction of diphenyltellurium dichloride with silver 3-butoxycarbonyl-2-propenoate (section 4-3-2).

The reaction of di-p-ethoxyphenylditelluride with benzoyl peroxide gave a white solid. The infra-red analysis, Table 3-2, of this material from a KBr disc shows the tellurium-oxygen vibration at 710cm^{-1}, 680cm^{-1} and 555cm^{-1}. This data and elemental analysis, Table 3-1, suggest the following empirical formula $[(P\text{-}C_2H_5O\ C_6H_4TeO)_2O]$. This may be attributed to a rapid hydrolysis of initially formed tribenzoate in moist air leading to the formation of an "anhydride". The I.R. data are identical to the data that were obtained for the product of the reaction of p-ethoxytellurium trichloride and silver benzoate which formed the same anhydride(81,121).

The reaction of diphenyltelluride with cumene hydroperoxide gave diphenyltelluroxide and α,α- dimethylbenzyl alcohol. The infra-red spectrum of the former, Table 3-2, shows a broad band at 770-480cm^{-1} which indicates the presence of a tellurium-oxygen bond(122). The latter was identified by GLC (see Table 3-4).

The experiment was repeated with excess of cumene hydroperoxide, After the reaction was complete, the remaining cumene hydroperoxide was determined by the iodine liberation method and the reaction was found to be stoichiometric.

From the above described reactions it seems likely that organotellurium (I) and (II) compounds act as decomposers of peroxides to produce stable products such as "anhydride" and diphenyltellurium dibenzoate respectively. Moreover, it has been found that these compounds react with organic peroxides stoichiometrically.

The reaction of some organotellurium compounds with hydrogenchloride, chlorohydrocarbon and peroxide can be summarised as follows:
A - The organotellurium compounds have the ability to react with the hydrogen chloride (which is split from the poly(vinylchloride), upon heating).
B - Diphenyltellurium diacetate is capable of replacing the chlorine atoms of chlorohydrocarbon with carboxylate groups which are more thermally stable than the chlorine. Such labile chlorine groups may reasonably be assumed to lead to initiation of degradation of the poly(vinylchloride) during processing, and thus such an exchange might be expected to result in stabilisation.
C - Organotellurium (I,II) have the ability to react with organic peroxides to give organotellurium (IV). Such organotellurium compounds promote the decomposition of peroxides to form stable products rather than chain-initiating free radicals.

CHAPTER FOUR

SYNTHESIS OF NEW ORGANOTELLURIUM COMPOUNDS

4-1 Experimental

4-1-1 Diphenyltellurium Maleate

Diphenyltelluroxide(123) was prepared by treatment of diphenyltellurium dibromide with a 5% solution of sodium hydroxide at 50°C, and was recrystallised from water. Diphenyltelluroxide (0.01 mole) was allowed to react with an equimolar amount of maleic anhydride (0.01 mole) in dry chloroform from which ethanol had been removed. The reaction was carried out under dinitrogen with stirring for one hour at room temperature, followed by evaporation of the solvent. The crude product was recrystallised from chloroform and hexane. The pure diphenyltellurium maleate, a white solid, has a melting point of 115-117°C. The yield was 95% .

4-1-2 Diphenyltellurium β - mercaptopropionate

Diphenyltelluroxide (0.05 mole) was dissolved in anhydrous toluene ($50cm^3$) in a $250cm^3$ round bottomed flask and β-mercaptopropionic acid (0.05 mole) added. The mixture was stirred under reflux for 3 hours to complete the reaction. Water was removed by continuous azeotropic distillation collected in a Dean and Stark's trap. Toluene was removed by rotary evaporation. The product was purified by preparative thin layer chromatography and column chromatography, using toluene, to give pure diphenyltellurium β - mercaptopropionate which is a yellow viscous fluid. The yield of the product was 90%.

4-1-3 Di-p-ethoxyphenyltellurium β - mercaptopropionate

Di-p-ethoxyphenyltelluroxide(124) was prepared by boiling di-p-ethoxyphenyltellurium dichloride with 2N-aqueous sodium hydroxide. Di-p-ethoxyphenyltellurium β - mercaptopropionate was prepared in the same manner as [4-1-2] from di-p-ethoxyphenyltelluroxide (0.05 mole) and β - mercaptopropionic acid (0.05 mole). The crude material was recrystallised from benzene and hexane to give pure di-p-ethoxyphenyltellurium β - mercaptopropionate, a yellowish solid yield 70%, m.p. 85-87°C.

4-1-4 Telluracyclopentane bis(monobutyl maleate)

Silver 3-butoxycarbonyl-2-propenoate (0.02 mole), prepared by the reaction of silver nitrate with 3-butoxycarbonyl-2-propenoic acid in an ammonia solution, was added in small portions to a continuously stirred solution of telluracyclopentane-1,1-diiodide (125) (0.01 mole) in dry dioxane ($50cm^3$) at room temperature. The reaction was carried out under dinitrogen. After 5 hours of reflux with stirring, a yellow precipitate was formed. Filtration was followed by evaporation of dioxane. The crude material was purified by preparative thin layer chromatography and column chromatography, using chloroform, to give pure telluracyclopentane bis(monobutyl maleate), a yellow oil with a strong odour, yield 89%.

4-1-5 Diphenyltellurium bis(monobutyl maleate)

This compound was prepared in the same way as [4-1-4] from diphenyltellurium dichloride(87) (o.ol mole) and silver 3-butoxycarbonyl-2-propenoate(0.02 mole). Diphenyltellurium bis(monobutyl maleate), yield 85%, was a colourless oil.

4-1-6 Diaryltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone) (Aryl = Ph or EtOC$_6$H$_4$)

4-Ethoxythioglycollate-2-hydroxybenzophenone was prepared from the reaction of 2-hydroxy-4-oxyethanol benzophenone and thioglycollic acid(126).

4-Ethoxythioglycollate-2-hydroxybenzophenone (0.02 mole) together with diarytelluroxide (0.01 mole) anhydrous toluene (100cm^3) were placed in a 250cm^3 round bottomed flask fitted with a reflux condenser and a Dean and Stark's trap, permitting the water to be removed continuously whilst refluxing over an oil bath. After a period of approximately 3 hours, the calculated amount of water was eliminated. Toluene was stripped from the mixture by rotary evaporation and the product isolated as a viscous brown oil. The crude product was purified by preparative thin layer and column chromatography, using toluene. The product was collected as a viscous brown oil, yield 90%.

4-1-7 New methods for the preparation of Dicetyltelluride

This compound was prepared by the reaction of a mixture of cetylchloride (0.08 mole), tellurium powder (0.04 mole) and sodium or potassium iodide (0.16 mole) in N,N-dimethylformamide ($\simeq$ 30cm^3). The mixture was stirred and heated gently. Gentle refluxing was continued for 2 hours. After the reaction was complete, the solution was filtered. The filtrate was poured into distilled water (500cm^3) and extracted with diethylether. The combined diethylether extracts were dried over calcium chloride. The diethylether was evaporated to give a red-brown oil.

Aqueous sodium sulphide was added to the red-brown oil. The mixture was heated at 80°C for approximately one hour until the red-brown colour disappeared. The solution was poured into distilled water (500cm^3) and extracted with diethylether. The diethylether was washed several times with water. The combined diethylether extracts were dried over calcium chloride and concentrated to dryness on a rotary evaporator

The crude product was treated with activated copper powder in dry dioxane under dinitrogen for 6 hours. The hot solution was filtered and the filtrate was evaporated to dryness. The crude product was recrystallised from acetone by using charcoal to give a very pale pink colour of dicetyltelluride, m.p.42-43°C (lit.43-44°C)(67). yield 72%.

4-1-8 Dicetyltellurium dichloride

To a solution of dicetyltelluride (0.01 mole) in diethylether ($20cm^3$) thionyl chloride (0.03 mole) in diethylether ($15cm^3$) was added drop wise with stirring. The mixture was stirred for another 4 hours, in an ice bath, after which the diethylether was evaporated. The crude product was recrystallised from acetone to give dicetyltellurium dichloride.

Dicetyltellurium dichloride was treated with tetraethylammoniumbromide (to remove any trichloride impurity as $Et_4\overset{+}{N}\,\overset{-}{[(cetyl)\,TeCl_3Br]}$) in chloroform. The mixture was shaken at room temperature for 2 hours, after which, the solution was filtered and the chloroform was evaporated. The crude product was recrystallised from acetone to give dicetyltellurium dichloride, a white solid, yield 65%, m.p. 34°C.

4-1-9 Dicetytellurium diacetate

Two different procedures were carried out for the preparation of this compound.

1 - A solution of dicetyltelluride (o.ol mole) in dry benzene was added slowly to a stirred solution of freshly prepared lead tetraacetate (0.01 mole) in in the same solvent ($50cm^3$). The mixture was stirred at room temperature for 5 hours under dinitrogen. Filtration followed by evaporation of benzene gave the crude material, which was recrystallised from diethylether to give dicetyltellurium diacetate, a white solid, m.p. 56-57°C, yield 90%.

2 - Silver acetate (0.02 mole) was added in small portions to a stirred solution of dicetyltellurium dichloride (0.01 mole) in dry dioxane ($50cm^3$) at room temperature. The mixture was refluxed for 4 hours. Filtration of silver chloride was followed by evaporation of dioxane from the filtrate. The crude material was recrystallised from diethylether to give dicetyltellurium diacetate, m.p. 56-57°C, yield 75%.

4-1-10 Dicetyltellurium maleate

Freshly prepared silver maleate(103) (0.01 mole) was added in small portions to a stirred solution of dicetyltellurium dichloride (0.01 mole) in dry chloroform at room temperature. The mixture was shaken for 24 hours. Filtration followed by evaporation of chloroform from the filtrate and recrystallisation of the crude product from petrolium-ether gave dicetyltellurium maleate, a white solid, m.p. 93-94°C with decomposition at 150°C, yield 76%.

4-1-11 Attempt to prepare Octyltellurium derivates

A - Dioctyltelluride

Two different procedures were carried out in order to prepare this compound.

1 - This experiment followed the procedure reported by McWhinnie et al(72) for the preparation of diaryl tellurides. By adding 1-bromooctane (48.25g) to magnesium (6.1g) in an ethereal solution and subsequently of dry benzene ($100cm^3$) was added. The temperature of the solution was lowered to 0°C and vigorous stirring was maintained. Tellurium tetrachloride (13.5g) in dry benzene ($200cm^3$) was added slowly to the stirred solution and then the reaction mixture was refluxed for 2 hours. The cooled solution was added to a saturated ammonium chloride solution ($400cm^3$). Directly

the solution turned black and gave tellurium metal.

2 - A solution of 1-bromooctane (0.01 mole) in dry diethylether (500cm^3) was added gradually with vigorous stirring in an inert atmosphere (under dinitrogen) to a suspension prepared from very small pieces of lithium (0.02 mole) in diethylether (200cm^3). After all the halogen derivative had been added, the mixture was refluxed with stirring for 1 hour. It was then cooled and excess tellurium powder (0.01 mole) was added to it in small portions with cooling and vigorous stirring, the solution changed from colourless to a yellowish colour. The mixture was refluxed with stirring for 3 hours. After that, 1-bromooctane (0.01 mole) was added slowly and refluxed for 5 hours. The lithium halide was separated from the mixture by filtration, during this stage the solution started to turn black and gave tellurium metal.

B - Dioctyltellurium dihalides

1 - Dioctyltellurium dichloride. The experiment, to prepare dioctyltelluride by using an organolithium compound (as above) was repeated. The lithium halide was separated from the mixture by filtration under dinitrogen. The thionyl chloride was added slowly to the solution. The solution was stirred for 3 hours in an ice bath, after which, the diethylether was evaporated by passing dinitrogen. Then

petroleum-ether was added to the crude product to give a white precipitate. The white precipitate turned black during isolation. giving tellurium metal.

2 - Dioctyltellurium diiodide. A mixture of tellurium powder (0.02 mole), 1-bromooctane (0.04 mole) and sodium or potassium iodide (0.08 mole) in 2-ethoxyethanol was heated gently and refluxed for 2 hours. The solution changed from colourless to a red-brown colour. The hot solution was filtered. The solution was poured into water (200cm^3) and extracted with diethylether. During this stage some of the compound started to give a black precipitate. The diethylether was dried over calcium chloride and evaporated to give a red-brown oil. Or after cooling, the reaction mixture was filtered and the solvent evaporated to give a red-brown oil. In both cases. petroleum-ether was added to the crude product (red-brown oil) to give a red-brown precipitate. After filtration the precipitate started to turn black, giving tellurium metal.

The same reaction was carried out by using 1-bromohexane instead of 1-bromooctane and gave a similar result.

C - Octyltellurium trihalide

A mixture of tellurium powder (0.02 mole), 1-bromooctane

(0.04 mole) and tetraethylammonium bromide (0.08 mole) in 2-methoxyethanol ($50cm^3$) was refluxed for 24 hours. The solution changed from colourless to a red-brown colour. The hot solution was filtered and the precipitate collected. The solid was recrystallised from 2-methoxyethanol to give a greenish solid which, on drying, melted with decomposition at 270°C.

A solution of bromine in chloroform was slowly added drop wise to a solution of the above solid in chloroform and was stirred for 2 hours resulting in a yellow-orange precipitate. The solution was filtered and the precipitate was dried which melted with decomposition at 320°C.

The same reaction was carried out by using 1-bromohexane instead of 1-bromooctane and gave an identical product which was identified by the melting point and elemental analysis.

4-1-12 Bis(diethyldithiocarbamato)tellurium (II)

Tetraethylthiuram disulphide (0.01 mole) was added to tellurium powder (0.01 mole) in xylene ($30cm^3$). The mixture was heated gently with stirring and refluxed for about 20 minutes. The hot solution was filtered. The solution was then cooled to give red crystals of bis(diethyldithiocarbamato) tellurium (II) which were dried, m.p. 162°C (lit 164°C)(135). The yield was 99%. This compound can also be prepared by the thermal decomposition of Te(dtc)$_4$ (See section 5B-1-1).

4-2 Results

4-2-1 Analysis

Elemental analyses of organotellurium compounds are listed in Table 4-1.

4-2-2 Molecular weight measurements

The molecular weights of new organotellurium compounds were determined by freezing point depression in solvents, such as nitrobenzene and benzene and the results are tabulated in Table 4-2.

4-2-3 Infra-red spectra

The infra-red spectra, as KBr discs,CsI discs, and Nujol mulls between two polyethylene plates or sheets, in the range of 4000cm^{-1} - 200cm^{-1} are shown in Table 4-7 and in Figs 4.1 to 4.4 .

4-2-4 'H NMR spectra

The 'H n.m.r. spectra of organotellurium compounds were measured in a suitable solvent and are presented in Table 4-8 and shown in Figs 4.5 to 4.7 .

4-2-5 Mass spectra

The mass spectra of diphenyltellurium maleate, diphenyltellurium β-mercaptopropionate, telluracyclopentane bis-(monobutyl maleate) and di-p-ethoxyphenyltellurium β-mercaptopropionate are tabulated in Tables 4-3, 4-4, 4-5 and 4-6 respectively. These tables contain only the important ions and ions with high relative abundance.

Table 4-1. - Analytical data for new organotellurium compounds.

Compound	Found			Calculated		
	%C	%H	%X	%C	%H	%X
Diphenyltellurium maleate	48.0	3.20	-	48.6	3.03	-
Diphenyltellurium β -mercaptopropionate	46.5	3.80	8.40^{+}	46.7	3.63	8.31^{+}
Di-p-ethoxyphenyltellurium β -mercaptopropionate	47.5	4.70	7.00^{+}	48.2	4.65	6.76^{+}
Telluracyclopentane bis(monobutyl maleate)	44.9	6.10	-	45.7	5.80	-
Diphenyltellurium bis(monobutyl maleate)	52.5	5.10	-	53.9	5.13	-
Diphenyltellurium di(4-ethoxythioglycollate-2-hydroxy-benzophenone)	59.3	4.10	6.80^{+}	58.4	4.24	6.78^{+}
Dicetyltelluride	64.9	11.5	21.0^{*}	66.5	11.4	22.0^{*}

Table 4-1 Cont'd.

Compound	Found			Calculated		
	%C	%H	%X	%C	%H	%X
Di-p-ethoxyphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)	57.9	4.90	5.70^{+}	58.2	4.65	6.20^{+}
Dicetyltellurium dichloride	61.0	11.2	10.2^{Δ} 18.5^{*}	59.4	10.2	10.8^{Δ} 19.3^{*}
Dicetyltellurium diacetate $(C_{16}H_{33})_2Te + Pb\ (O\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3)_4$	61.3	10.9	-	62.2	10.4	-
Dicetyltellurium diacetate $(C_{16}H_{33})_2TeCl_2 + 2AgO\text{-}\underset{\overset{\|}{O}}{C}\text{-}CH_3$	61.1	10.6	-	62.2	10.4	-
Dicetyltellurium maleate	61.6	10.1	-	62.5	9.84	-
Tetraethylammonium tribromotellurate (II) 1-bromohexane + Te $\xrightarrow{Et_4N\ Br}$ 1-bromooctane + Te $\xrightarrow{\prime\prime}$	20.0 20.2	4.20 4.40	2.90° 2.80°	19.3	4.04	2.81°

Table 4-1. Cont'd.

Compound	Found %C	Found %H	Found %X	Calculated %C	Calculated %H	Calculated %X
Tetraethylammonium pentabromotellurate (IV)						
reaction of 1-bromohexane	14.8	3.00	2.30^{o}	14.6	3.00	2.13^{o}
reaction of 1-bromooctane	15.0	3.10	2.00^{o}			
Bis(diethyldithiocarbamato)tellurium (II)	28.5	4.80	6.3^{o} 29.2^{+}	28.4	4.72	6.61^{o} 30.4^{+}
From heating Tetrakis(diethyldithiocarbamato)tellurium (IV)	28.8	5.00	6.5^{o} 29.0			
Tetrakis(diethyldithiocarbamato)tellurium (IV)	33.3	5.8	7.70^{o} 34.4^{+}	33.3	5.56	7.78^{o} 35.6^{+}
Tetraethylthiuramdisulphide from heating Tetrakis(diethyldithiocarbamato)tellurium (IV)	40.4	6.80	9.20^{o} 43.2^{+}	46.5	6.75	9.45^{o} 43.2^{+}

Δ - Chlorine. o - Nitrogen.

+ - Sulphur. ✱ - Tellurium.

Table 4-2. Molecular weight of new organotellurium compounds.

Compound	M (monomers)	M (dimer)	M (obs)	Exp.Error
Diphenyltellurium maleate	395	790	810^{+}	+20
Diphenyltellurium β - mercaptopropionate	385	770	800^{*}	+30
Di-p-ethoxyphenyltellurium β - mercaptopropionate	473	946	914^{*}	-32
Dicetyltelluride	580	-	560^{*}	-20
Dicetyltellurium maleate	691	1382	950^{*}	
Diphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)	943	-	920^{+}	-23

* - Benzene

\+ - Nitrobenzene

TABLE 4-3.

Mass spectral data for diphenyltellurium maleate relative to ^{130}Te, ^{16}O, ^{12}C, ^{1}H.

Species	m/e	R.I. (%)
$C_{12}H_{10}\overset{+}{T}e_2$	414	7
$C_{15}H_{12}O_3\overset{+}{T}e$	370	50
$C_{16}H_{12}O_2\overset{+}{T}e$	366	35
$C_{15}H_{12}O_2\overset{+}{T}e$	354	20
$C_{14}H_{12}O\ \overset{+}{T}e$	326	15
$C_{12}H_{10}O\ \overset{+}{T}e$	298	25
$C_{12}H_{10}\overset{+}{T}e$	284	100
$C_{12}H_{1\overset{+}{0}}$	154	100
$C_6H_5\overset{+}{T}e$	207	100
$C_6H_5^+$	77	100
$\overset{+}{T}e = C = O$	158	100
$C_4H_3O_4^+$	115	35
$C_2H_3^+$	27	50
CO_2^+	44	100

TABLE 4-4.

Mass spectral data for diphenyltellurium β-mercaptopropionate relative to ^{130}Te, ^{32}S, ^{16}O, ^{12}C, ^{1}H.(15eV)

Species	m/e	R.I.(%)
$C_{30}H_{28}O_4S_2Te^+$	776	10
$C_{12}H_{10}Te_2^+$	414	40
$C_{15}H_{14}O_2Te^+$	356	25
$C_{12}H_{10}Te^+$	284	100
$C_6H_5Te^+$	207	100
$C_6H_5^+$	77	100
$C_3H_5O_2S^+$	105	50
$\overset{+}{Te} = C = O$	158	100
CO_2^+	44	100

TABLE 4-5.

Mass spectral data for telluracyclopentane bis(monobutyl maleate) relative to ^{130}Te, ^{16}O, ^{12}C, ^{1}H.

Species	m/e	R.I. (%)
$C_{12}H_{18}O_4Te^+$	357	35
$C_8H_{10}O_3Te^+$	284	100
$C_7H_{10}O_2Te^+$	256	10
$C_4H_8O\ Te^+$	202	100
$C_4H_8Te^+$	186	100
$C_4H_7^+$	55	100
$\overset{+}{Te} = C = O$	158	100
$C_8H_{11}O_4^+$	171	100
$C_4H_9O^+$	73	100
$\overset{+}{C}O$	28	100

TABLE 4-6.

Mass spectral data for di-p-ethoxyphenyltellurium β- mercaptopropionate relative to $^{130}Te, ^{32}S, ^{16}O, ^{12}C, ^{1}H$.

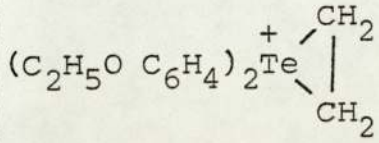
Species	m/e	R.I. (%)
 $(C_2H_5O\ C_6H_4)_2\overset{+}{Te}(CH_2)_2$	400	18
$(C_2H_5O\ C_6H_4)_2\overset{+}{Te}$	372	100
$C_2H_5O\ C_6H_4\overset{+}{Te}C_6H_5$	328	50
$C_2H_5O\ C_6H_4\overset{+}{Te}$	251	100
$(C_2H_5O\ C_6H_4-C_6H_4O\ C_2H_5)^+$	242	100
$(C_2H_5O\ C_6H_4-C_6H_4\ OH)^+$	214	100
$HOC_6H_4\overset{+}{Te}$	**223**	100
$(HO\ C_6H_4-C_6H_4OH)^+$	186	100
$(C_6H_5OH)^+$	93	100
$(C_6H_5OC_2H_5)^+$	121	100
$(C_6H_5)^+$	77	100
$C_3H_5O^+S$	105	100
$\overset{+}{Te} = C = O$	158	100

Table 4-7. Infra-red data of some new organotellurium compounds.

Compound	[Cm^{-1}]	Assignment [ν]
Diphenyltellurium maleate	1665 1625 (s)	as[COO]
	1315 1235 (s)	s[COO]
	1720 (s) 1175 (s)	as s bridge carboxylate
Diphenyltellurium β-mercaptopropionate	1650 (s)	as[COO]
	1255 (s)	s[COO]
	1725 (s) 1190 (s)	as s bridge carboxylate
	265 (s)	[Te-S]
Di-p-ethoxyphenyltellurium β-mercaptopropionate	1645 (s)	as[COO]
	1240 (s)	s[COO]
	1720 (m) 1170 (s)	as s bridge carboxylate
	220 (w)	[Te-S]

Table 4-7. Cont'd.

Compound	[Cm^{-1}]		Assignment [ν]
Telluracyclopentane bis(monobutyl maleate)	1670 1620	(s)	as[COO]
	1210 1170	(s)	s[COO]
	1730	(s)	[C = O] ester
	540	(w)	[Te-C]
Diphenyltellurium bis(monobutyl maleate)	1660 1615	(s)	as[COO]
	1215 1170	(s)	s[COO]
	1730	(s)	[C = O] ester
Diphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)	3350	broad	[OH]
	1740	(s)	[C = O] ester
	265	(m)	[Te-S]

Table 4-7. Cont'd.

Compound	$[\mathrm{Cm}^{-1}]$	Assignment [ν]
Di-p-ethoxyphenyltellurium di(4-ethoxythioglycollate-2-hydroxy-benzophenone	3350 broad 1740 (s) 225 (s)	[OH] [C = O] ester [Te-S]
Dicetyltelluride	2960 (s) 1470 (s) 490 (¼-multiplier with 5-expansion)	[C-H] stretching [C-H] deformation [Te-C]
Dicetyltellurium dichloride	490 (¼-multiplier with 5-expansion) 255 (m)	[Te-C] [Te-Cl]
Dicetyltellurium diacetate	1640 (s) 1290 (s)	as[COO] s [COO]

Table 4-7. Cont'd.

Compound	$[Cm^{-1}]$	Assignment $[\nu]$
Dicetyltellurium maleate	1645 1610 (s)	as[COO]
	1315 1250 (s)	s[COO]
	1670 (m) 1150. (m)	as s bridge carboxylate
Telluriumdioxide	650 broad	[Te-O]
Bis(diethyldithiocarbamato) tellurium (II)	225 (w)	[Te-S]

s - strong
m - medium
w - weak

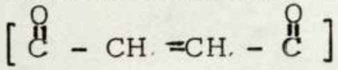
Table 4-8. 'H NMR data of some new organotellurium compounds.

Compound	Solvent	Chemical shifts δ ppm VS.TMS		Assignment
Diphenyltellurium maleate	$CDCl_3$	7.2 - 7.9	(m)	Aromatic protons
		5.96- 6.2	(m)	Alkene protons $[\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}]$
Diphenyltellurium β - mercaptopropionate	$CDCl_3$	2.7	(q)	methylene protons $[\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S]$
		7.2 - 7.9	(m)	Aromatic protons
Di-p-ethoxyphenyltellurium β -mercaptopropionate	$CDCl_3$	1.39	(t)	Methyl protons
		4.00	(q)	Methylene protons
		2.7	(q)	Methylene protons $[\overset{O}{\overset{\|}{C}}-CH_2-CH_2-S]$
		6.6 - 7.8	(m)	Aromatic protons
Telluracyclopentane bis(monobutyl maleate)	DMSO	0.9	(t)	Aliphatic protons $[O-CH_2-CH_2-CH_2-CH_3]$
		1.45	(m)	
		3.55	(m)	
		4.1	(t)	
		2.4	(s)	C_8H_4Te protons
		3.15	(s)	
		6.01- 6.12	(d)	Alkene protons $[-\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}-]$
		6.31- 6.42	(d)	

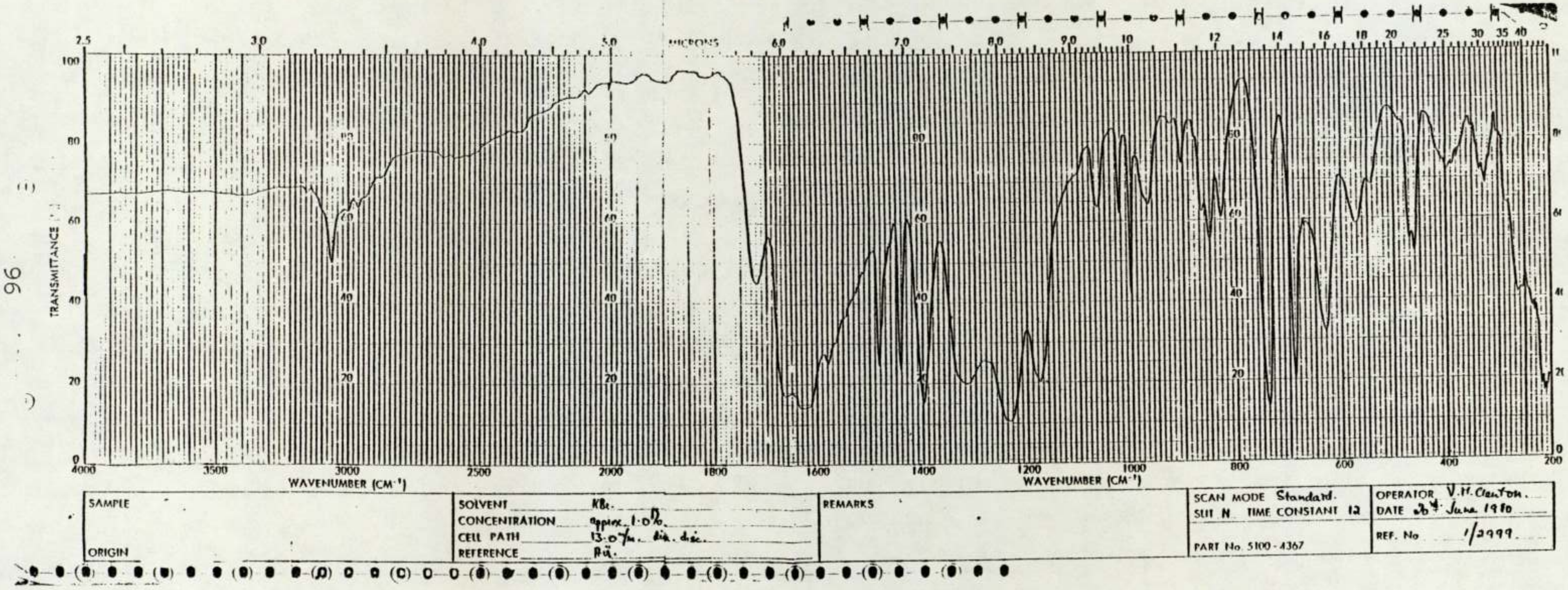
Table 4-8. Cont'd.

Compound	Solvent	Chemical shifts σ ppm VS.TMS		Assignment
Diphenyltellurium bis(monobutyl maleate)	$CDCl_3$	0.9	(t)	Aliphatic protons $[O - CH_2 - CH_2 - CH_2 - CH_3]$
		1.5	(m)	
		3.95	(t)	
		3.55	(m)	
		5.8 - 6.0	(d)	Alkene protons $[\overset{O}{C} - CH = CH - \overset{O}{C}]$
		6.1 - 6.3	(d)	
		7.3 - 7.8	(m)	Aromatic protons
Diphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)	$CDCl_3$	6.2 - 7.7	(m)	Aromatic protons
		4.15	(s)	Methylene protons $[O - CH_2 - CH_2 - O]$
		4.4	(s)	
		2.25	(s)	Methylene protons $[S-CH_2-\overset{O}{\overset{\|}{C}}]$
Di-p-ethoxyphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)	$CDCl_3$	1.3	(t)	Methyl protons
		3.7 - 4.1	(q)	Methylene protons
		6.3 - 7.8	(m)	Aromatic protons
		4.2	(s)	Methylene protons $[O - CH_2-CH_2-O]$
		4.4	(s)	
		2.3	(s)	Methylene protons $[-S-CH_2-\overset{O}{\overset{\|}{C}}]$

Table 4-8. Cont'd.

Compound	Solvent	Chemical shifts ppm VS.TMS		Assignments
Dicetyltelluride	$CDCl_3$	0.9 - 1.6	(m)	Aliphatic protons
Dicetyltellurium dichloride	$CDCl_3$	0.9 - 1.6	(m)	Aliphatic protons
Dicetyltellurium diacetate	$CDCl_3$	0.9 - 1.6 2.1	(m) (s)	Aliphatic protons Acetate protons
Dicetyltellurium maleate	$CDCl_3$	0.9 - 1.6 6.25	(m) (s)	Aliphatic protons Alkene protons  $[\overset{O}{\overset{\|}{C}} - CH = CH - \overset{O}{\overset{\|}{C}}]$

s - singlet
d - doublet
t - triplet
q - quartet
m - multiplet



SAMPLE

ORIGIN

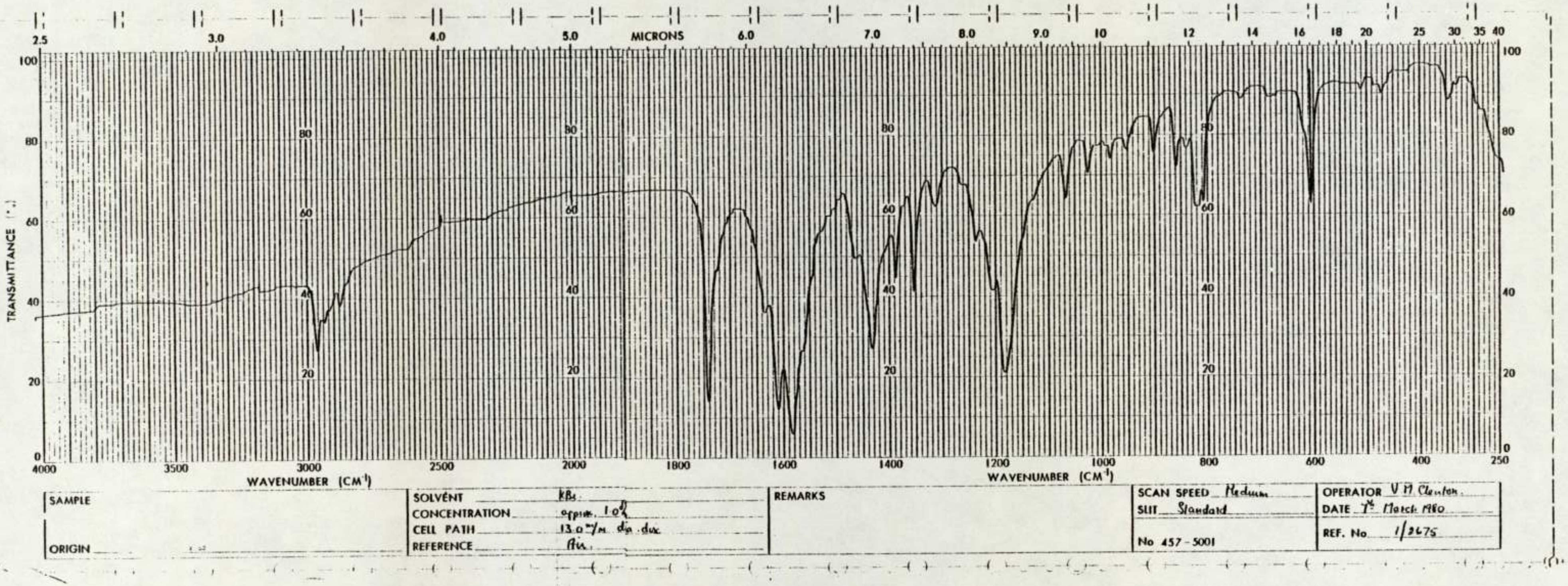
SOLVENT KBr.
CONCENTRATION approx. 1·0%.
CELL PATH 13·0 m/m. dia. disc.
REFERENCE Air.

REMARKS

SCAN MODE Standard.
SLIT N TIME CONSTANT 12
PART No. 5100 - 4367

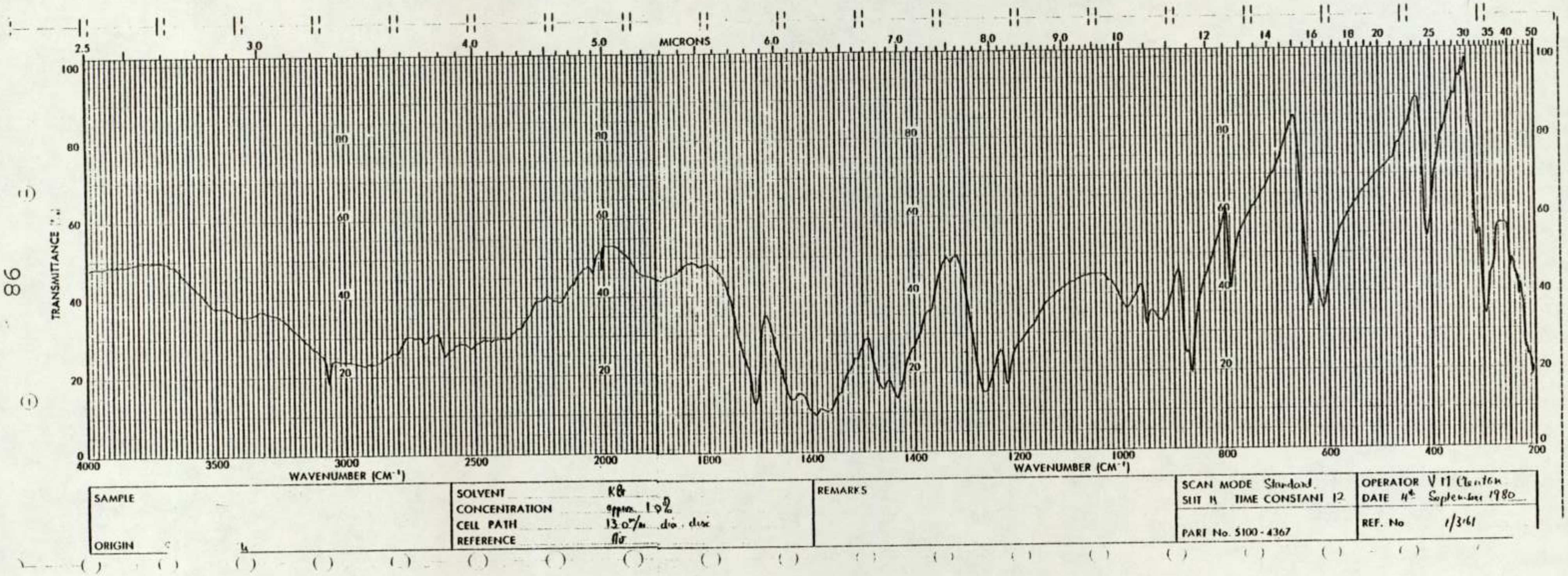
OPERATOR V.H. Clenton.
DATE 26th June 1980
REF. No 1/2999.

Fig 4.1(a) Infra-red spectrum of diphenyltellurium maleate



SAMPLE
ORIGIN
SOLVENT KBr.
CONCENTRATION approx. 1.0%
CELL PATH 13.0 m/m dia. disc
REFERENCE Air.
REMARKS
SCAN SPEED Medium
SLIT Standard
No 457 - 5001
OPERATOR V H Clenton.
DATE 7th March 1980
REF. No 1/2675

Fig 4.1(b) Infra-red spectrum of silver 3-butoxycarbonyl-2-propenoate



SAMPLE

ORIGIN

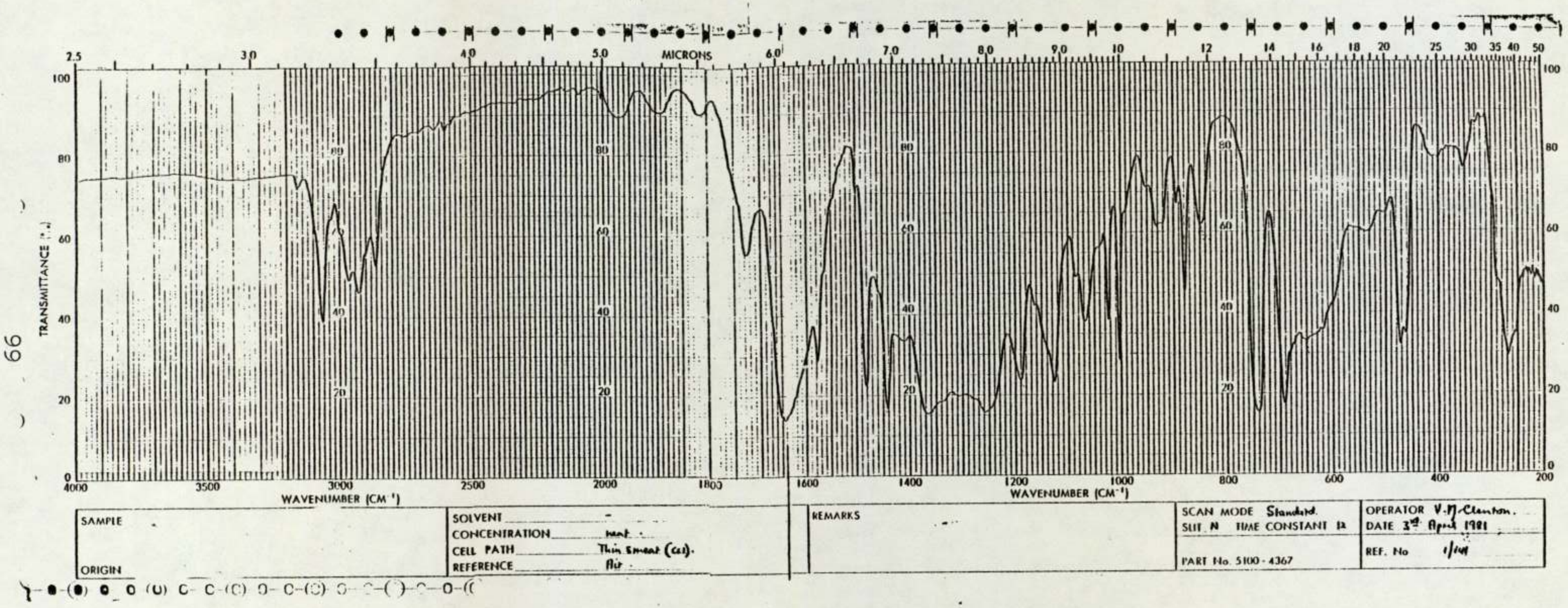
SOLVENT KBr
CONCENTRATION approx 1%
CELL PATH 13.0 m/m dia. disc
REFERENCE Air

REMARKS

SCAN MODE Standard.
SLIT N TIME CONSTANT 12
PART No. S100-4367

OPERATOR V H Clenton
DATE 4th September 1980
REF. No 1/3161

Fig 4.1(c) Infra-red spectrum of maleic acid



SAMPLE

ORIGIN

SOLVENT -

CONCENTRATION neat

CELL PATH Thin smear (csi).

REFERENCE Air

REMARKS

SCAN MODE Standard.

SLIT N TIME CONSTANT 12

PART No. 5100-4367

OPERATOR V.M. Clenton.

DATE 3rd April 1981

REF. No 1/141

Fig 4.2(a) Infra-red spectrum of diphenyltellurium β -mercaptopropionate

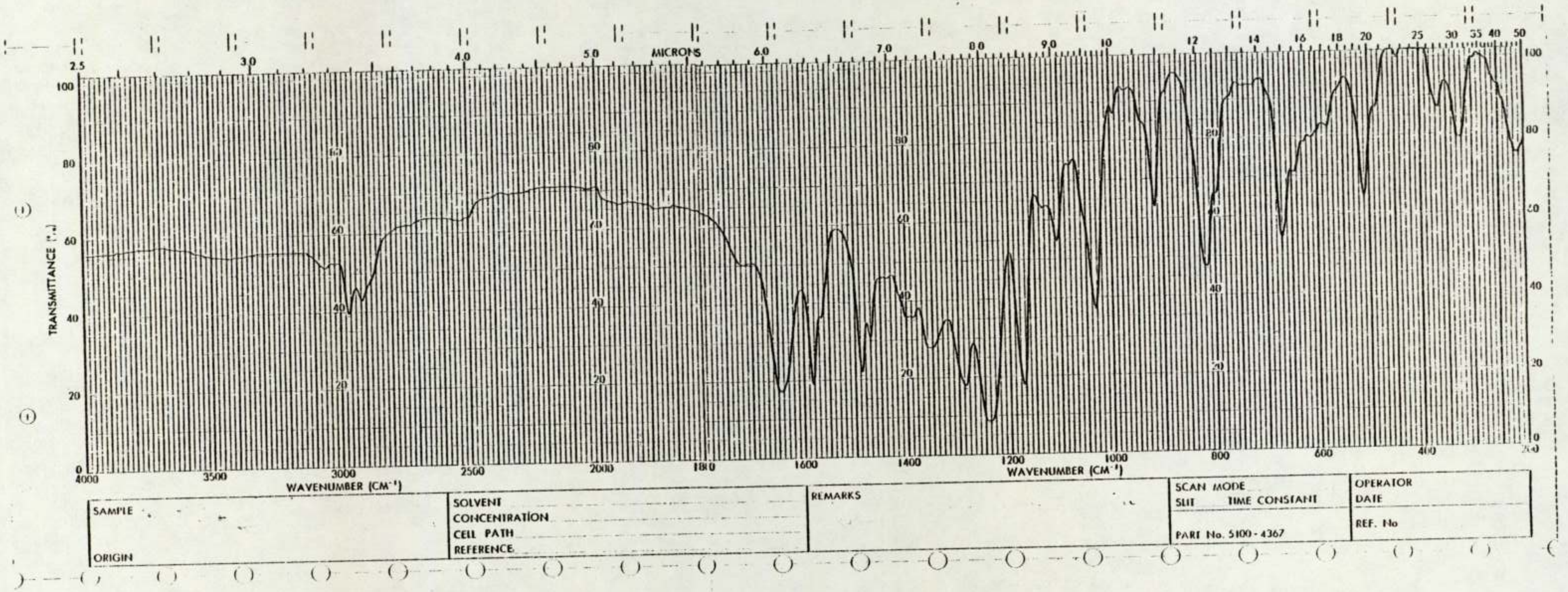


Fig 4.2(b) Infra-red spectrum of di-p-ethoxyphenyltellurium β -mercaptopropionate

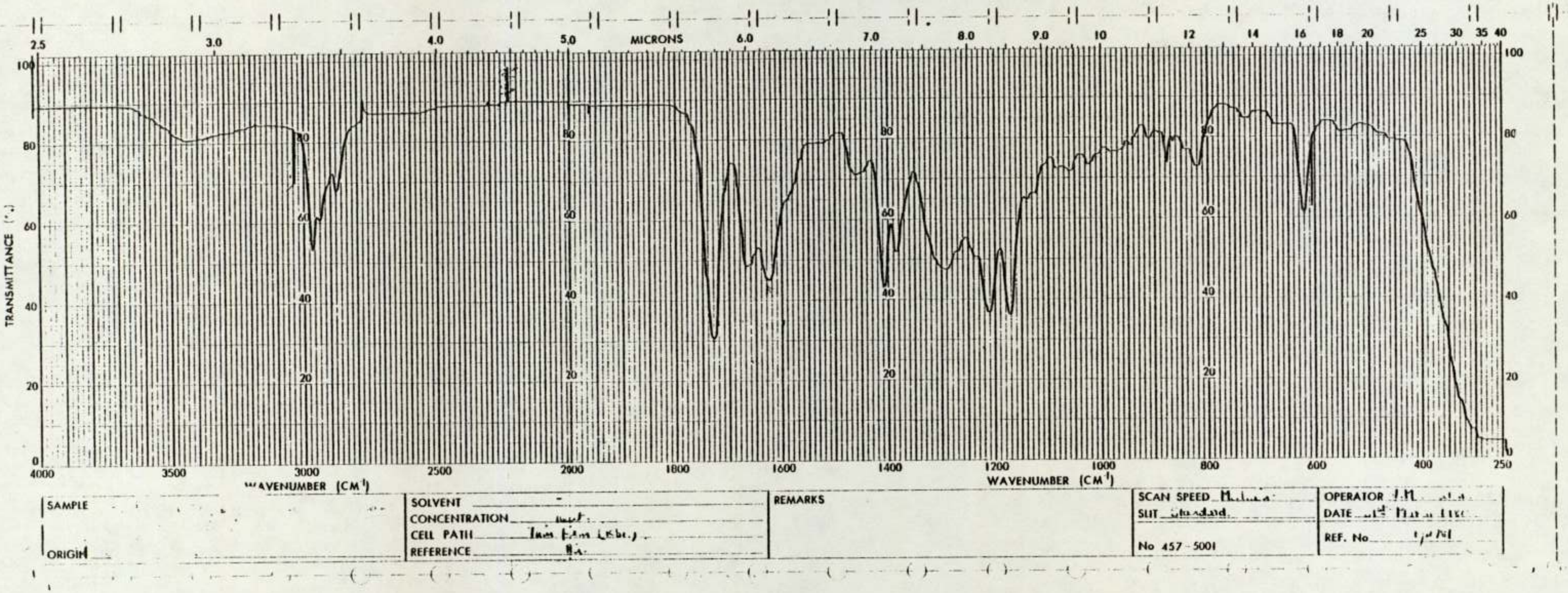


Fig 4.3(a) Infra-red spectrum of Telluracyclopentane bis(monobutyl maleate)

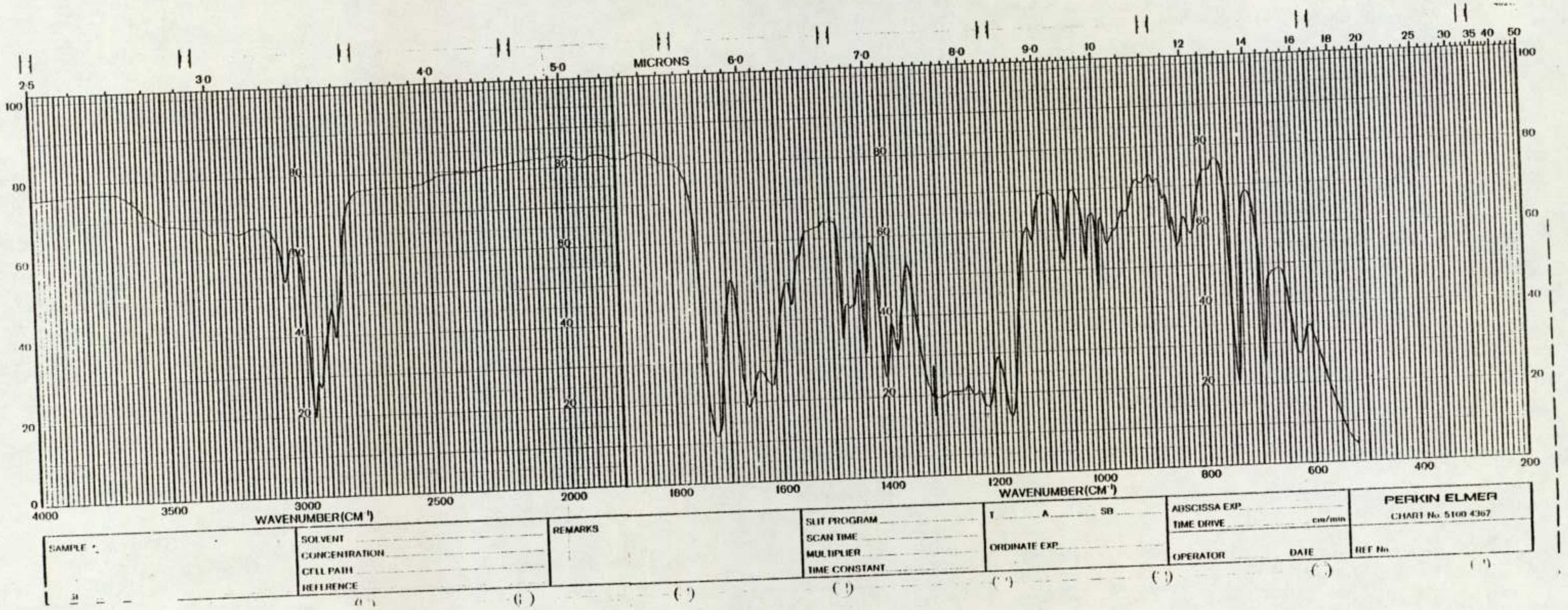
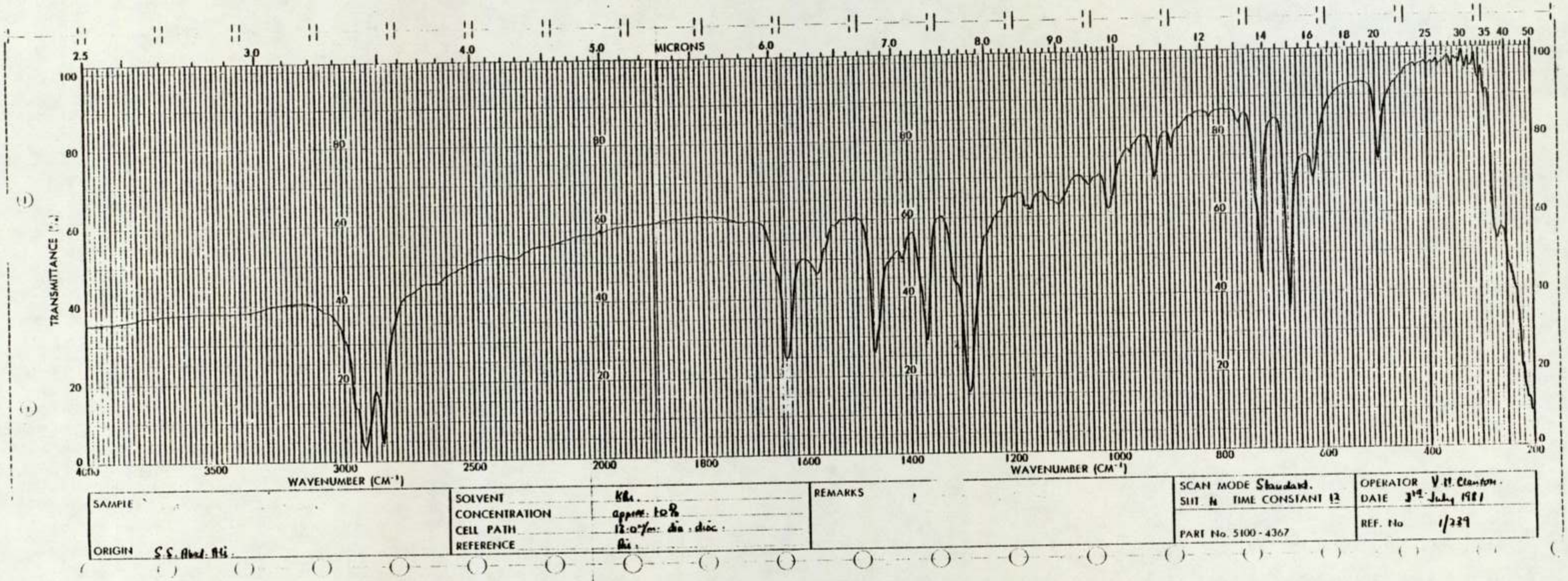


Fig 4.3(b) Infra-red spectrum of Diphenyltellurium bis(monobutyl maleate)



SAMPLE

ORIGIN S.S. Abd. Ali.

SOLVENT KBr.

CONCENTRATION approx. 1.0%

CELL PATH 13.0 m/m. dia. disc.

REFERENCE Air.

REMARKS

SCAN MODE Standard.

SLIT N TIME CONSTANT 13

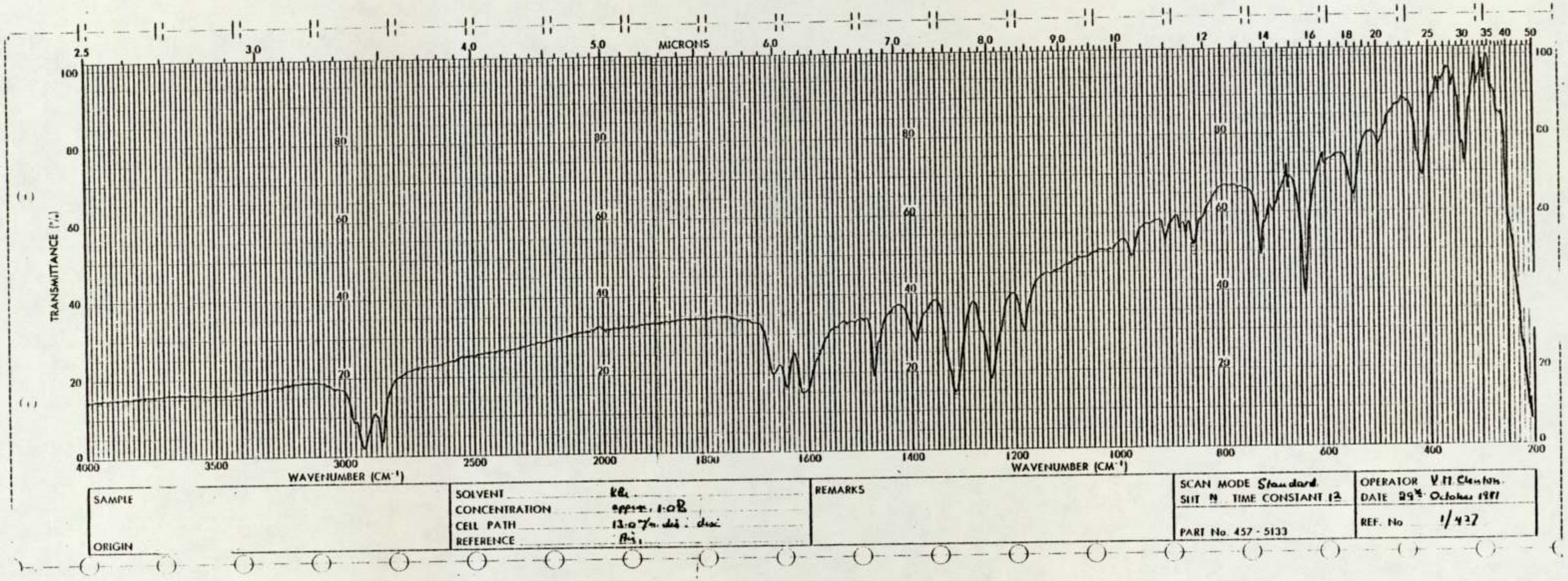
PART No. 5100 - 4367

OPERATOR V.H. Clanton.

DATE 3rd July 1981

REF. No 1/239

Fig 4.4(a) Infra-red spectrum of Dicetyltellurium diacetate



SAMPLE

ORIGIN

SOLVENT KBr.
CONCENTRATION approx. 1.0%
CELL PATH 13.0mm dia. disc
REFERENCE Air.

REMARKS

SCAN MODE Standard
SLIT N TIME CONSTANT 12
PART No. 457 - 5133

OPERATOR V.M. Clinton
DATE 29th October 1981
REF. No 1/437

Fig 4.4(b) Infra-red spectrum of Dicetyltellurium maleate

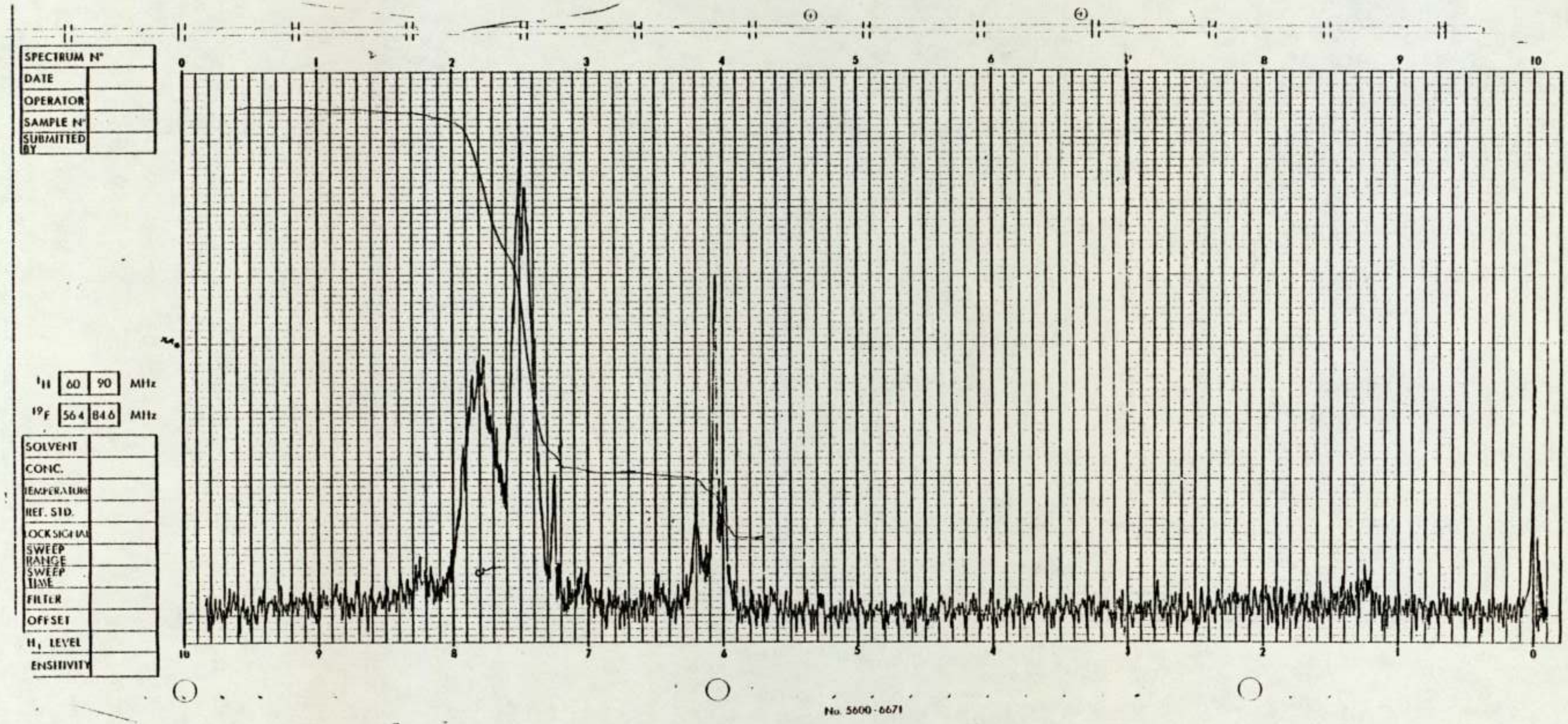


Fig 4.5 ^{1}H NMR spectrum of Diphenyltellurium maleate

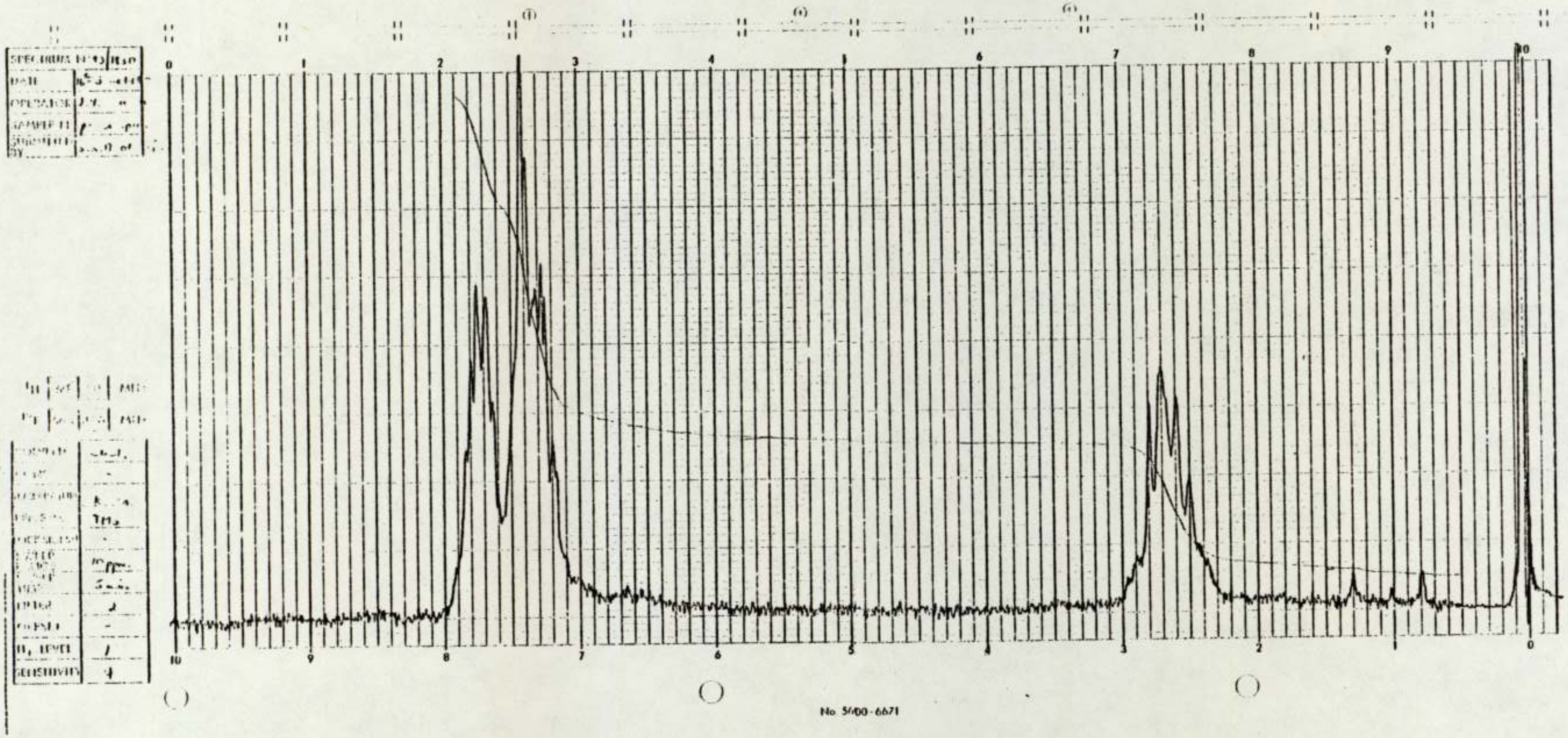


Fig 4.6 ^{1}H NMR spectrum of Diphenyltellurium β-mercaptopropionate

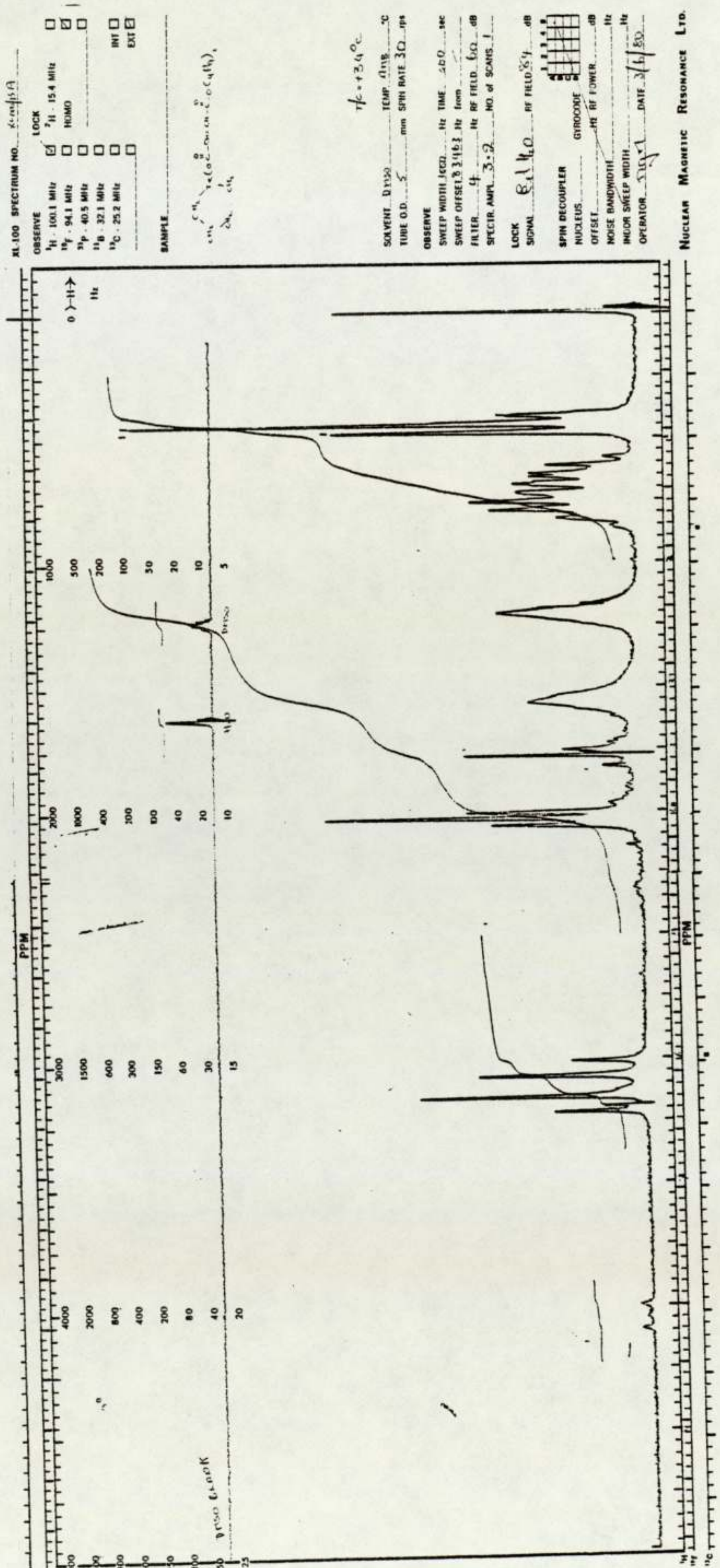


Fig 4.7 ^{1}H NMR spectrum of Telluracyclopentane bis(monobutyl maleate)

4-3 Discussion

A large number of literature reports of infra-red and Raman spectroscopic investigations of orgenotellurium compounds exist. The tellurium-carbon (alkyl), tellurium-chlorine and tellurium-sulphur stretching frequencies are located in the regions 530-450cm^{-1} (127), 287-255cm^{-1} (72) and 262-215cm^{-1} (128) respectively. The infra-red spectrum of organotellurium carboxylates provide some useful information on the type of interaction between the carboxylate groups and the tellurium atom. Carboxylate groups may act as unidentate ligands, or, symmetrical or unsymmetrical bidentate ligands. The separation of the two infra-red active carboxylate stretching frequencies, νas [COO] and νs [COO] has previously been used to measure the degree of ester-like character for organotin carboxylate(119) and organotellurium carboxylates.(83) For example, the separations (Δ) of the two frequencies, Δ = 316cm^{-1} and Δ = 227cm,$^{-1}$ are suggested to imply unidentate(119) and unsymmetrically bidentate(120) acetate groups respectively.

4-3-1 Diphenyltellurium maleate and diaryltellurium β - mercaptopropionate (Aryl = Ph or $EtOC_6H_4$)

The elemental analyses of these compounds are in good agreement with calculated values as shown in Table 4-1. The quantity of water eliminated during the formation of diaryltellurium β - mercaptopropionate matched the theoretical quantity. Molecular weight measurements on these compounds in freezing solvents were carried out, and the results clearly indicated that the compounds must be formulated as dimers, Table 4-2.

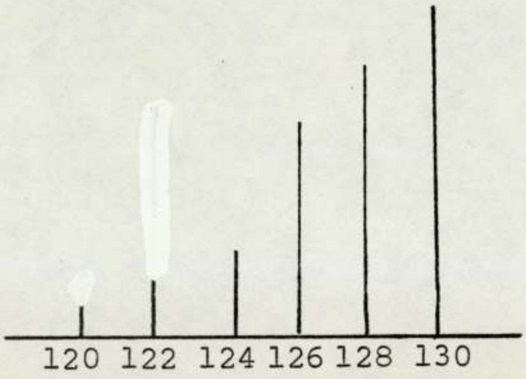
The infra-red spectral data for these compounds are given in Table 4-7. The spectrum of diphenyltellurium maleate, Fig 4.1 (a), shows a strong absorption, possibly a poorly resolved doublet, at1625cm^{-1} with a shoulder at 1665cm^{-1} is due to νas [COO] . A similar feature is observed in the spectrum of silver 3-butoxycarbonyl-2-propenoate, and that of maleic acid, Fig 4.1 (b) and (c), showed well resolved doublets at 1580cm^{-1}; 1610cm^{-1} and 1567cm^{-1} with a shoulder at 1640cm^{-1} respectively. The strong well resolved doublet at 1235cm^{-1} and 1315cm^{-1} is due to νs [COO] which is different from νs [COO] of silver 3-butoxycarbonyl-2-propenoate and of maleic acid.

The infra-red spectrum of diaryltellurium β - mercaptopropionate, Fig 4.2 (a) and (b), shows bands at 1650cm^{-1}-1645cm^{-1} and 1255cm^{-1}- 1240cm^{-1} due to νas [COO] and νs [COO] respectively. Bands appear at 265cm^{-1} in diphenyltellurium β - mercaptopropionate and at 220cm^{-1} in di-p-ethoxyphenyltellurium β - mercaptopropionate which could be due to ν[Te-S] (128).

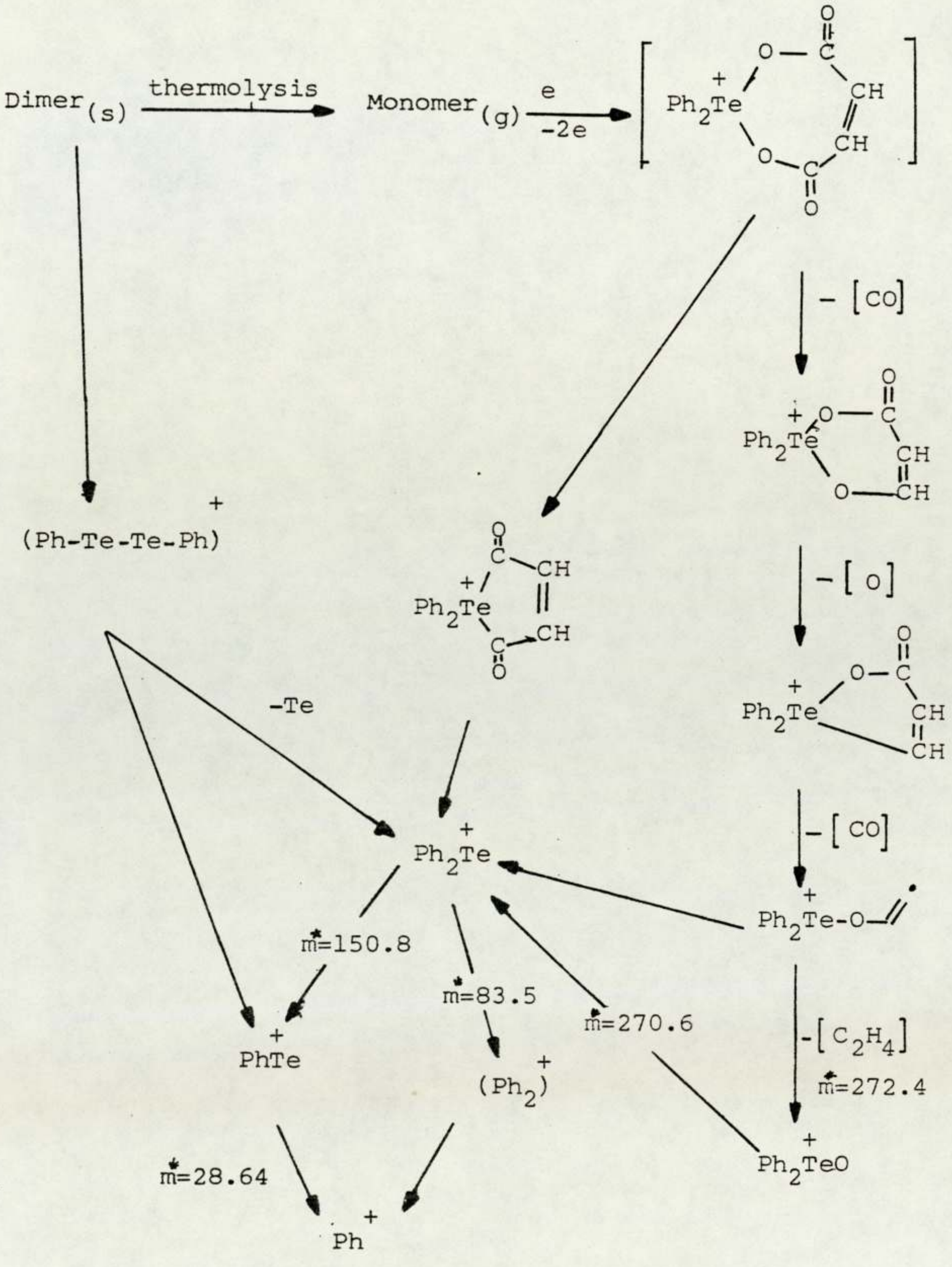
The diphenyltellurium maleate and diaryltellurium β - mercaptopropionate show two strong absorptions at $1725 cm^{-1}$ - $1720 cm^{-1}$ and $1190 cm^{-1}$ - $1170 cm^{-1}$ which could also be due to the ν_{as} [COO] and ν_s [COO] respectively. Also, these bands are not observed in the spectrum of diaryltellurium dichloride. The [COO] in plane rock, out of plane rock and scissor vibration for diphenyltellurium maleate appear at $570 cm^{-1}$, $630 cm^{-1}$ and $850 cm^{-1}$ while for diaryltellurium β - mercaptopropionate they appear at $510 cm^{-1}$, $670 cm^{-1}$ and $715 cm^{-1}$ respectively.

The 'H n.m.r. spectra of solutions of these compounds in deuterated chloroform were recorded with TMS as the internal standard, as shown in Figs 4.5 and 4.6 (Table 4-8). The multiplet resonance appearing at δ 6.6-7.8ppm is due to the aromatic protons. Diphenyltellurium maleate shows a singlet at δ 5.9-6.3 ppm superimposed on a weak multiplet which is due to the alkene protons of the ligand. The diaryltellurium β - mercaptopropionate gives a quartet appearing at δ 2.5, 2.6, 2.7 and 2.8 ppm which is due to the overlaping of two triplets, the two triplets corresponding to the methylene protons of the ligand ($S - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}}$). The spectrum of di-p-ethoxyphenyltellurium β - mercaptopropionate shows two resonances centred at δ 1.38 [triplet 1:2:1] and 4 ppm [quartet 1:3:3:1] which are due to methyl and methylene protons of the ethoxy groups respectively. The 'H n.m.r spectra of these compounds are helpful in showing the correct ratio of aromatic to aliphatic protons and hence supporting the stoichiometry and purity of the material.

The mass spectral data of diphenyltellurium maleate are given in Table 4-3. Tellurium has eight naturally occuring isotopes, which give rise to a characteristic isotope pattern for each ion containing tellurium atoms. Such isotope clusters are of great help in identifying tellurium containing ions. The peaks observed in the mass spectrum of diphenyltellurium maleate are : ^{120}Te, ^{122}Te, ^{123}Te, ^{124}Te, ^{125}Te, ^{126}Te, ^{128}Te and ^{130}Te corresponding to most abundant natural isotopes of tellurium such as



The fragmentation patterns of diphenyltellurium maleate may be represented by the following scheme:-



(Species in square brackets not observed)

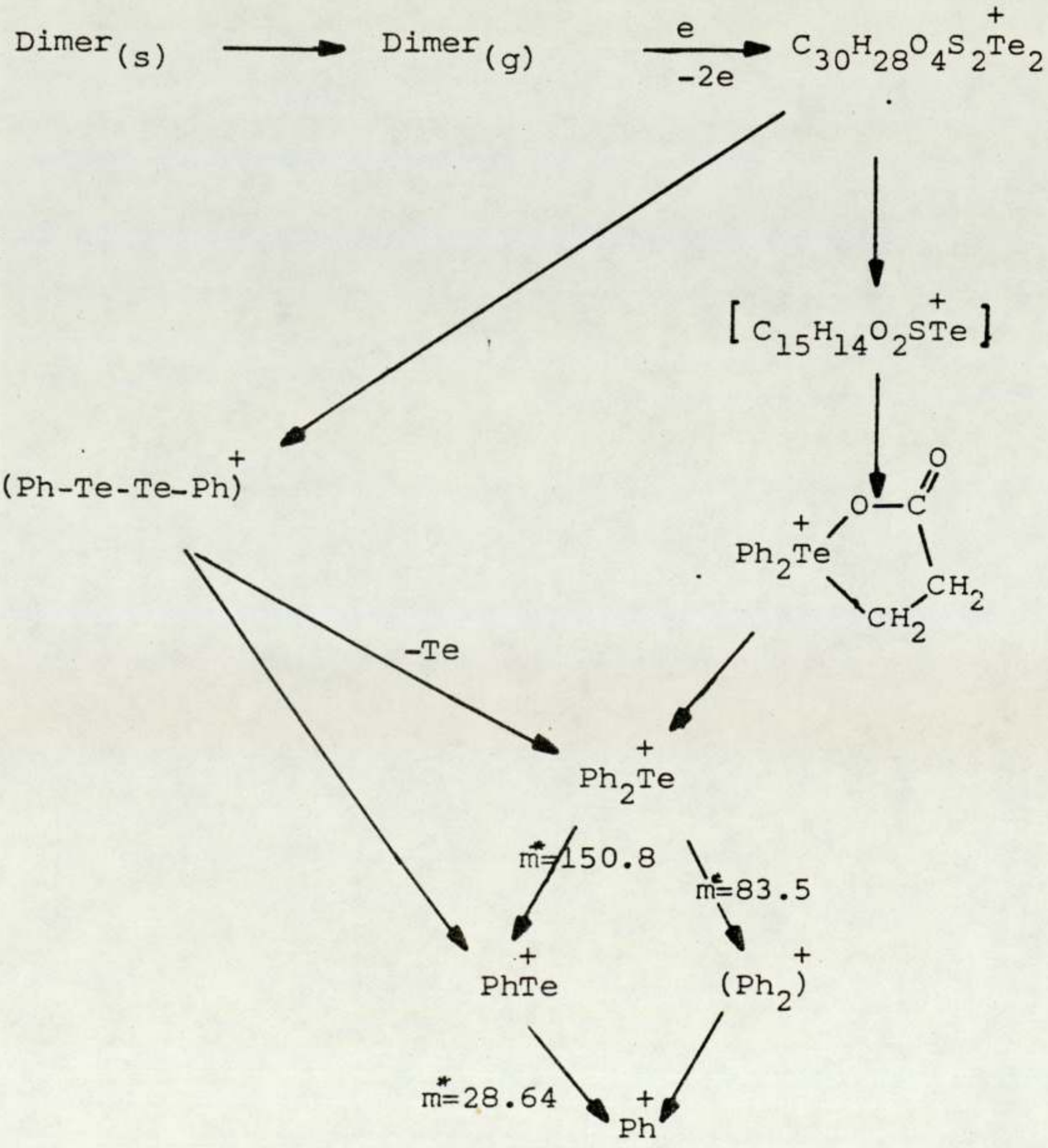
Unfortunately there was no evidence to support all the steps in the scheme from the metastable ions, but some stages are supported by the observation of metastable ions as indicated.

The molecular weight measurements (Table 4-2) show that this compound is dimeric. However, it seems that the dimer undergoes decomposition in to a monomer via thermolysis. It was expected that the molecular ion of the monomer should appear at m/e = 398 in the mass spectrum of the compound. However, no parent ion for the monomer was seen.

The mass spectrum of this compound showed the presence of what is possibly a tetraorganotellurium ion, $C_{16}H_{12}O_2\overset{+}{Te}$, m/e = 366, however, no metastable ion was observed to relate this ion to a specific fragmentation. It is known that tetraalkyl and dialkyldiaryltellurium compounds are thermally unstable. The mass spectrum also shows the presence of diphenylditelluride ion at m/e = 414. The formation of ditelluride ion, as shown in the mass spectrum, is very interesting, since it supports the view that diphenyltellurium maleate is a dimer, McWhinnie et al(136) pointed out that ditelluride ions could not occur from the monomer, but only from dimer or oligomer molecules.

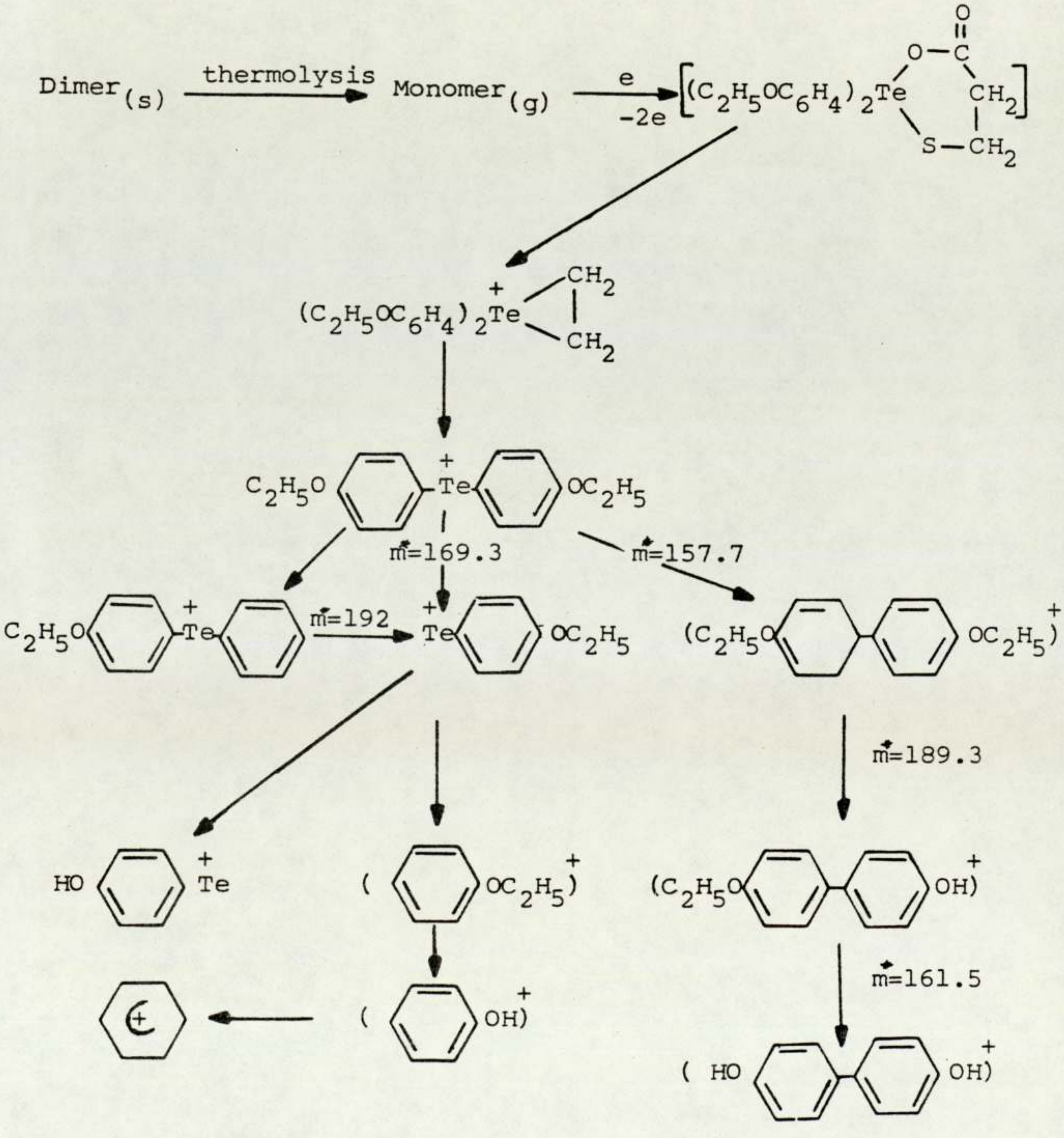
The mass spectral data of diphenyltellurium β - mercaptopropionate are shown in Table 4-4. The mass spectrum of this compound showed ions appearing at m/e = 776 which corresponds to the dimer (as shown by molecular weight measurements Table 4-2) of this compound. The interesting feature of the mass spectrum is the formation of the ditelluride ion at m/e = 414 which is further evidence to support the dimer hypothesis.

A possible fragmentation pattern of this compound is shown in the following scheme:-



(Species in square brackets not observed)

The mass spectral data for di-p-ethoxyphenyltellurium β - mercaptopropionate are shown in Table 4-6. The further fragmentations of the organic ions are complicated because there is more than one possible route. The most probable fragmentation pattern of this compound is shown below. Some stages are supported by the observation of metastable ions as indicated.

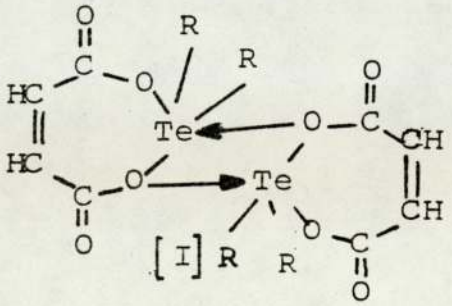


(Species in square brackets not observed)

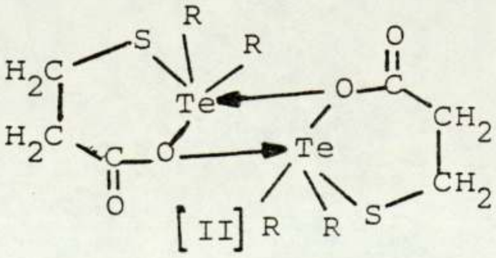
The molecular weight measurements (see Table 4-2) show that the diphenyltellurium maleate and diaryltellurium β-mercaptopropionate are dimeric. Quite recently McWhinnie et al (85) have reported that phenylmethyltellurium phthalate is monomeric in chloroform solution and is thus similar to diaryl derivatives reported by Tamagaki et al.(84) The results reported here are, however, similar to that for diphenyltellurium phthalate reported by Dance.(129) Dance later confirmed his results after the appearance of Tamagaki's contribution.(130) It seems likely that there are monomeric and dimeric forms of some of these materials. The structures of the monomeric and dimeric forms are of some interest. It is convenient to regard the structure of an organotellurium compound R_2TeX_2 (X is an electronegative group) as ψ - trigonal bipyramidal, however, both crystallography(79) and, for example ^{125}Te mössbauer spectroscopy(100) indicate that the tellurium-carbon bonds have high tellurium p-character, although the $X\hat{Te}X$ angle is generally close to 180°. Reduction of the $X\hat{Te}X$ angle, which would presumably be necessary on steric grounds in the case of monomeric $Ph(CH_3)Te(C_8H_4O_4)$, is likely to increase the s-character of the tellurium-carbon bonds.(131)

McWhinnie et al(85) studied the coupling constant between the methyl protons and ^{125}Te, in diphenyltellurium dichloride and phenylmethyltellurium phthalate. In fact both compounds give identical coupling constants (25HZ), thus implying similar S and P character within the tellurium-carbon bonds in both compounds. Evidence gained from Dreiding models supports McWhinnie's suggestion that the tellurium-oxygen bond in a ψ-trigonal bipyramidal monomer must be strained and off the tellurium-oxygen axis.

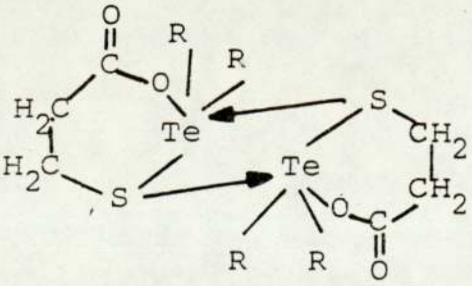
On the basis of the molecular weight measurements, mass spectra and infra-red spectra, the diphenyl tellurium maleate and diaryltellurium β- mercaptopropionate must be dimeric. Thus both monomer and dimer seem to be established for diorganotellurium carboxylates. The dimer structure should be such that ready dissociation to monomers can occur in which case the structure proposed by Dance(129) is unattractive. Possible structures for these compounds are given below.



[I]



[II]



[III]

An infra-red study of these compounds gave evidence to support the postulated structures. The splitting of the carboxylate band in diphenyltellurium maleate may be essentially due to the different environment between the carboxylate groups within the dimer. Diaryltellurium β - mercaptopropionate showed no splitting at the carboxylate vibration, hence the two carboxylate groups in the dimer are equivalent. The infra-red spectra of these compounds reveal two bands which could be due to the ester-like structure. These bands may arise due to the interaction between the carboxylate groups of one monomeric species with tellurium atom of another monomeric species via ester-like bridge. The postulated structure (I) has the advantage over Dance's (as stated early in Chapter 1) model in that it can readily explain the existance of monomeric species (i.e. by splitting the ester-like bridge). The diaryltellurium β - mercaptopropionate could have either of the two structures (II) and (III). However, the infra-red spectroscopy shows the ester-like vibration and on the basis of dissociation of the dimer to the monomeric species the structure (III) would not favour the dissociation. It is, therefore, probable that the diaryltellurium β - mercaptopropionate has structure (II).

If the diphenyltellurium maleate was truly dimeric, we would expect an AB pattern in the n.m.r. which is due to a slight difference between the alkene protons;

whereas the monomer of this compound should give a singlet peak. However, 'H n.m.r studies of this compound produced multiplet peaks with a singlet peak which might perhaps be due to the dissociation of the dimer to the monomer that led to this overlap.

$$\text{Dimer} \rightleftharpoons 2\ \text{Monomer}$$

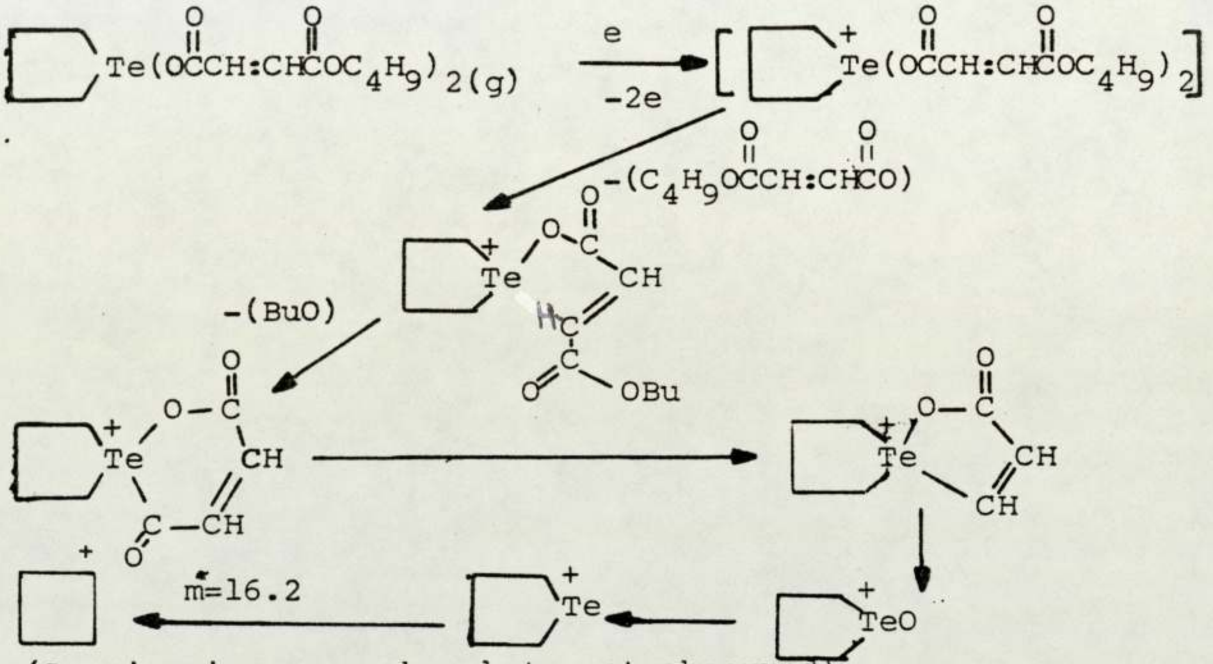
In recent years the structure determination by X-ray crystallography has become common place, unfortunately we were unable, despite repeated and strenuous efforts, to grow suitable single crystals of diphenyltellurium maleate and diaryltellurium β-mercaptopropionate , so no crystallographic confirmation of the structure was possible. However, it may be possible in the future to test our postulates further by a ^{125}Te n.m.r. or by a ^{125}Te Mössbauer study.

4-3-2 Diorganotellurium bis(monobutyl maleate) [R=cyclopentane or Ph]

The elemental analyses were in good agreement with the calculated values (Table 4-1). The infra-red spectra of these compounds are very similar, Fig 4.3 (a) and (b). The strong well resolved doublets at 1620cm^{-1}- 1670cm^{-1} and 1170cm^{-1} - 1210cm^{-1} are due to the ν_{as}[COO] and ν_{s}[COO] respectively. However, there could be a slightly different environment for the two carboxylate groups. Thus it is conceivable that the "non-bonded" oxygen atom of one group is closer to the central tellurium atom than the corresponding oxygen atom of the other group. Telluracyclopentane bis(monobutyl maleate) shows a weak band at $450cm^{-1}$ which could be due to a ν [Te-C].

The 'H n.m.r. data for these compounds are given in Table 4-8. Both the spectra show AB spectrum at δ 5.8-6.5 ppm (J_{AB} = 11 - 12 HZ) due to the alkene protons. This could mean that the two protons are in different environments which could be due to the two carboxylate groups, one attached to the tellurium atom and the other one attached to aliphatic group. Two triplet resonances appear at δ 4-4.2 and 0.7-1 ppm in both of the spectra which are due to the methylene (d) bonded to oxygen and methyl (a) protons respectively ($O-\overset{d}{C}H_2-\overset{c}{C}H_2-\overset{b}{C}H_2-\overset{a}{C}H_3$). The multiplet resonances centred at δ 3.55 ppm and 1.45 ppm are associated with methylene protons (c) and (b) respectively. The diphenyltellurium bis(monobutyl maleate) shows multiplets resonances at δ 7.3-7.9 ppm due to the aromatic protons while telluracyclopentane bis(monobutyl maleate) spectrum shows two singlet peaks at δ 2.4 and 3.12 ppm assigned to $-CH_2-C$ and to $-CH_2-Te$ protons respectively. One possibility for the absence for the triplet peaks in the 'H n.m.r. spectrum could be in the torsional flexing of the ring resulting in a smearing of environmental effects hence two singlet peaks appear.

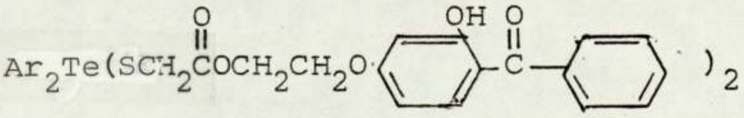
The mass spectral data for telluracyclopentane bis(monobutyl maleate) are shown in Table 4-5. The fragmentation patterns of this compound may be represented by the following scheme:-



(Species in square brackets not observed)

Although the molecular ion peak of this compound at m/e 528 was not observed, the pattern of fragmentation was found to be related to that of diphenyltellurium maleate.

4-3-3 Diaryltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)(Aryl = Ph or EtO C_6H_4).



The infra-red spectra of these compounds are given in Table 4-7. The weak ν (S-H) for free acid which occurs at 2590cm^{-1}, is absent and new bands appear at 265cm^{-1}

and 225cm^{-1} which are due to the ν[Te-S] in diphenyl and di-p-ethoxyphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone) respectively. However, the ν[Te-S] in the diphenyl compound may overlap with ν [Te-C(phenyl)].

The 'H n.m.r. spectra of these compounds were similar (Table 4-8) and helpful in showing the correct ratio of aromatic to aliphatic protons and hence supporting the stoichiometry of the materials. The spectrum shows a multiplet at δ 6.2-7.7 ppm which are due to the aromatic protons. The two singlets at δ 4.15 ppm and δ 4.3 ppm are due to protons of the methylene groups $[O\text{-}CH_2\text{-}CH_2\text{-}O]$. This indicates that the protons of the two methylene groups are equivalent. A single peak at δ 3.5 ppm are due to the protons of the methylene group $[S\text{-}CH_2\text{-}\overset{\overset{O}{\|}}{C}]$. However, in the case of di-p-ethoxyphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone) the spectrum shows a triplet at δ 1.3 ppm and quartet at δ 3.9 ppm which are due to methylene and methyl protons of the ethoxy groups respectively.

Molecular weight measurements on diphenyltellurium-di(4-ethoxythioglycollate-2-hydroxybenzophenone) in freezing nitrobenzene, were carried out, and the result matched the theoretical value for the monomer (Table 4-2).

4-3-4 Dicetyltelluride.

The preparation of this compound has been reported(67), using sodiumtelluride prepared from elemental sodium and tellurium in liquid ammonia, which then reacted with cetylchloride and gave dicetyltelluride. However, sodium telluride was difficult to prepare and the reaction was performed under a dinitrogen atmosphere to protect the sodiumtelluride from oxidation. The dicetyltelluride was prepared by a new method, from the reaction of cetylchloride with tellurium in the presence of sodium or potassium iodide. The reaction gave dicetyltellurium diiodide which was reduced to dicetyltelluride by sodium sulphide. The new method was found to be easier than the method described previously. The elemental analyses (Table 4-1) and molecular weight measurement (monomer) in freezing benzene (Table 4-2) of this compound matched the theoretical values. The dicetyltelluride was pale pink in colour suggesting the presence of some dicetylditelluride. To purify this, the pink coloured compound was treated with active copper under a dinitrogen atmosphere to oxidise the dicetylditelluride to dicetyltelluride, by the removal of tellurium.

Comparison of infra-red spectra of the prepared dicetyltelluride (Table 4-7) with that of the starting material, cetylchloride, shows strong absorption appearing at $2960cm^{-1}$ and $1470cm^{-1}$ which are characteristic of C-H stretching and C-H deformation respectively. However, the infra-red spectrum of dicetyltelluride showed that the absorption at $650cm^{-1}$ due to ν [C-Cl] had disappeared hence proving complete reaction of cetyltelluride with tellurium in the presence of sodium or potassium iodide. A band which appeared at $490cm^{-1}$ could be due to ν[Te-C] .

Proton n.m.r. obtained from $CDCl_3$ solution (Table 4-8) shows resonances at δ 0.8-1.6 ppm corresponding to the aliphatic protons of the cetyl group. The triplet at δ 3.5 ppm, of the cetyl chloride, due to the $-CH_2-Cl$ has disappeared demonstrating complete reaction of the tellurium with cetyl chloride.

4-3-5 Dicetyltellurium dichloride

As was mentioned before, the dicetyltelluride could contain some dicetylditelluride. However, it is known that thionylchloride converts the diorganotelluride and diorganoditelluride to diorganotellurium dichloride and organotellurium trichloride respectively. Therefore, in order to remove any cetyltellurium trichloride impurity, the precipitate of the reaction between dicetyltelluride and thionylchloride is reacted with tetraethylammonium bromide (in chloroform) to remove the trichloride as an anionic species tellurium (IV), $[Et_4\overset{+}{N}]\,[RTeX_3\overset{-}{Br}]$,. The infra-red spectrum and the melting point of the salt were identified to that of tetraethylammonium bromide, hence showing there was no trichloride impurity. This result supported the absence of dicetylditelluride.

Infra-red spectrum of dicetyltellurium dichloride (Table 4-7) in a Nujol mull supported in polyethylene sheets was recorded and a ν[Te-Cl] was assigned at $255cm^{-1}$ which is in agreement with those reported by McWhinnie et al$^{(72)}$ in their studies on ν[Te-Cl] . Furthermore, the band at $490cm^{-1}$ may be due to the ν[Te-C] .

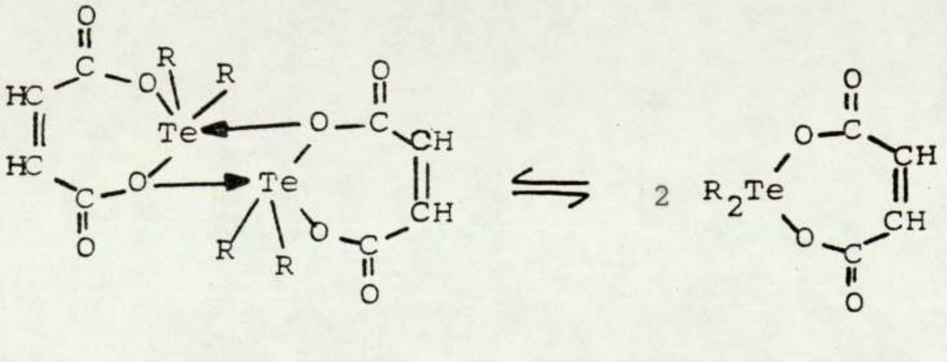
4-3-6 Dicetyltellurium dicarboxylate.

Dicetyltellurium diacetate has been synthesised by the oxidation of dicetyltelluride with lead tetraacetate (yield 90%) and also by the reaction of dicetyltellurium dichloride with silver acetate (yield 75%). However, in view of the cost of silver acetate and of the lower yield this seems to be less attractive than using lead tetraacetate.

Dicetyltellurium diacetate and dicetyltellurium maleate thus obtained were **satisfactorily** characterized by elemental analyses, and IR and n.m.r. spectra. The data is summarised in Tables 4-1, 4-7 and 4-8. Molecular weight measurements of dicetyltellurium maleate in freezing benzene were carried out and the values (Table 4-2) indicate that an equilibrium exists between dimer and monomer.

The infra-red spectra for these compounds are shown in Figs 4.4(a) and 4.4(b) respectively. The spectrum of dicetyltellurium diacetate showed two strong bands at $1640cm^{-1}$ and $1290cm^{-1}$ which are due to νas [COO] and νs [COO] respectively. The spectrum of dicetytellurium maleate is similar in major respects to that of diphenyltellurium maleate. Bands at $1640cm^{-1}$, $1610cm^{-1}$ and $1315cm^{-1}$, $1245cm^{-1}$ which are due to νas[COO] and ν s[COO] respectively. Moreover, the two other bands at $1670cm^{-1}$ and $1180cm^{-1}$ could be due to the ν as [COO] and νs [COO] ester-like respectively. The band at $495cm^{-1}$ may be due to the ν[Te-C] .

'H.n.m.r spectra of these compounds in deuterated $CDCl_3$ (Table 4-8) showed resonances at δ0.8-1.9 ppm which were assigned to the cetyl protons. The dicetyltellurium diacetate showed one sharp singlet peak at δ2.16 which was assigned to methyl protons of the acetate group while the dicetyltellurium maleate showed a singlet peak at δ6.25 ppm which is due to the alkene protons. Molecular weight measurement yield a value intermediate between monomer and dimer structure. This could be due to partial dissociation of the dimer structure to yield monomer as shown below:-



However, the n.m.r. gave a singlet peak which may also be due to the dimer dissociating to produce monomeric species on a time scale equivalent to that of lattice relaxation or it could be due to a dynamic exchange phenomenona so giving only one equivalent structure for the dimer.

4-3-7 Attempt to prepare octyltellurium derivates.

In fact, the reason for the preparation of octyltellurium derivates was that dicetyltellurium maleate decomposed at 150°C while the processing temperature for the polymer (PVC) is 170°C (see chapter 5). As described in the experimental section no compound was isolated. The product was extremely air sensitive and could not be handled without decomposition. However, it is known that the dialkyltellurides, low molecular weight aliphatic members, are light and air sensitive.

Gysling(132) has recently succeeded in preparing diorganotellurium dichloride $((CH_3)_3\ SiCH_2)_2\ TeCl_2$ Which showed no signs of decomposition on prolonged storage in air. As a result of this reaction on the ability of the halogen to stabilise the diorganotelluride, it was decided to use thionylchloride. Unfortunately, addition of the halogen to dioctyltelluride failed to produce dioctyltellurium dichloride (see 4-1-11 B). However, the white solid was directly decomposed to a black material.

It seemed reasonable to attempt to prepare dioctyltelluride dihalide by the procedure used to prepare dicetyltellurium dihalide (see 4-1-11 B). The red-brown precipitate undergoes decomposition to give a black material. The black material is not soluble in common organic solvents (such as $CHCl_3$, benzene, etc.,.) but it dissolved in H_2SO_4 to give a violet solution. It does not melt below 360^0C and is probably tellurium metal. It seems that the dioctyltellurium dihalide is extremly air and light sensitive.

Petragnani et al$^{(133)}$ have prepared salts containing $[ArTeX_2]^-$ by the reaction of ArTeX with tetraorganylphosphonium halides. It appeared possible to attempt preparation of the $[Et_4N]^+$ $[\text{Octyl TeBr}_2]^-$ by using tetraethylammoniumbromide instead of sodium or potassium iodide. However, octyltellurium tribromide could be obtained by adding bromine to $[Et_4N]^+$ $[\text{Octyl TeBr}_2]^-$. The reaction gave the tetraethylammonium tribromotellurate (II) $[Et_4NTeBr_3]$ instead of the $[Et_4N]^+$ $[\text{Octyl-TeBr}_2]^-$. 1-Bromohexane was also used instead of 1-bromooctane and the product of the reaction was also Et_4NTeBr_3 . Tetraethylammonium pentabromotellurate (IV) $[Et_4NTeBr_5]$ was obtained by treatment of Et_4NTeBr_3 with bromine in chloroform. Et_4NTeBr_5 has been prepared by mixing$^{(134)}$ a solution of tellurium tetrabromide or tellurium dioxide with a solution of tetraethylammonium bromide and treated with hydrobromic acid. The analytical data for tetraethylammonium tribromotellurate (II) and tetraethylammonium pentabromotellurate (IV) were quite satisfactory and are given in Table 4-1.

The tetraethylammonium tribromotellurate (II) and tetraethylammoniumpentabromotellurate (IV) were unstable in the presence of water. The former gave tellurium, possibly by disproportionation [2Te (II)→Te(O) + Te(IV)] , the latter was hydrolysed to TeO_2. The tellurium was characterized by dissolving in H_2SO_4 to give a violet solution. The tellurium dioxide, the product of hydrolysis, was characterized by infra-red and was identical to an authentic sample of tellurium dioxide.

4-3-8 Bis(diethyldithiocarbamato)tellurium (II)

The preparation of this compound has been reported(135). This method required close attention for long periods. A new method was used to prepare this compound in which tetraethylthiuramdisulphide and tellurium have been used to give a higher yield (99%). The analytical data (Table 4-1) were quite satisfactory. The infra-red shows a band at 230cm^{-1} assigned to the ν [Te-S].

In summary, the following compounds have been prepared.

- Diphenyltellurium maleate
- Diaryltellurium β-mercaptopropionate [Aryl=Ph or $EtOC_6H_4$].

- Diorganotellurium bis(monobutyl maleate) (R=cyclopentane or Ph)
- Diaryltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone) [Aryl=Ph or $EtOC_6H_4$].
- Dicetyltelluride.
- Dicetyltellurium dichloride.
- Dicetyltellurium maleate.
- Tetraethylammonium tribromotellurate (II)
- Tetraethylammonium pentabromotellurate (IV)
- Bis(diethyldithiocarbamato) tellurium (II).

As verified by elemental analyses, molecular weight measurements, 'H.n.m.r, IR and mass spectra. Diphenyltellurium maleate and diaryltellurium β-mercaptopropionate were shown to exist as dimers whilst dicetyltellurium maleate was shown to be in equilibrium between dimer and monomer forms. The dimer could be formed via an ester-like bridge.

CHAPTER FIVE

5A - STABILISATION OF POLY(VINYLCHLORIDE) PVC

5A - 1 Experimental

PVC formulations were prepared by tumble mixing additives with the polymer in the appropriate ratio. When lubricants were incorporated in the formulation, the internal lubricant, calcium sterate (0.8%) was used in conjunction with the external lubricant, waxE (0.65%). Lubricants reduce the severity of the mechano-chemical process by lowering internal friction and preventing adhesion of the polymer to the machine surface(21,169). The mixture was processed in a RAPRA torque rheometer. The processing operation was carried out at 170°C for 2.5, 5, 10 and 15 minutes in a closed mixer. The additive-free polymer was also processed at 2.5, 5, 10 and 15 minutes. The processed polymer was compressed into films and then examined for the effect of processing, photo and thermal-oxidation as described previously in Chapter 2.

5A - 2 Results and discussion

5A - 2 - 1 Effect of organotellurium compounds during processing

During thermal degradation of PVC hydrogen chloride is

Table 5.1 Code of the compounds used in this chapter

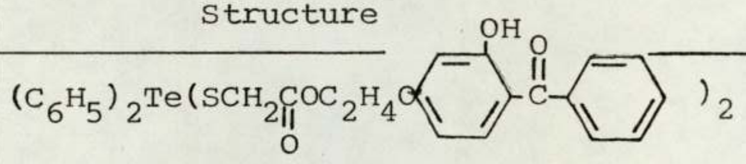
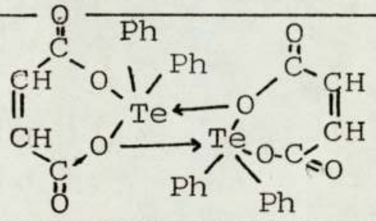
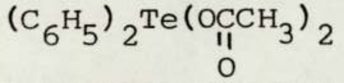
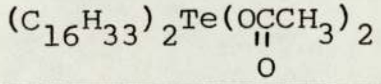
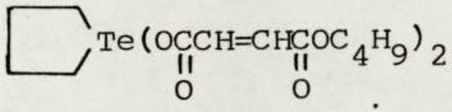
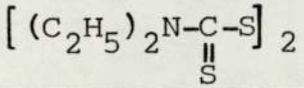
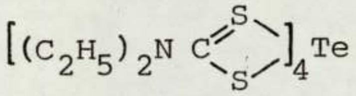
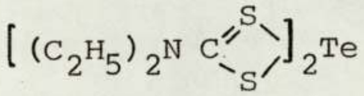
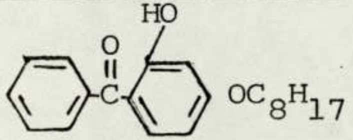
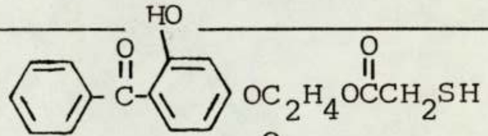
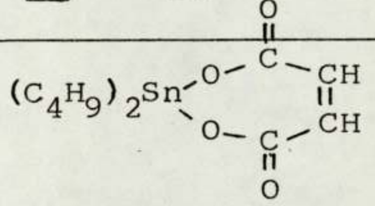
Compounds	Structure	Code
Diphenyltellurium di(4-ethoxythioglycollate-2-hydroxybenzophenone)$_2$		DPTeE
Diphenyltelluride	$(C_6H_5)_2Te$	DPTe
Dicetyltelluride	$(C_{16}H_{33})_2Te$	DCTe
Diphenyltellurium maleate		DPTeM
Diphenyltellurium diacetate	 $(C_6H_5)_2Te(OCCH_3)_2$	DPTeA
Dicetyltellurium diacetate	 $(C_{16}H_{33})_2Te(OCCH_3)_2$	DCTeA
Telluracyclopentane bis(monobutyl maleate)		TeCM

Table 5.1-Cont'd

Compounds	Structure	Code
Tetraethylthuiram disulphide	 $\left[(C_2H_5)_2N{-}\underset{\underset{S}{\Vert}}{C}{-}S\right]_2$	TETD
Tetrakis(diethyldithiocarbamato) tellurium (IV)		Te(dtc)$_4$
Bis(diethyldithiocarbamato) tellurium (II)		Te(dtc)$_2$
4-Octyloxy-2-hydroxybenzo-phenone		HOBP
4-Ethoxymercaptoacetato-2-hydroxybenzophenone		EBHPT
Dibutyltin maleate		DBTM

evolved and the dehydrochlorination reaction is usually the focus of attention.(3,11,13,14,27,137) It was not feasible, however, to directly measure the hydrogen chloride evolved during processing in the torque rheometer. In practise, therefore, discolouration is normally the first and most important effect of degradation and the change of colour together with the formation of olefinic unsaturation has been used for the study of the degradation in the presence of thermal stabilisers.(139,17,21,26)

The change in colour during processing at varying periods (2.5, 5, 10 and 15 minutes) was measured using a Colormaster and the procedure is described in Chapter 2. A plot of the total colour difference vs the processing time at 170°C is shown in Fig 5.1 . PVC without additives gave the highest level of discolouration. The two lubricants did not show a significant effect on the level of discolouration, though the total level of discolouration was slightly lower than the control. When DPTeM was used in combination with lubricants, the level of discolouration was reduced drastically. As the concentration of this compound was increased the level of discolouration was decreased. A similar set of curves was obtained for colour formation for DPTeA and DPTeE in combination with lubricants as shown in Figs 5.2 and 5.3 respectively.

Fig 5.4 compares the change of colour during processing of PVC containing organotellurium compounds with lubricants, and its effects as compared with DBTM (a commercial PVC stabiliser) with lubricants, PVC with lubricants and PVC without additives. The PVC without additives showed that the level of discolouration rose rapidly during the first 2.5 minutes of processing. The level of discolouration continued to rise at a slower linear rate after this time. The PVC with lubricants showed a similar behaviour to PVC without additives, but the level of discolouration is slightly lower. When organotellurium compounds were used together with lubricants, the level of discolouration during the first 2.5 minutes of processing was substantially reduced. After 2.5 minutes the level of discolouration was noted to rise steadily but slowly up to 10 minutes of processing and after this time at a very much slower rate. The DPTeM was a somewhat better stabiliser than DPTeA. The DPTeE was somewhat more effective than DPTeM at longer processing times. DBTM in combination with lubricants was found to have very similar discolouration characteristics to organotellurium compounds, though the latter produced a lower level of discolouration.

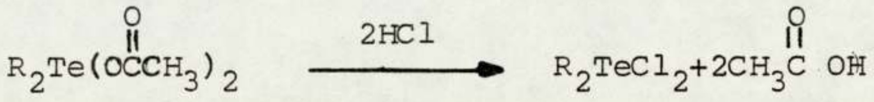
The unsaturation formed as a result of hydrogen chloride evolution was measured by using the method described in Chapter 2. Plots of the unsaturation formed as a function of time during the processing of PVC formulations containing DPTeM, DPTeA DBTM in combination with lubricants were compared with PVC with lubricants and of

PVC without additives are shown in Fig 5.5 . Unsaturation formation shows a parallel trend to colour formation (Fig 5.4).

The infra-red spectra of DPTeM and DPTeA alone have strong absorptions at 1640-1575cm^{-1} and 1630cm^{-1} respectively. Whereas this part of the spectrum of pure PVC has no such peaks. Therefore, the peaks at 1640-1575cm^{-1} and 1630cm^{-1} observed during the processing can be assigned to asymmetric carboxylate stretching of DPTeM and DPTeA respectively. The carboxylate peaks are plotted in Fig 5.6 as an index I_{COO} 1560cm^{-1} for DPTeM and I_{COO} 1630cm^{-1} for DPTeA vs processing time. The carboxylate peaks decreased with the processing time. At the same time the ester groups at 1735cm^{-1} increased (Fig 5.7). This was mentioned in Chapter 3 and is due to replacement of the chlorine atoms by carboxylate groups.

Organotellurium compounds show a pronounced concentration effect in their capacity to prevent an increase in the level of discolouration in unplasticised PVC during processing, especially during long term processing (Figs 5.1, 5.2 and 5.3). The loss in effectiveness is associated with consumption of the stabiliser during processing (Fig 5.6). These observations strongly suggest that the activity of organotellurium compounds as processing stabilisers is largely dependant on their ability to neutralise the liberated hydrogen chloride effectively.

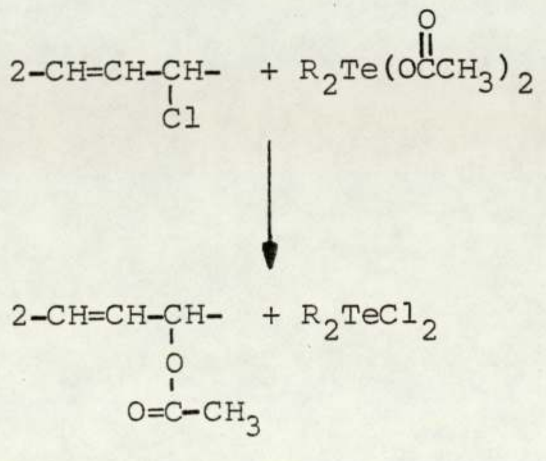
It was shown in Chapter 3 that these compounds possess the property of being able to react with hydrogen chloride chemically. The following reactions probably indicate the main function of organotellurium compounds as stabilisers.



$$R_2Te(O\overset{O}{\overset{\|}{C}}CH_3)_2 \xrightarrow{2HCl} R_2TeCl_2+2CH_3\overset{O}{\overset{\|}{C}}\,OH$$

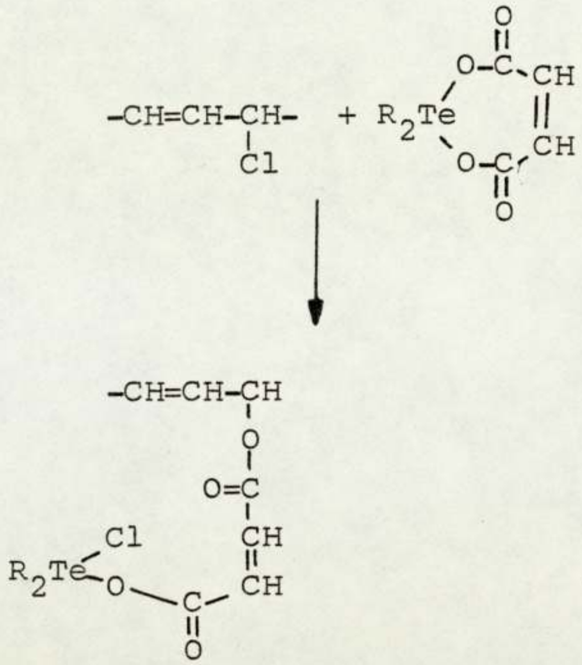
$$R_2Te(SR^1)_2 \xrightarrow{2HCl} R_2TeCl_2+2R^1SH$$

The DPTeA and DPTeM significantly decrease the formation of olefinic unsaturation and the level of discolouration during the processing of PVC (Figs 5.4 and 5.5). Moreover, they were seen to replace labile chlorine atoms by carboxylate moieties. Evidence to support this is that DPTeA has the ability to replace the chlorine atoms in model compounds (see Chapter 3). Secondly, the carboxylate infra-red absorption decreases and ester groups are formed (Figs 5.6 and 5.7) during processing. The formation of ester groups during processing may be described by the following reactions:



$$2\text{-}CH{=}CH\text{-}\underset{Cl}{\underset{|}{CH}}\text{-} + R_2Te(O\overset{O}{\overset{\|}{C}}CH_3)_2 \longrightarrow 2\text{-}CH{=}CH\text{-}\underset{O=C-CH_3}{\underset{|}{\underset{O}{\underset{|}{CH}}}}\text{-} + R_2TeCl_2$$

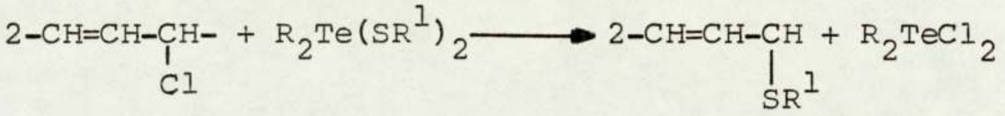
or



It is well known that DBTM is a good stabiliser for PVC. One of its principal modes of action is believed to be the reaction of the maleate group with conjugated unsaturation in the PVC via Diels-Alder type reactions(45) (as was mentioned in Chapter 1). By analogy, DPTeM is a better stabiliser than DPTeA (Fig 5.4) since the maleate group can undergo the same type of Diels-Alder reaction.

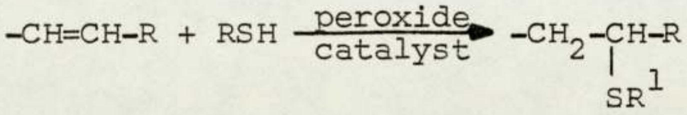
As was mentioned previously, Chapter 1, DOTG has the ability to neutralise hydrogen chloride and replace labile chlorine atoms. However, the effectiveness of DPTeE to prevent the colour change during the processing of PVC (Fig 5.3) may be (analogous to DOTG) due to its ability to react with both hydrogen chloride resulting from the degradation and labile chlorine atoms as follows:

$$R_2Te(SR^1)_2 + 2HCl \longrightarrow R_2TeCl_2 + R^1SH$$



$$2\text{-CH=CH-}\underset{\text{Cl}}{\underset{|}{\text{CH}}}\text{-} + \text{R}_2\text{Te(SR}^1)_2 \longrightarrow 2\text{-CH=CH-}\underset{\text{SR}^1}{\underset{|}{\text{CH}}} + \text{R}_2\text{TeCl}_2$$

Scott(17,26) has shown that the addition of thiols to the unsaturation in the polymer proceeds by a radical catalysed reaction involving the conversion of free thiol to thioyl radicals:

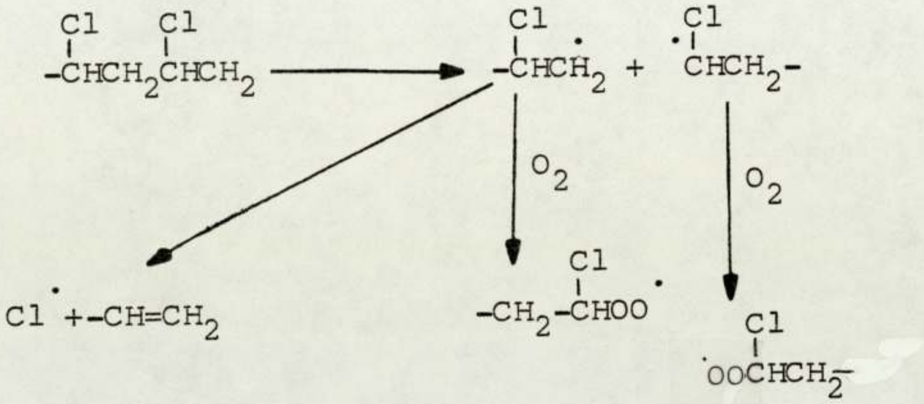


$$\text{-CH=CH-R} + \text{RSH} \xrightarrow[\text{catalyst}]{\text{peroxide}} \text{-CH}_2\text{-}\underset{\text{SR}^1}{\underset{|}{\text{CH}}}\text{-R}$$

The reaction of DPTeE with hydrogen chloride could lead to the corresponding EBHPT which simultaneously adds to the developed double bond in PVC during processing as in the case of thiols.(140-142) The behaviour of DPTeE is probably similar to the tin mercaptides which are known to exhibit effective decomposition of hydroperoxide.(26,47)

Fig 5.2, curve 'e' shows the effect of DPTe in combination with lubricants during processing of PVC. The DPTe is not a good stabiliser compared to other organotellurium compounds. It is possible that telluronium species were initially formed from the reaction of DPTe with PVC, and upon heating, diphenyltellurium dichloride is formed (as explained in model compound,Chapter 3). Alternatively, DPTe may decompose peroxides (as explained experimentally in Chapter 3) and competition between these two separate reactions leads ultimately to DPTe being a poor stabiliser for PVC.

Scott et al(21,26) have shown that the formation of hydrogen chloride, unsaturation and hydroperoxides are formed very rapidly in PVC during the first minutes of processing; when the applied shearing forces acting on the polymer are highest.



Hence, the initial rapid colour change and formation of unsaturation within the first 2.5 minutes of processing (Figs 5.4 and 5.5) is due to the three species as explained above.

5A-2-2 Effect of organotellurium compounds during thermal-oxidation

Fig 5.8 shows the discolouration in PVC films containing different concentrations of DPTeA (1%, 2% and 3%) in combination with lubricants, processed for 5 minutes, during thermal-oxidative ageing at 140°C. The control without additives had the deepest initial colour and under thermal-oxidative conditions accumulation of further discolouration occurs rapidly. The two lubricants did not have a significant effect on the level of discolouration. PVC containing 1% DPTeA show an induction period to colour formation followed by a rapid increase in discolouration (auto-accelerator). As the concentration of DPTeA increased the induction period to colour formation increased. A similar set of curves were obtained for DPTeM in combination with lubricants as shown in Fig 5.9 .

Fig 5.10 compares the change of colour during thermal-oxidation of PVC samples, processed for 5 minutes, containing organotellurium compounds with DBTM, PVC in combination with lubricants and of PVC without additives. The stabilising effects are in the following order:-
PVC without additives < PVC with lubricants < 3% DPTeA < 3% DPTeM < 3% DCTeA < 3% TeCM < 2% DBTM.

The stability effects of organotellurium compounds during thermal-oxidation are similar to that during processing and similar mechanisms are involved; notably neutralisation of hydrogen chloride, replacement of labile chlorine atoms and for DPTeM and TeCM reaction with conjugated unsaturation. DPTeA shows less stabilising activity in thermal-oxidation of PVC than DCTeA. The same behaviour was found in diaryltin and dialkyltin derivatives(143,144), and may be due to the fact that dicetyltellurium dichloride is a poorer catalyst (Lewis acid) for dehydrochlorination than diphenyltellurium dichloride during PVC degradation. The auto-accelerator shown by DPTeA and DPTeM could be due to the diphenyltellurium dichloride. Diorganotellurium dichloride is a product of the reaction of diorganotellurium diacetate with hydrogen chloride and labile chlorine atoms (as described experimentally in Chapter 3).

5A-2-3 Effect of organotellurium compounds during UV exposure

The change in colour during photo-oxidation of PVC samples processed for 5 minutes, with DPTeA at different concentrations (1%, 2% and 3%) in combination with lubricants is shown in Fig 5.11 . The PVC films without additives which had substantial initial colour darkened rapidly during the photo-oxidation. The colour change of PVC films containing DPTeA in the early stages of exposure increased rapidly, but after about 50 hours of exposure further discolouration was relatively slow (auto-retardation). Auto-retardation after initial rapid photo-oxidation may be due to the formation of a light screening surface layer consisting mainly of long conjugated unsaturation sequences.(21) The colour change at the later stages of photo-oxidation was higher at higher concentrations of DPTeA. A similar set of curves were obtained for colour formation in PVC films containing different concentrations (1%, 2% and 3%) of DPTeM, Fig 5.12 .

Carbonyl formation during photo-oxidation of PVC samples containing DPTeM and DPTeA at varying concentrations in combination with lubricants are shown in Figs 5.17 and 5.16 respectively. The rate of carbonyl formation is similar to that of colour change.

Figs 5.15, 5.16 curve 'e' and 5.17 curve 'e' show the effect of DCTeA and TeCM together with lubricants on photo-oxidation of PVC films. These compounds did not cause a rapid increase in the level of the discolouration or rate of carbonyl formation.

On UV exposure of PVC films containing DPTeM and DPTeA, a pro-oxidant effect is observed with a simultaneous disappearance of the carboxylate peak at 1640-1575cm^{-1} in the early hours of irradiation (Fig 5.20). This is an indication that these compounds were photolysed in the early stages of UV irradiation. The photo-pro-oxidant effect shown by these compounds may be caused by the phenyl groups. However, DPTe showed less stabiliser activity than DCTe during the photo-oxidation of PP (Fig 5.31). This may also suggest that the pro-oxidant behaviour is due to the phenyl groups.

The combination of HOBP with DPTeM at different percent ratio (2%:1%, 1.5%:1.5% and 1%:2%) showed an induction period to colour formation(Fig5.14)(reduction in the rate photo-oxidation compared with DPTeM alone) followed by increasing colour formation. The stabilising effect in terms of induction period, increased as the concentration of HOBP was increased in the system. The carbonyl formation for the above formulations is shown in Fig 5.18. At 2%:1% ratio a reduced rate of carbonyl formation was observed compared to DPTeM alone. The rate of carbonyl formation rising slowly with time of irradiation. The reduction in the rate of carbonyl formation increased as the concentration of HOBP increased.

Thus the stabilising effect observed for the combination is due to the screening behaviour of HOBP(48,142,145,146) which prevents the decomposition of DPTeM and protects the polymer from UV light. Fig 5.20 shows that the carboxylate peak at 1640-1575cm^{-1} decreased during the irradiation. This result may suggest that the DPTeM remaining in the polymer after processing might now react with hydrogen chloride. It could also be that the maleate group reacts with reactive sites (chlorine atoms) and with conjugated unsaturation.

DPTeE at different concentrations (1%, 2% and 3%) processed for 5 minutes shows an induction period for colour formation (Fig 5.13) and reduction in the rate of photo-oxidation (Fig 5.19) compared to DPTeM and DPTeA. However, DPTeE shows similar behaviour to the combination of HOBP/DPTeM. It seems likely that the

2-hydroxybenzophenone moiety acted as a light screen to protect the phenyl groups and the polymer from the UV light. Scott et al (142) have shown that EBHPT has the ability to react with developing unsaturation and peroxide in the PVC during photo-oxidation. However, the effect of DPTeE could be due to its reaction with hydrogen chloride during the photo-oxidation to give EBHPT. Then EBHPT reacts with unsaturation and peroxide as Scott pointed out.

Fig 5.15 compares colour formation during the photo-oxidation of PVC samples (processed for 5 minutes) containing organotellurium compounds, varying ratios of DPTeM/HOBP were compared with DBTM, PVC in combination with lubricants and PVC without additives. The level of discolouration (stabilising effect) of these compounds is in the following order:-
PVC with additives < PVC with lubricants < 3% DPTeA up to 100 hours < 3% DPTeM up to 100 hours < 3% DCTeA < 3% TeCM < 2% DPTeM: 1% HOBP < 1.5% DPTeM: 1.5% HOBP ≤ 3% DPTeE < 1% DPTeM: 2%HOBP ≤ 2% DBTM

Organotellurium compounds have been shown to be good stabilisers during processing and thermal oxidation for PVC, though not quite as efficient as DBTM (a commercial stabiliser for PVC). In general, organotellurium compounds do not lead to good UV stabilising properties in PVC, but when used in combination with HOBP or when analogues of HOBP is incorporated into the organotellurium molecule a marked improvement in activity was observed.

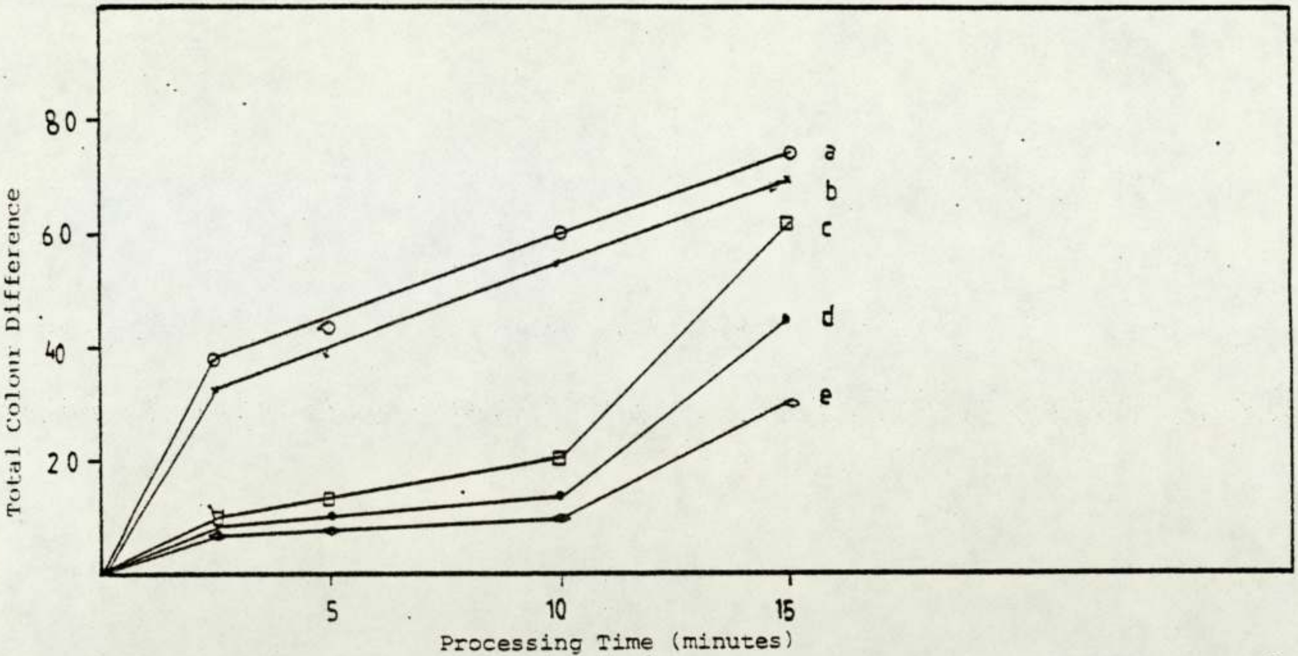


Fig 5.1 Colour formation in PVC during processing at 170°C (closed mixer) a- PVC without additives, b-PVC with lubricants, c- 1% DPTeM, d-2% DPTeM, e- 3% DPTeM (c-e with lubricants)

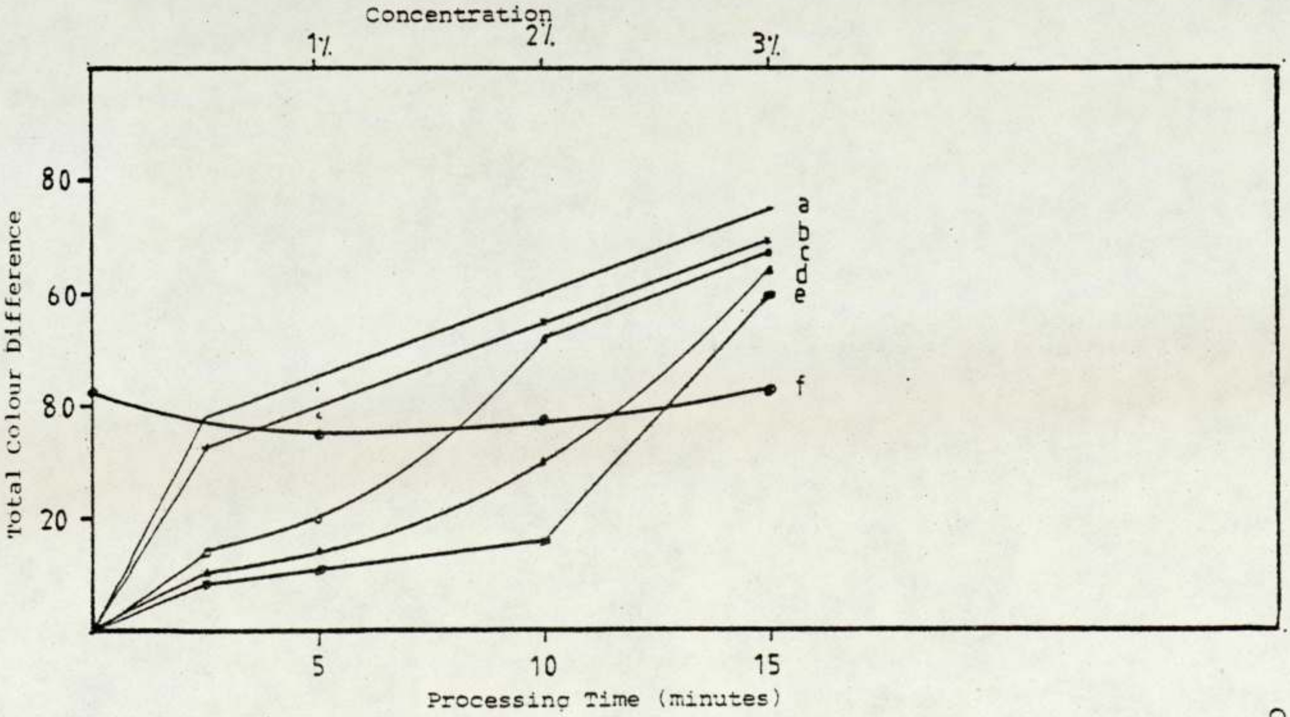


Fig 5.2 Colour formation in PVC during processing at 170°C (closed mixer) a- PVC without additives, b-PVC with lubricants, c- 1% DPTeA, d- 2% DPTeA, e-3% DPTeA, f-DPTe (5 mins processed) (c-f with lubricants)

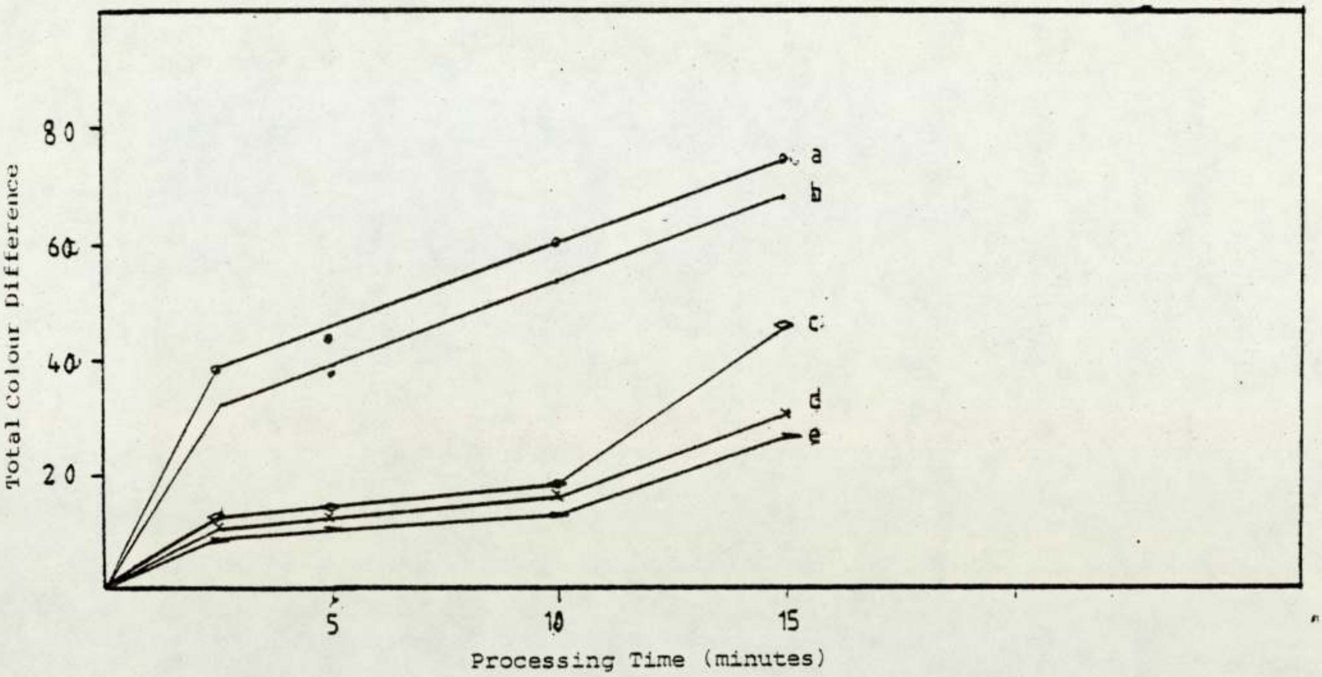


Fig 5.3 Colour formation in PVC during processing at 170°C (closed mixer) a- PVC without additives, b- PVC with lubricants, c- 1% DPTeE, d- 2% DPTeE, e- 3% DPTeE (c-e with lubricants)

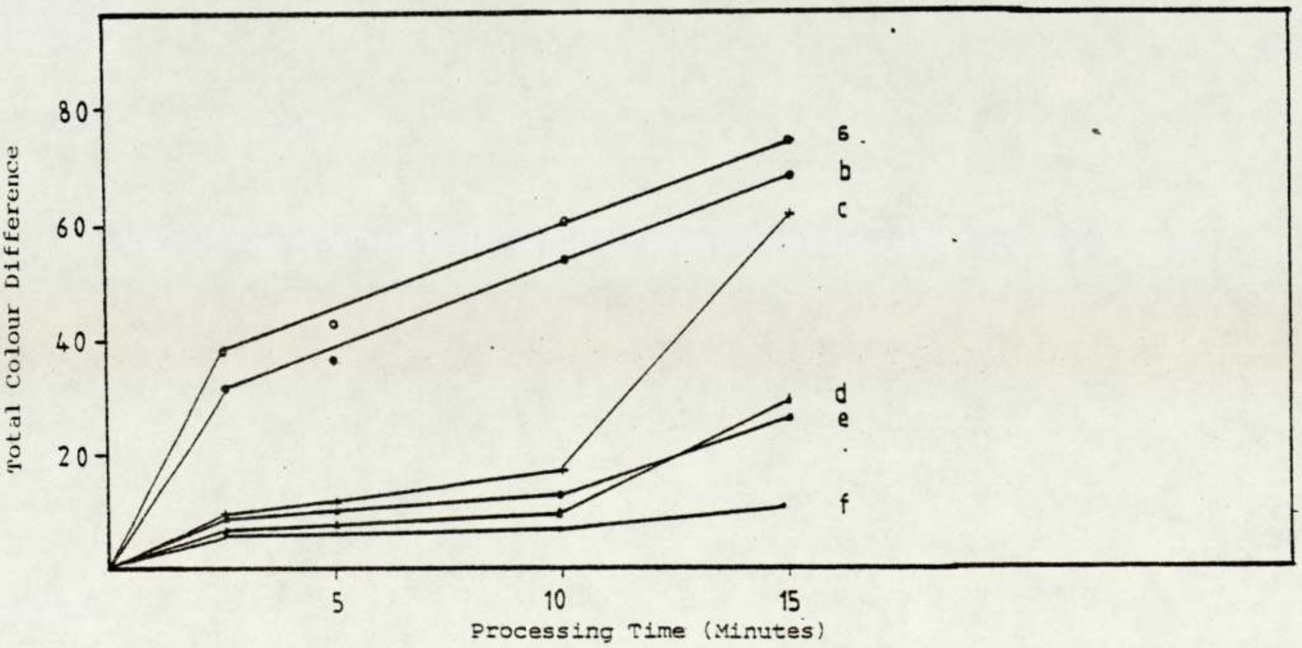


Fig 5.4 Colour formation in PVC during processing at 170°C (closed mixer) a- PVC without additives, b-PVC with lubricants, c- 3% DPTeA, d- 3% DPTeM, e- 3% DPTeE, f- 2% DBTM (c-f with lubricants)

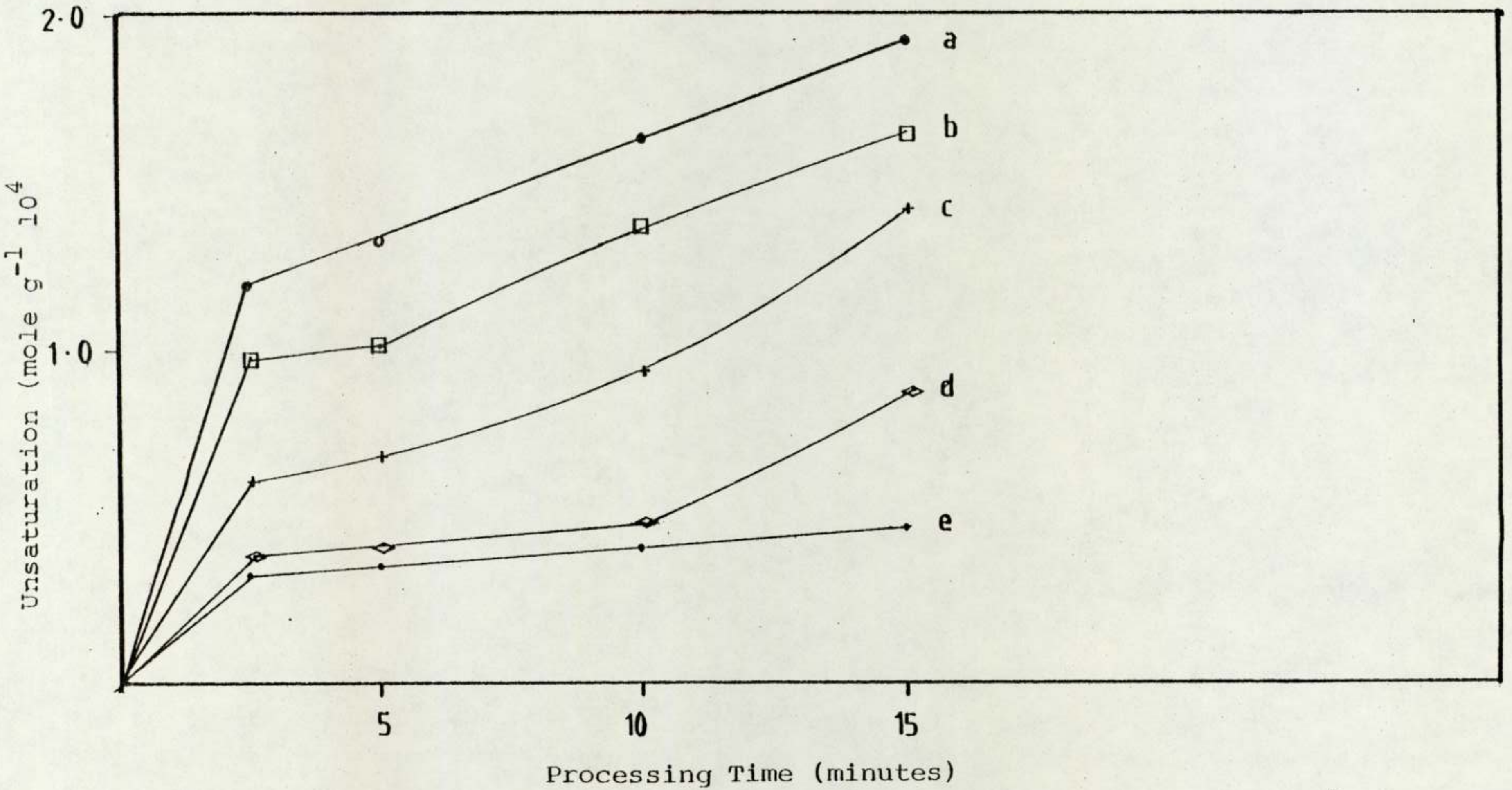


Fig 5.5 Formation of unsaturation in PVC during processing at 170^{o}C (closed mixer)
a - PVC without additives, b - PVC with lubricants, c - 3% DPTeA
d - 3% DPTeM, e- 2% DBTM (c-e with lubricants)

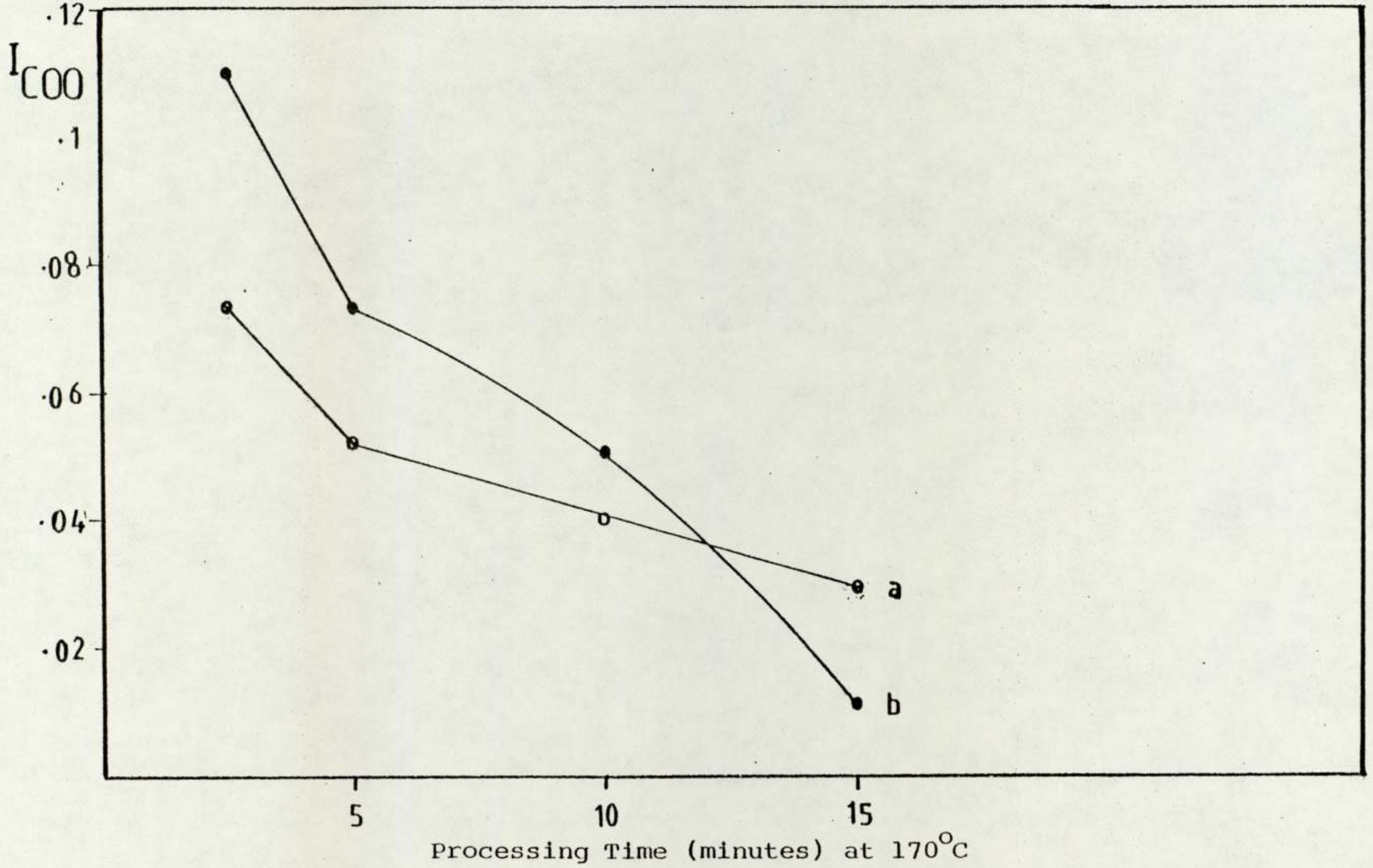


Fig 5.6 Carbonyl index of PVC processed with organotellurium compounds.
a - 3% DPTeM at 1560cm^{-1}, b- 3% DPTeA at 1630cm^{-1}

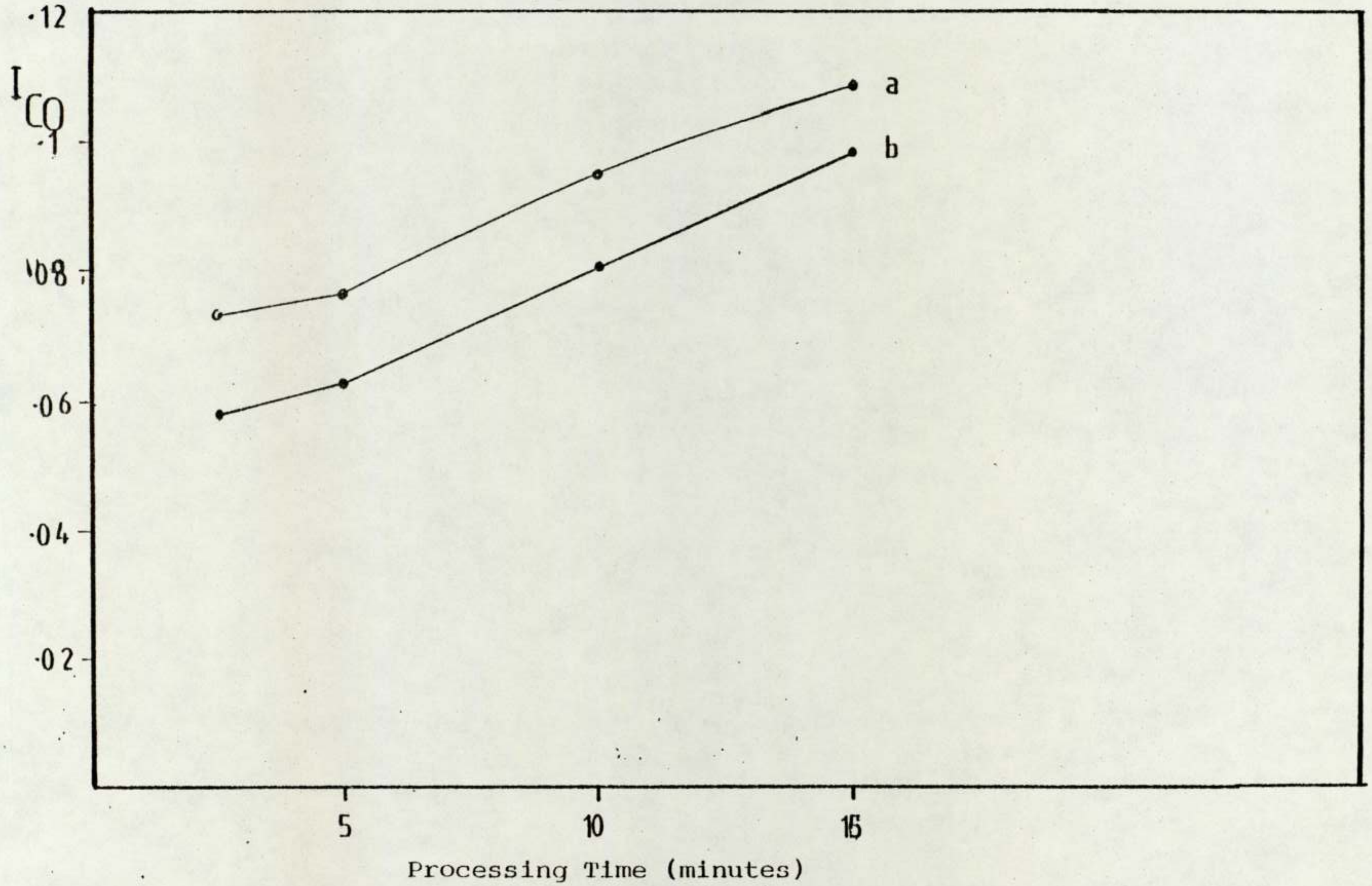


Fig 5.7 Carbonyl Index I_{CO} 1735 cm^{-1} of PVC processed with organotellurium compounds. a- 3% DPTeM, b- 3% DPTeA

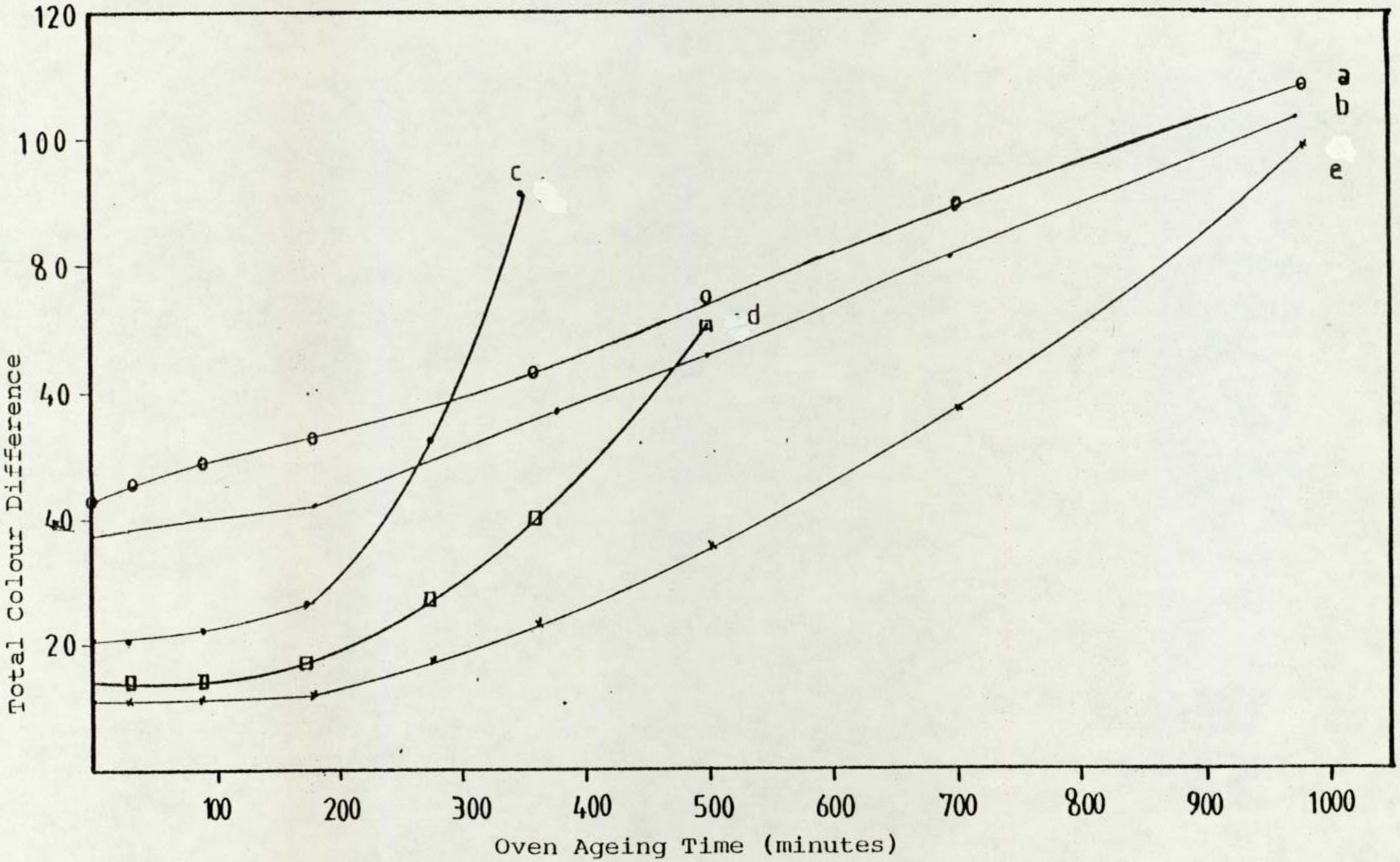


Fig 5.8 Colour formation during oven ageing of PVC at 140^{O}C (processing time 5 minutes). a - PVC without additives, b- PVC with lubricants, c - 1% DPTeA, d- 2% DPTeA, e- 3% DPTeA, (c-e with lubricants)

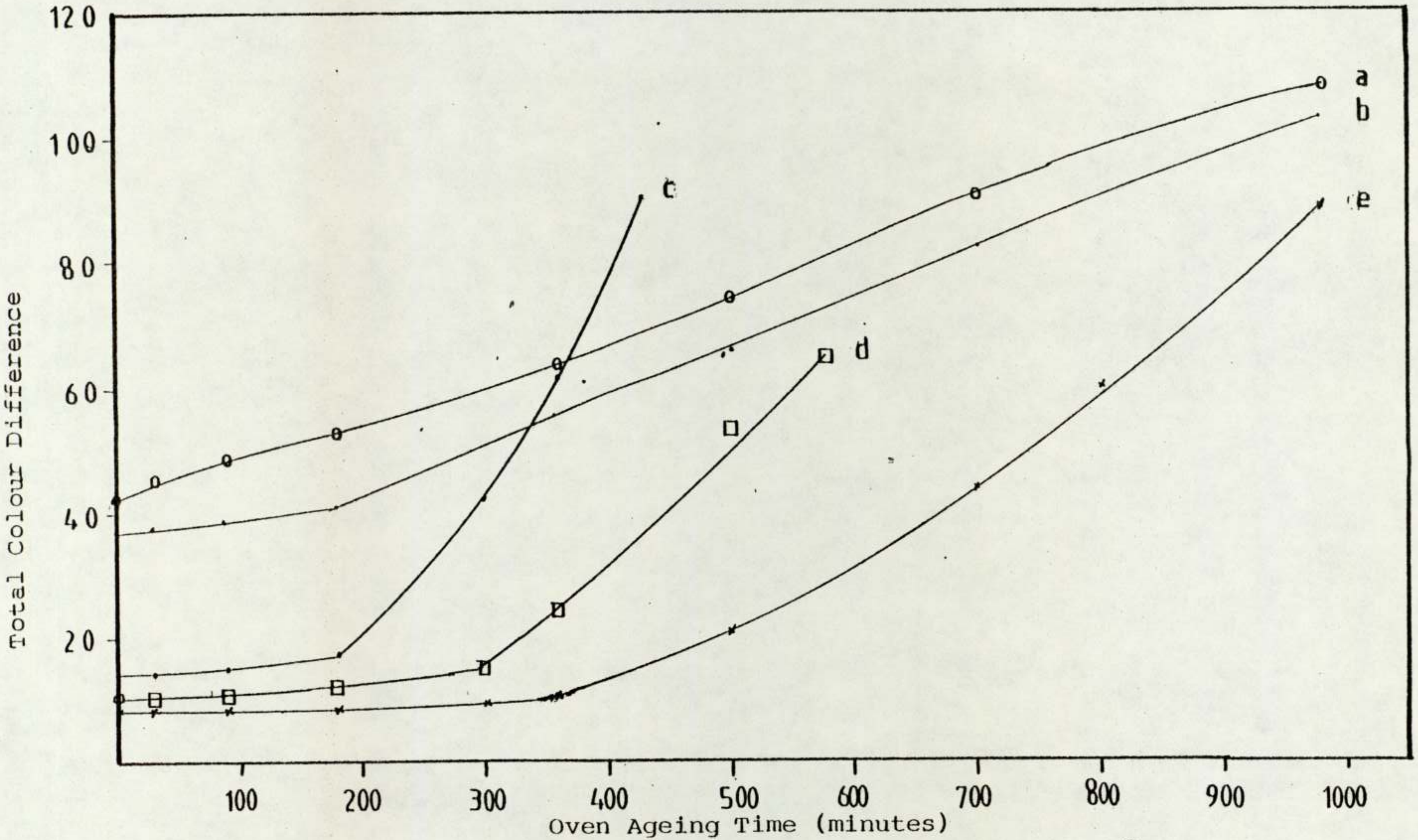


Fig 5.9 Colour formation in PVC during oven ageing at 140^0C (processing time 5 minutes). a - PVC without additives, b - PVC with lubricants, c - 1% DPTeM, d- 2% DPTeM, e- 3% DPTeM (c-e with lubricants)

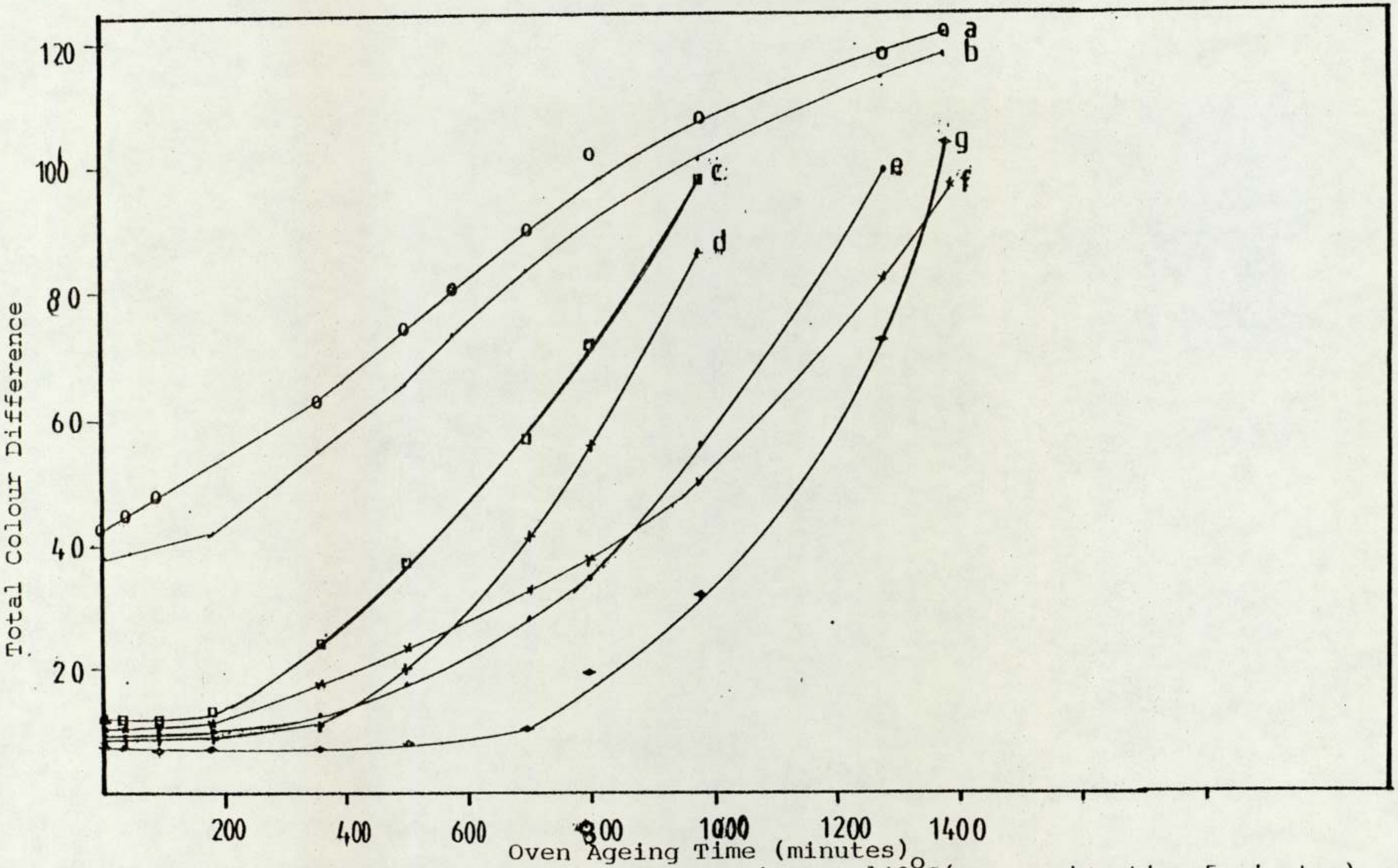


Fig 5.10 Colour formation in PVC during oven ageing at 140°C (processing time 5 minutes)

a - PVC without additives, b- PVC with lubricants, c- 3% DPTeA, d- 3% DPTeM

e - 3% TeCM, f- 3% DCTeA, g- 2% DBTM (c-g with lubricants)

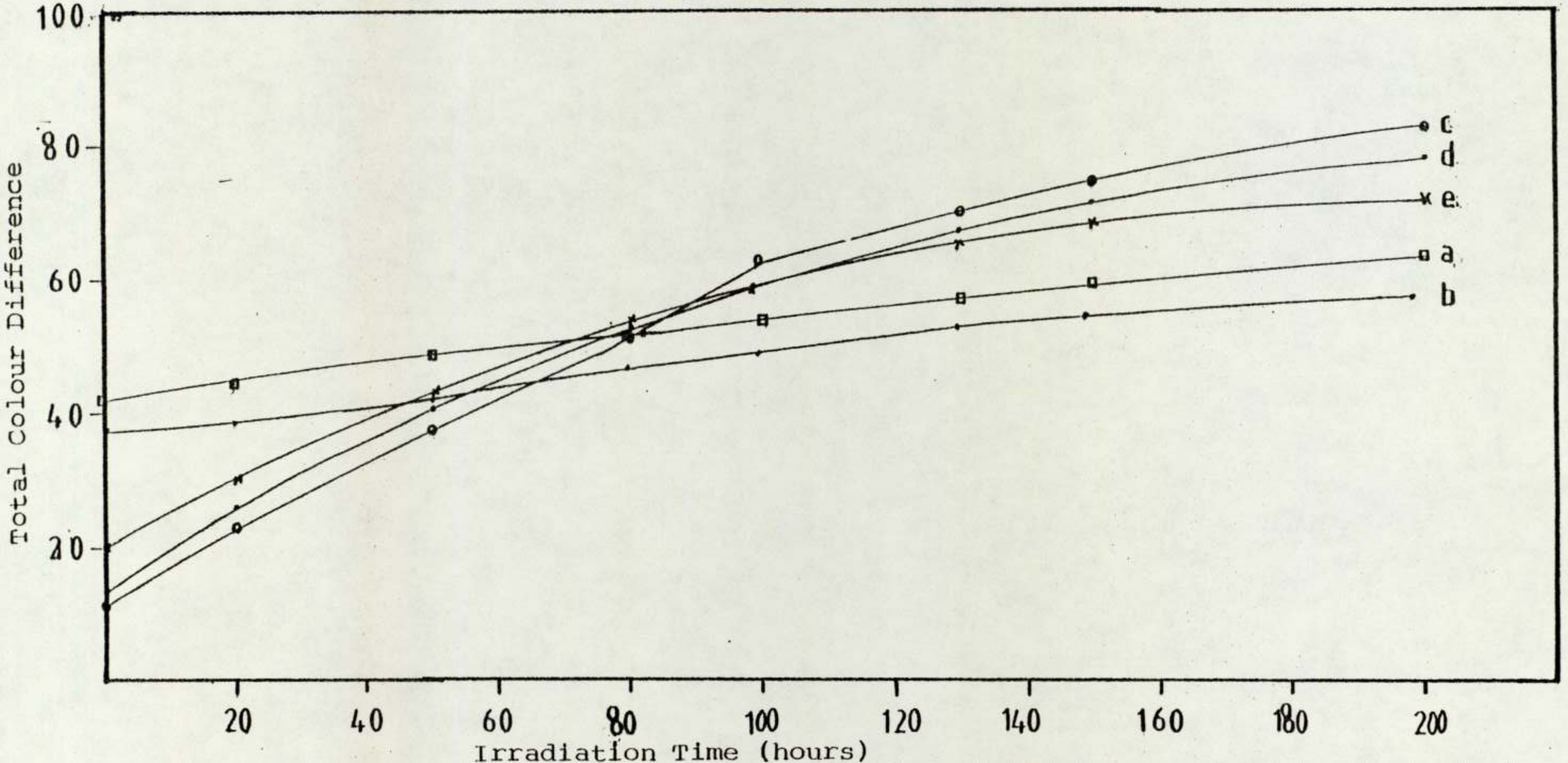


Fig 5.11 Colour formation during UV irradiation of PVC (processing time 5 minutes)
a - PVC without additives, b - PVC with lubricants, c - 1% DPTeA
d - 2% DPTeA, e - 3% DPTeA (c-e with lubricants)

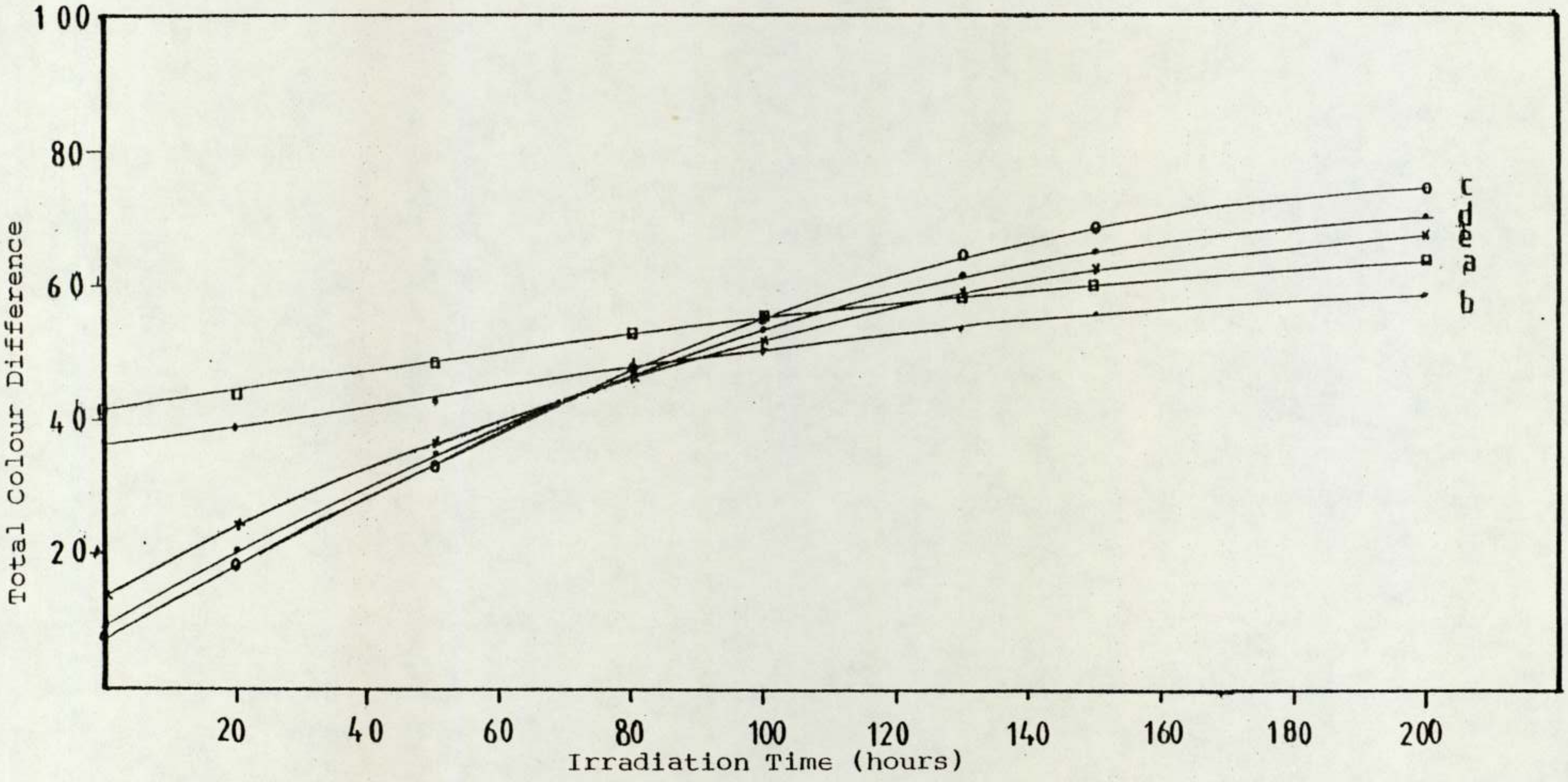


Fig 5.12 Colour formation during UV irradiation of PVC(processing time 5 minutes)
a - PVC without additives, b - PVC with lubricants, c - 1% DPTeM
d - 2% DPTeM, e - 3% DPTeM (c-e with lubricants)

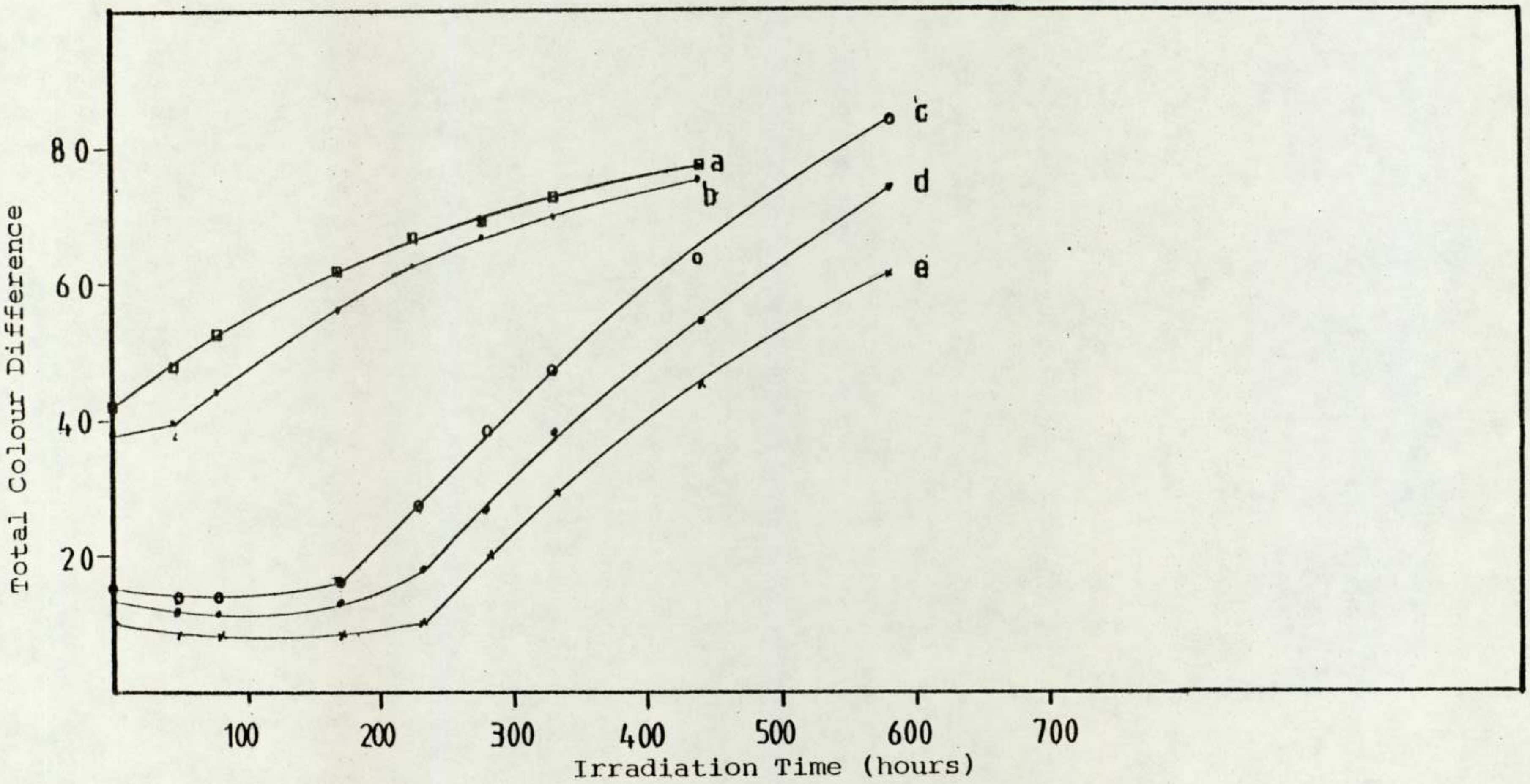


Fig 5.13 Colour formation during UV irradiation of PVC(processing time 5 minutes)

a - PVC without additives, b - PVC with lubricants, c - 1% DPTeE

d - 2% DPTeE, e - 3% DPTeE (c-e with lubricants)

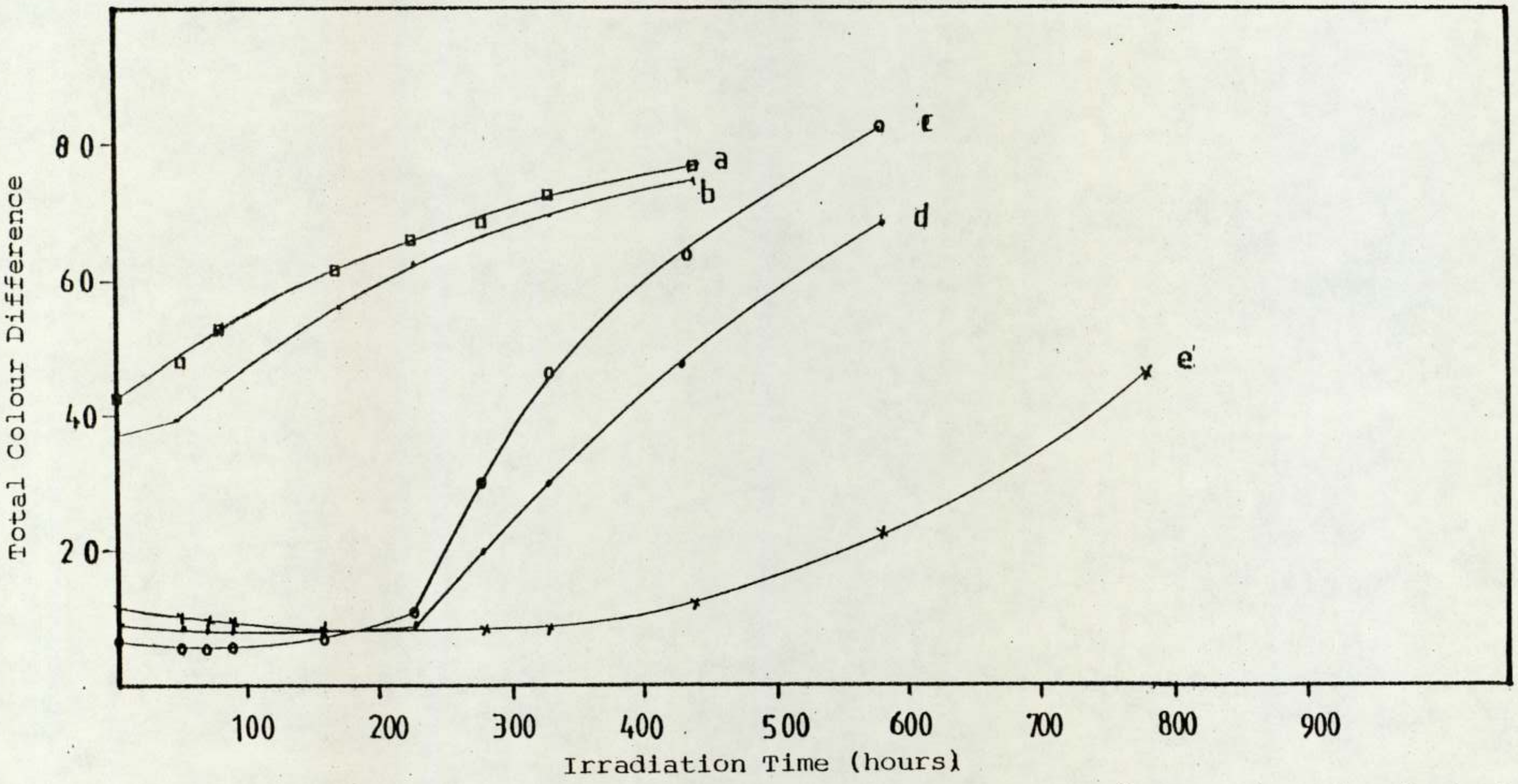


Fig 5.14 Colour formation during UV irradiation of PVC (processing time 5 minutes)

a - PVC without additives, b - PVC with lubricants, c - 2% DPTeM : 1% HOBP
d - 1.5% DPTeM : 1.5% HOBP, e - 1% DPTeM : 2% HOBP (c-e with lubricants)

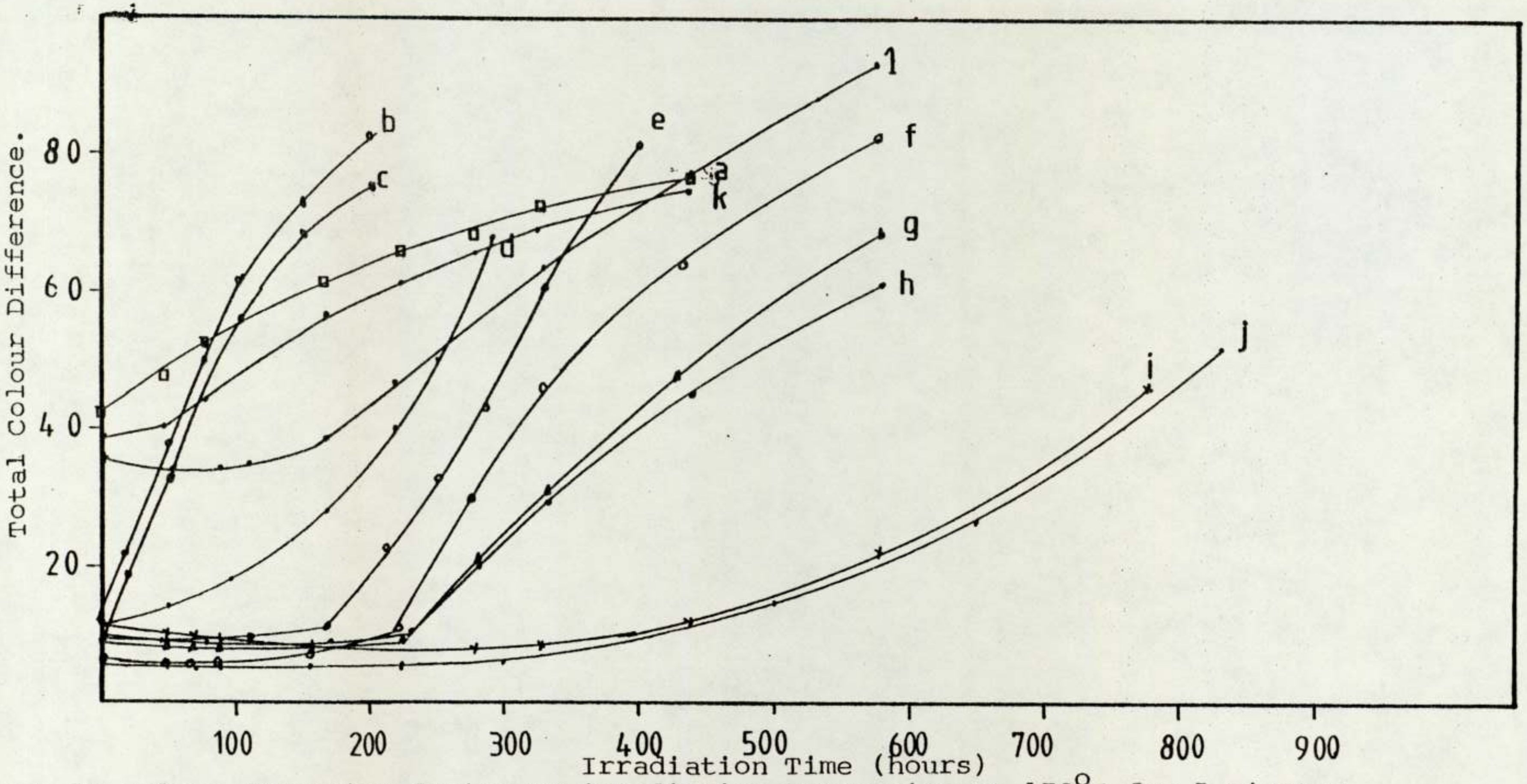


Fig 5.15 Colour formation during UV irradiation processing at 170°C for 5 minutes.
a - PVC without additives, b - PVC with lubricants, c - 3% DPTeA, d - 3% DPTeM
e - 3% DCTeA, f - 3% TeCM, g - 2% DPTeM:1% HOBP, h - 3% DPTeE, i - 1.5% DPTeM:1.5% HOBP
j - 1% DPTeM:2% HOBP, k - 2% DBTM, l - 1% HOBP(c-l with lubricants)

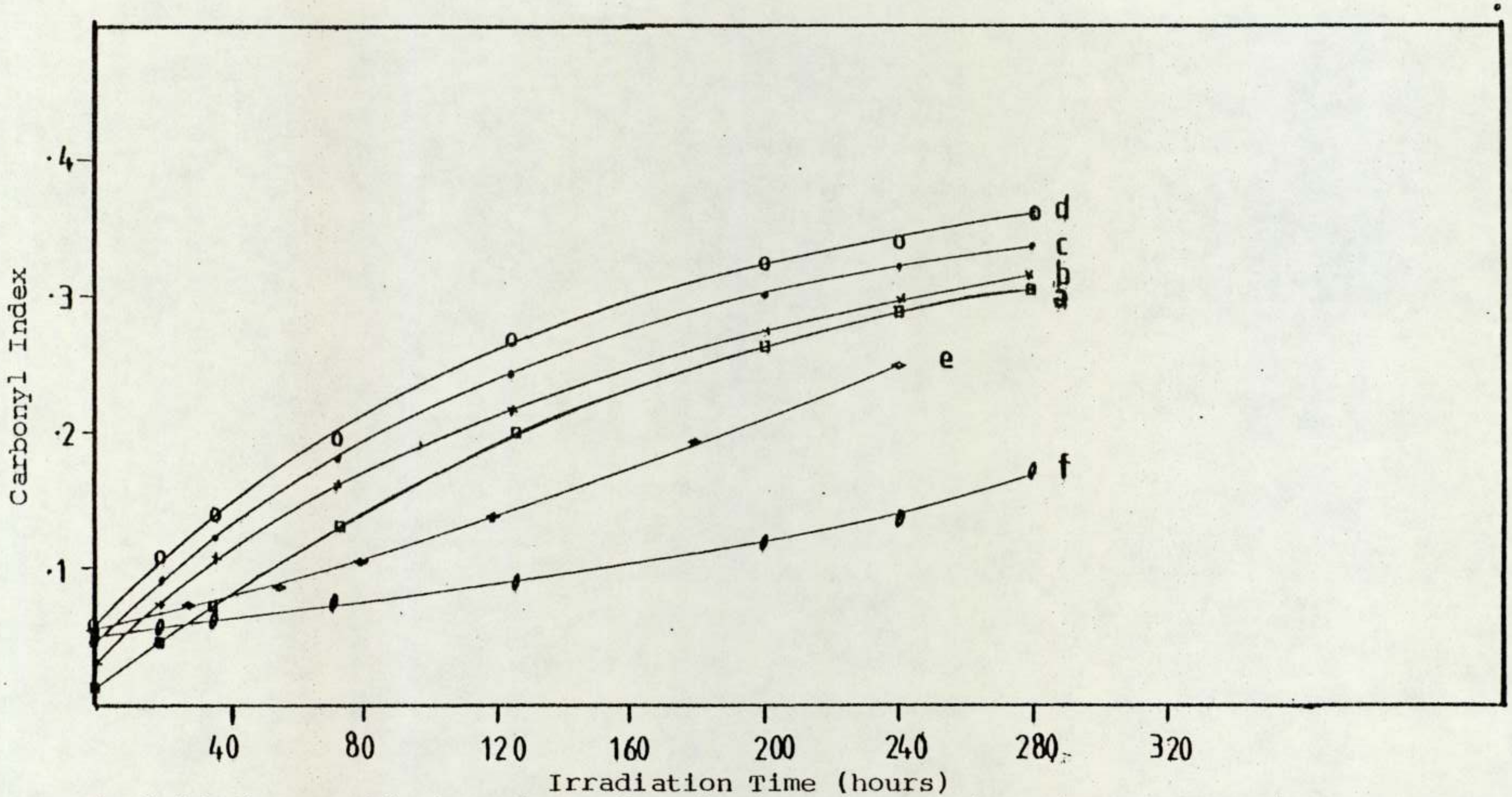


Fig 5.16 Photo-oxidation of PVC formulations (processing time 5 minutes)

a - PVC without additives, b - 1% DPTeA, c- 2% DPTeA, d - 3% DPTeA

e - 3% DCTeA, f - 2% DBTM (b-f with lubricants)

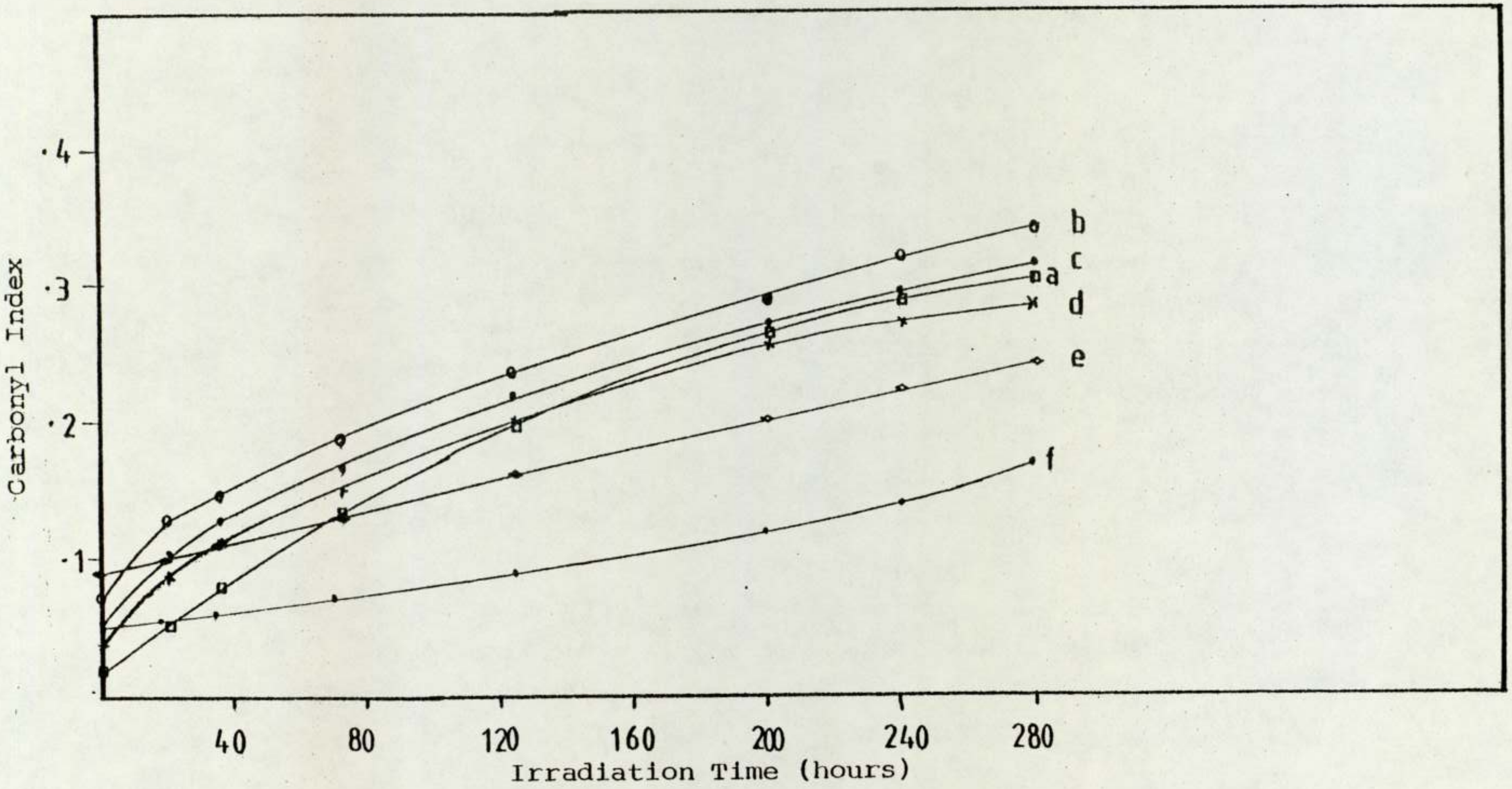


Fig 5.17 Photo-oxidation of PVC formulations (processing time 5 minutes)

a - PVC without additives, b- 3% DPTeM, c - 2% DPTeM, d - 1% DPTeM

e - 3% TeCM, f - 2% DBTM (b-f with lubricants)

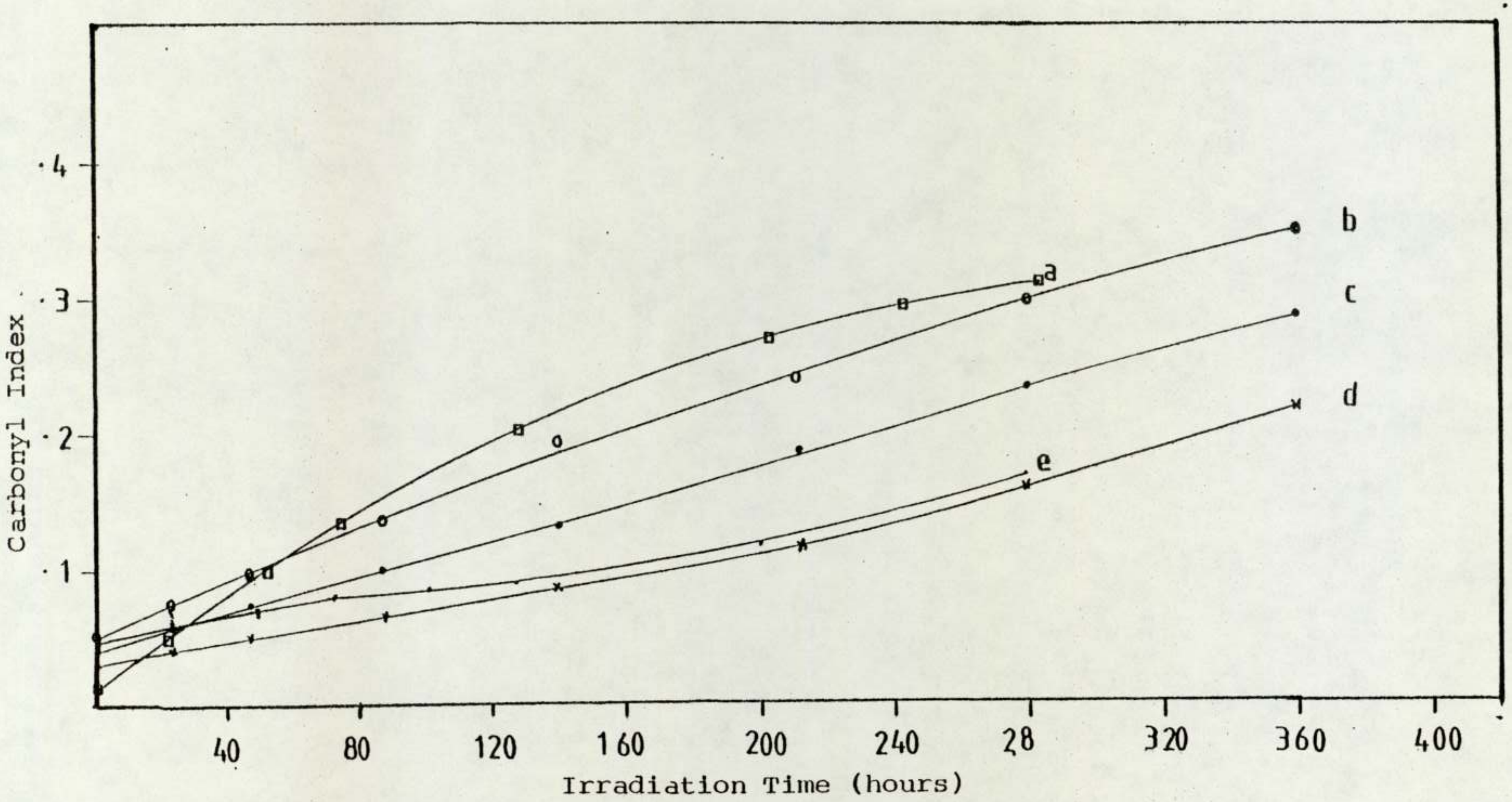


Fig 5.18 Photo-oxidation of PVC formulations (processing time 5 minutes)

a - PVC without additives, b - 2% DPTeM:1% HOBP, c- 1.5%DPTeM:1.5% HOBP

d - 1% DPTeM:2% HOBP, e - 2% DBTM (b-e with lubricants)

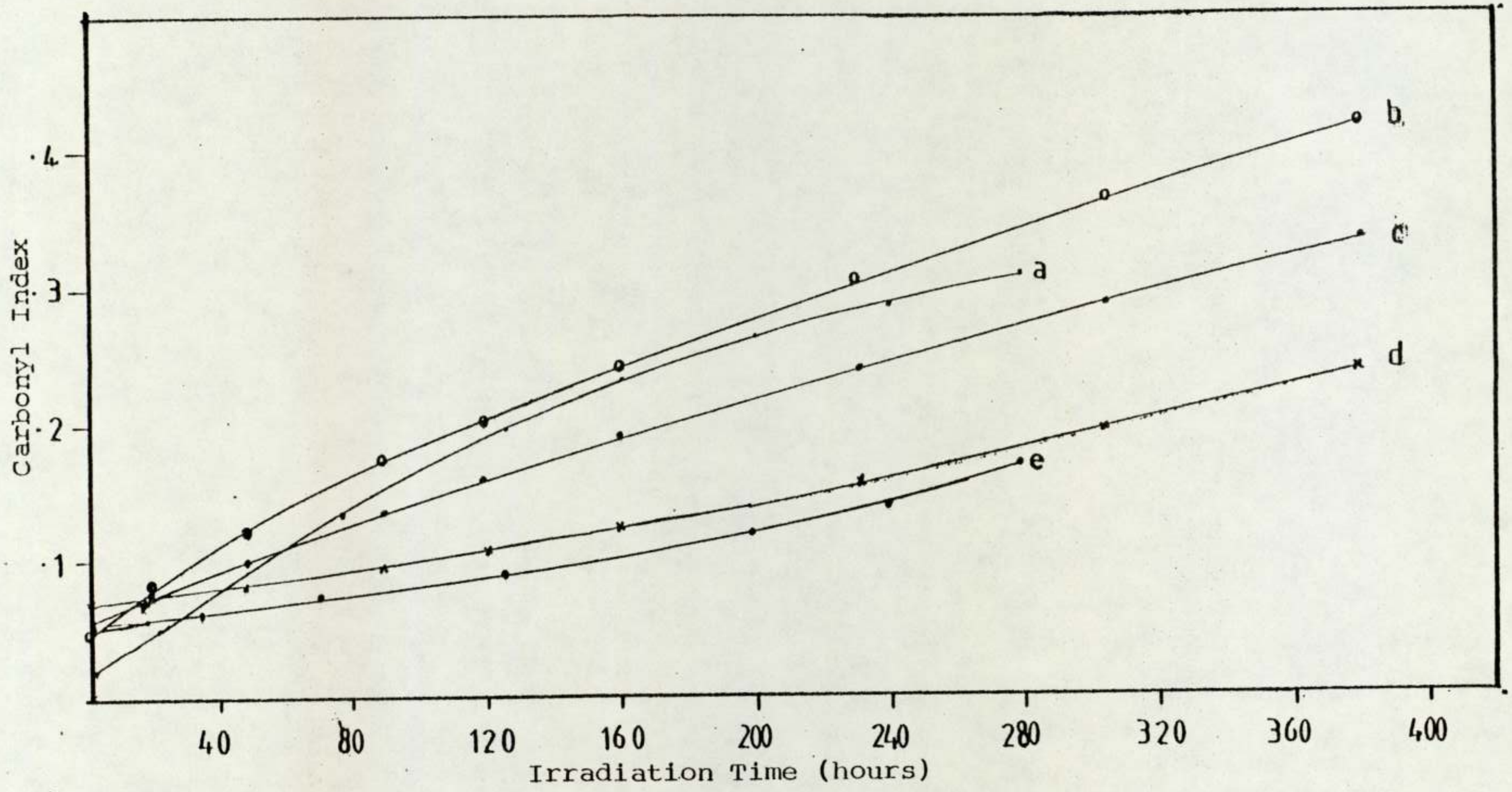


Fig 5.19 Photo-oxidation of PVC formulations (processing time 5 minutes)
a - PVC without additives, b - 1% DPTeE, c - 2% DPTeE, d - 3% DPTeE,
e - 2% DBTM (b-e with lubricants)

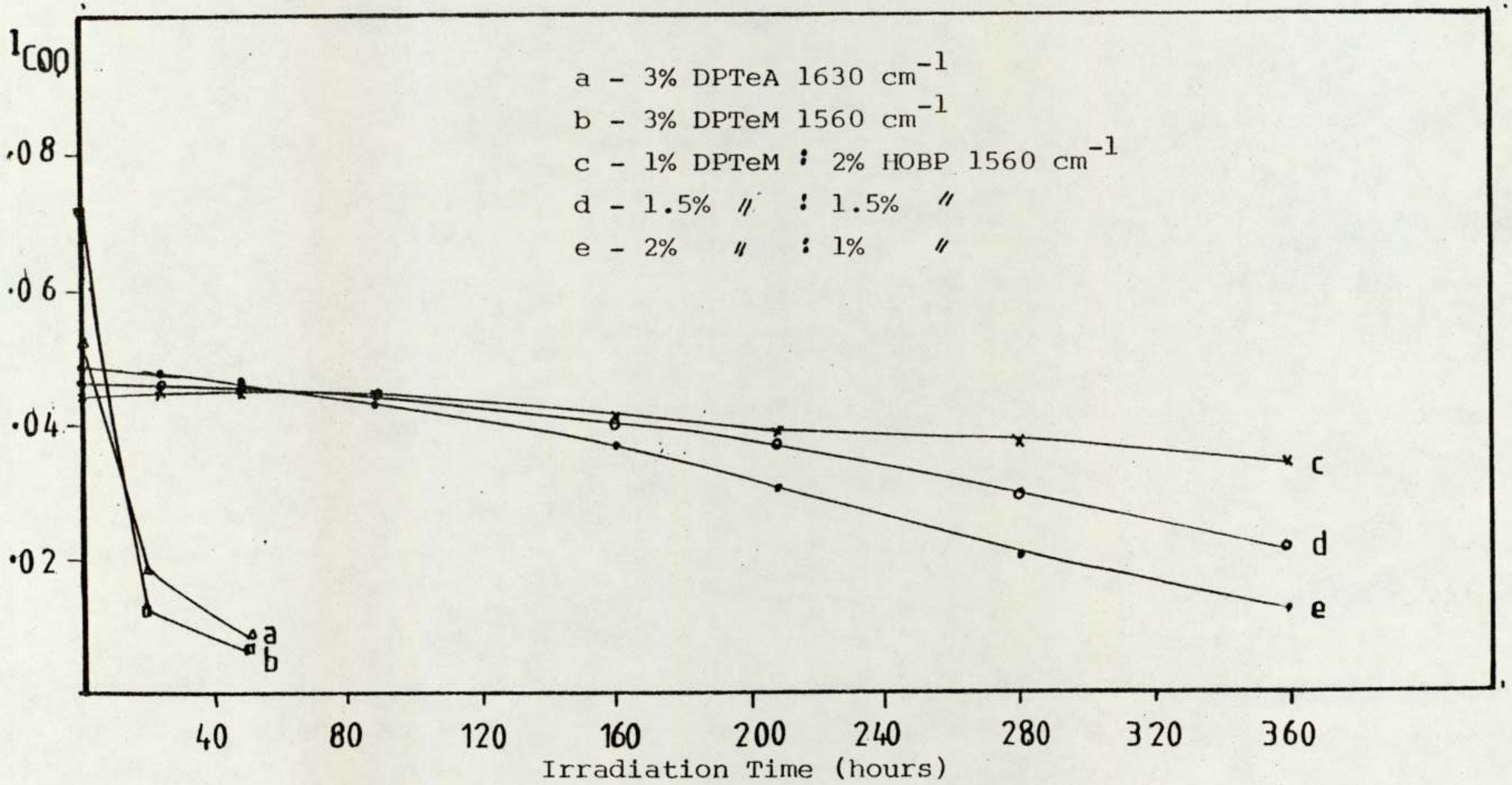


Fig 5.20 Decrease in carbonyl index at 1630 and 1560 cm^{-1} during UV exposure

5B-STABILISATION OF POLYPROPYLENE (PP)

It has been mentioned that (Chapter 1) sulphur containing compounds such as metal dithiocarbamates have been used as thermal and UV stabilisers for polyolefins. Te(dtc)$_4$ has been used in rubber to improve rubber compositions to ageing. It seems appropriate, therefore, to investigate the effect of Te(dtc)$_4$ and Te(dtc)$_2$ in PP as thermal and UV stabilisers.

5B-1 Experimental

PP was processed at 180°C with additives for various periods of time (5, 10 and 20 minutes) in a closed mixer and the processed samples were then compressed into films, as described in Chapter 2, to study the thermal and photo-oxidation.

5B-1-1 Thermal stability of Te(dtc)$_4$

Te(dtc)$_4$ (2gm) was dissolved in xylene ($\simeq$ 30ml). The mixture was gently heated and refluxed for about 5 hours. The colour of the mixture started to change from canary yellow to a red colour in the early stages of the reflux. The main products of the reaction were Te(dtc)$_2$ and TETD which were separated by preparative thin layer chromatography and column chromatography respectively, using $CHCl_3$. The products were identified by melting points and elemental analyses (Table 4-1).

5B-2 Results and discussion

The effect of $Te(dtc)_4$ and $Te(dtc)_2$ on the oxidation stability of PP during processing are compared with PP without additives in Fig 5.21 . Initial carbonyl and melt flow index of PP without additives showed a steady increase with processing time indicating that considerable oxidation took place during the processing. Whereas the initial carbonyl and melt flow index of PP containing $Te(dtc)_4$ and $Te(dtc)_2$ were found to be constant up to 20 minutes of processing. This indicates that both additives effectively inhibit oxidation of PP during processing.

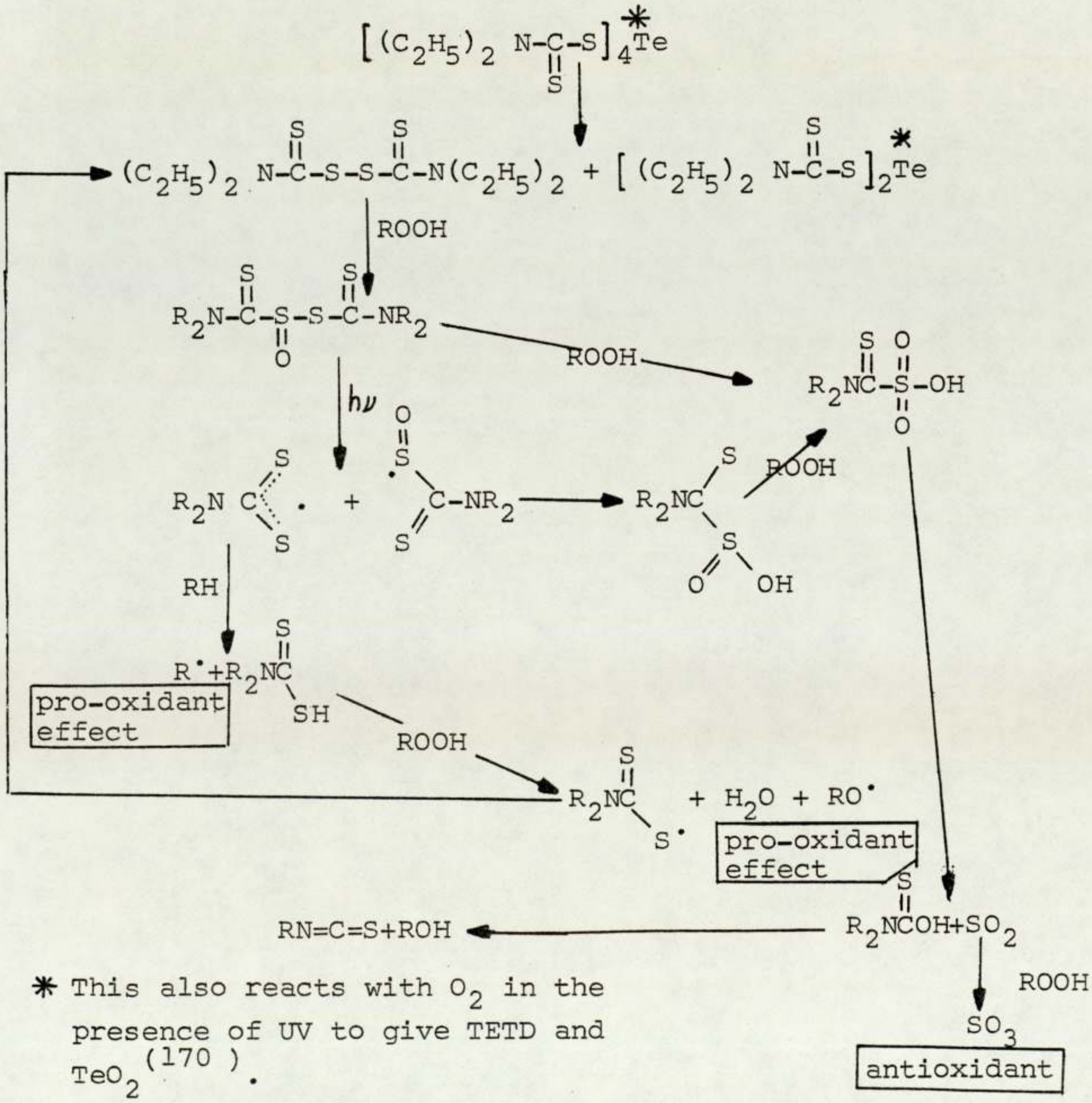
The effect of varying the concentrations (0.7×10^{-4} , 1.4×10^{-4} and 2.8×10^{-4} mole/100g) of $Te(dtc)_2$ and $Te(dtc)_4$ on photo-oxidation of PP in the form of compression moulded films all processed for 5 minutes at 180°C in a closed mixer are shown in Figs 5.22 and 5.23 respectively. On UV irradiation, it appears that the above additives at all concentrations show a stabilising action as evidenced by the length of the induction period and time to embrittlement (Table 4-2). The carbonyl values of PP containing $Te(dtc)_2$ and $Te(dtc)_4$ which are initially lower than that of PP without additives, remain constant during the induction period. At the end of the induction period, the rate of carbonyl formation (the rate of photo-oxidation) becomes auto-catalytic. Increasing the concentration of $Te(dtc)_2$ and $Te(dtc)_4$ in PP from 0.7×10^{-4} to 2.8×10^{-4} mole/100g increases the induction period and subsequently increases the UV life time of PP, Fig 5.39 (Table 5-2). This clearly suggests that the stabilising activity of $Te(dtc)_2$ and $Te(dtc)_4$ begins in the processing operation and is carried through to the initial UV exposure stage.

Fig 5.24 shows the effect of the severity of processing on PP containing the same molar concentration (2.8×10^{-4} mole/100g) of $Te(dtc)_2$ during the UV irradiation. On increasing the processing time results in a slight decrease in the photo-stability of PP. A similar set of curves were obtained for 0.7×10^{-4} and 1.4×10^{-4} mole/100g concentration of $Te(dtc)_2$ in PP as shown in Figs 5.25 and 5.26 respectively. However, Scott et al (147-149) have shown that the photo-oxidative stability of PP is markedly dependent on the previous thermal history which appears to depend primarily on the amount of hydroperoxide formed during processing. The slight reduction in the effectiveness of $Te(dtc)_2$ in the higher processing time could be due to the reaction of $Te(dtc)_2$ with peroxide in the system during processing which could reduce the concentration of the additive.

Fig 5.27 shows the effect of processing conditions on the photo-stability of PP containing 2.8×10^{-4} mole/100g of

$Te(dtc)_4$. It is clear that the severity of processing affects dramatically the photo-stability of PP. The induction period showed by 5 minutes processed sample is completely absent in the case of 10 and 20 minutes processed samples. Moreover, the PP samples containing $Te(dtc)_4$ which were subjected to a severe processing condition showed an initial pro-oxidant effect which increased with the severity of processing followed by a complete retardation. Finally, after the retardation period the rate of the carbonyl formation was found to increase in an auto-catalytic way as did that of the control and continued until the PP embrittled. As the processing time increased the photo-stability of PP increased and subsequently the life time also increased (Table 5-2). A similar behaviour is also observed at 0.7×10^{-4} and 1.4×10^{-4} mole/100g of $Te(dtc)_4$ (Figs 5.28 and 5.29 respectively).

It seems likely that the $Te(dtc)_4$ undergoes decomposition to TETD and $Te(dtc)_2$ during processing at a temperature of 180°C. Similar products were also isolated on heating the $Te(dtc)_4$ at 140°C (see section 5B-1-1). The addition of TETD to $Te(dtc)_2$ at equimolar (1.4×10^{-4} TETD + 1.4×10^{-4} $Te(dtc)_2$ mole/100g) give an entirely similar trend to that of $Te(dtc)_4$ in PP photo-oxidation, Fig 5.30. These results suggest that $Te(dtc)_4$ is decomposed in to $Te(dtc)_2$ + TETD during the high temperature processing. The increase in the UV stability of PP and the initial pro-oxidant effect observed during the photo-oxidation containing Te(dtc)$_4$ is certainly due to the TETD. It is well known(150-152,162) that most of the disulphides show initial pro-oxidant effects in the polymer. The following reaction scheme for TETD, mainly based on the comprehensive research of Scott et al(151,152) on the reaction of other dithiocarbamates, suggests the possible routes for the pro-oxidant and an increase in the UV stability of PP containing Te(dtc)$_4$.



✱ This also reacts with O_2 in the presence of UV to give TETD and TeO_2(170).

It is evident from the embrittlement time (Table 5-2) that $Te(dtc)_4$ is a better UV stabiliser in PP than $Te(dtc)_2$ at the same concentration. This could be due to decomposition of $Te(dtc)_4$ into TETD and $Te(dtc)_2$ during processing which subsequently affect the photo-oxidation of the polymer.

Fig 5.31 shows the effect of DCTe and DPTe at 2.8×10^{-4} mole/100g on PP during UV irradiation. The DPTe showed less stabilising effect than DCTe. This could be due to the phenyl groups as explained earlier. The role of the telluride could be to decompose peroxides as described experimentally in Chapter 3.

$$R2Te + ROOH \longrightarrow R_2TeO + ROH$$

The effects may also be due to the telluride acting as a radical trap(89).

The effect of varying the concentration (0.7×10^{-4}, 1.4×10^{-4} and 2.8×10^{-4} mole/100g) of $Te(dtc)_2$ on the thermal oxidative stability of PP films in a Wallace oven at 140°C is shown in Fig 5.32. The rate of carbonyl formation for PP without additives started to increase rapidly from the beginning of the thermal oxidation. Whereas the rate of carbonyl formation for the films containing $Te(dtc)_2$ 2.8×10^{-4} mole/100g remain constant up to $\simeq$ 31 hours. At the end of the induction period the rate of carbonyl increased rapidly until the PP embrittled. It appears from the results that as the concentration increases, the induction period increases and hence the thermal stability of the PP. A similar set of curves was obtained for $Te(dtc)_4$ on varying the concentration (0.7×10^{-4}, 1.4×10^{-4} and 2.8×10^{-4} mole/100g) on thermal oxidation of PP (Fig 5.33). Comparison of the effect of $Te(dtc)_2$ and $Te(dtc)_4$ at the same molar concentration on thermal oxidative stability of PP is shown in Figs 5.32 and 5.33. It appears that $Te(dtc)_4$ gives much better stability than $Te(dtc)_2$. This is due to the decomposition of $Te(dtc)_4$ at a higher temperature, 140°C, to TETD and $Te(dtc)_2$ since similar products were obtained on refluxing $Te(dtc)_4$ in xylene (section 5B-1-1). Fig 5.33 curve 'e' shows the effect of the mixture of TETD 1.4×10^{-4} and $Te(dtc)_2$ 1.4×10^{-4} mole/100g during the thermal oxidation of PP. The mixture gave a synergistic effect. However, the affect is similar to that of $Te(dtc)_4$ at 1.4×10^{-4} mole/100g.

The effect of the severity of processing conditions on the thermal oxidation of PP films containing the same molar concentration of $Te(dtc)_2$ and $Te(dtc)_4$, Figs 5.34 and 5.35 respectively showed similar behaviour to that during photo-oxidation.

$Te(dtc)_4$ and $Te(dtc)_2$ at 2.8×10^{-4} mole/100g showed an induction period during photo-oxidation (Figs 5.23 curve 'd' and 5.22 curve 'd' respectively) and thermal oxidation (Figs 5.33 curve 'f' and 5.32 curve 'd' respectively) which lasted just as long as the spectrum of these compounds could be observed in the polymer by UV spectrophotometry (Figs 5.36 and 5.37). This indicates that these additives are responsible for both thermal and photo-stability of PP.

The UV spectrum of $Te(dtc)_4$ in PP film (Fig 5.36) shows an increase in the UV absorption maximum at 258nm during the early stages of heat treatment in the oven at 140°C. However, the UV spectra of $Te(dtc)_2$ and $Te(dtc)_4$ are very similar in shape but the difference between the two spectra is that $Te(dtc)_2$ has higher intensity at 258nm than $Te(dtc)_4$ (Fig 5.38). The increase in the absorption at 258nm in $Te(dtc)_4$-PP film could be due to the formation of $Te(dtc)_2$ under heat treatment, since $Te(dtc)_4$ is found to decompose into $Te(dtc)_2$ and TETD on heating (section 5B-1-1).

The importance of hydroperoxides as initiators for photo-oxidation is now well established.(24,28,147,149, 148, 153-160,146) Not only is the rate of photo-oxidation a direct function of the initial (thermally produced) hydroperoxide concentration,(147,148) but the rate of photo-oxidation is proportional to the square root of the peroxide concentration during the initial stages of UV irradiation.(160,151) It follows then that additives which can remove peroxide during processing, heat and UV exposure will be efficient antioxidants and UV stabilisers(151).

Scott(50,54-56,150,151) has shown that many sulphur-containing antioxidants have the ability to suppress hydroperoxide formation in the polymer. However, the effect of metal dithiocarbamates (Zn and Ni) as stabilisers for polyolefins during processing, air oxidation and UV irradiation has shown to be associated with decomposition of the hydroperoxide.(151) Scott has also shown(150,151) the mechanism by which metal dithiocarbamates (Zn and Ni) destroy hydroperoxide to be catalytic involving a Lewis acid (probably sulphur trioxide or sulphuric acid) as mentioned in Chapter 1. However, the Lewis acid has been shown(151,150,50,3,161) to form by the reaction between hydroperoxide and dithiocarbamate.

It is clearly shown that in PP films containing $Te(dtc)_2$ and $Te(dtc)_4$, not only is the build up of carbonyl inhibited during processing but also during heating in an air oven and during UV irradiation. Furthermore, the initial rate of carbonyl formation in PP films containing $Te(dtc)_2$ and $Te(dtc)_4$ is much lower than the control without additives. It seems likely then that $Te(dtc)_2$ and $Te(dtc)_4$ are involved in the same mechanism of peroxide decomposition as the metal dithiocarbamate.

(Zn and Ni).

$Te(dtc)_4$ and $Te(dtc)_2$ were found to be good melt stabilisers for PP. These compounds exhibit better stability than bis(diethyldithiocarbamato)zinc(II), but were comparitively less efficient than bis(diethyldithiocarbamato)nickel(II) during photo-oxidation.(151) $Te(dtc)_4$ and $Te(dtc)_2$ have shown better stabiliser efficiency than bis(diethyldithiocarbamato)nickel(II) and bis(diethyldithiocarbamato)zinc(II) during thermal oxidation.(163)

Table 5-2

Sample	Processing Time(mins)	Embrittlement Time(Hours)
Control	5	80
$Te(dtc)_2$ 0.7 x 10^{-4}mole/100g	5	210
1.4 x 10^{-4}mole/100g	5	260
2.8 x 10^{-4}mole/100g	5	320
$Te(dtc)_2$ 0.7 x 10^{-4}mole/100g	10	198
1.4 x 10^{-4}mole/100g	10	245
2.8 x 10^{-4}mole/100g	10	300
$Te(dtc)_2$ 0.7 x 10^{-4}mole/100g	20	183
1.4 x 10^{-4}mole/100g	20	220
2.8 x 10^{-4}mole/100g	20	280
$Te(dtc)_4$ 0.7 x 10^{-4}mole/100g	5	231
1.4 x 10^{-4}mole/100g	5	272
2.8 x 10^{-4}mole/100g	5	360
$Te(dtc)_4$ 0.7 x 10^{-4}mole/100g	10	244
1.4 x 10^{-4}mole/100g	10	303
2.8 x 10^{-4}mole/100g	10	405
$Te(dtc)_4$ 0.7 x 10^{-4}mole/100g	20	273
1.4 x 10^{-4}mole/100g	20	361
2.8 x 10^{-4}mole/100g	20	464

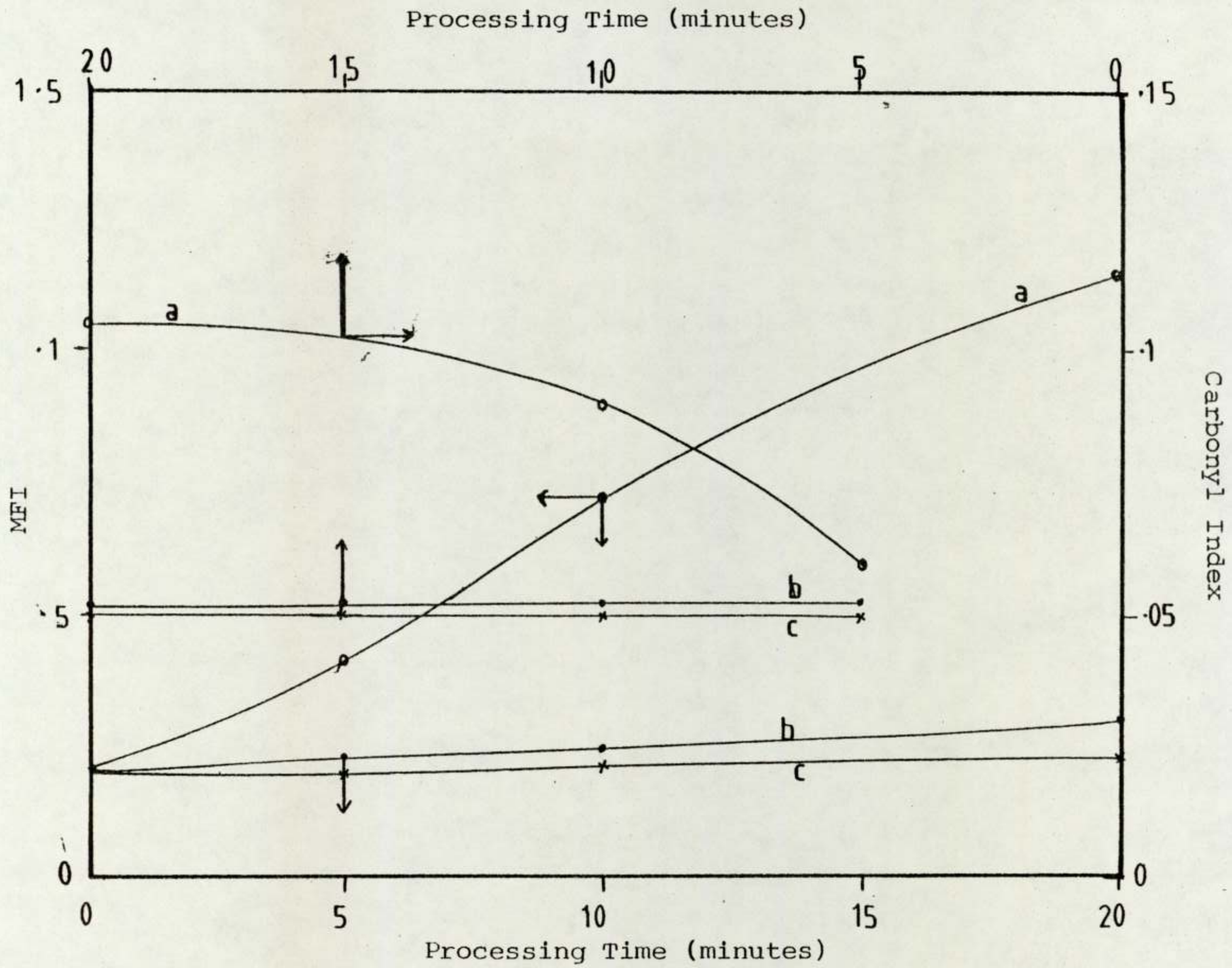


Fig 5.21 Effect of tellurium diethyldithiocarbamato on the change in melt flow index and carbonyl index of PP processed at 180°C (closed mixer)

a - PP(without additive)b - Te(dtc)$_2$ 2.8 x 10^{-4} mole/100g, c - Te(dtc)$_4$ 2.8 x 10^{-4} mole/100g

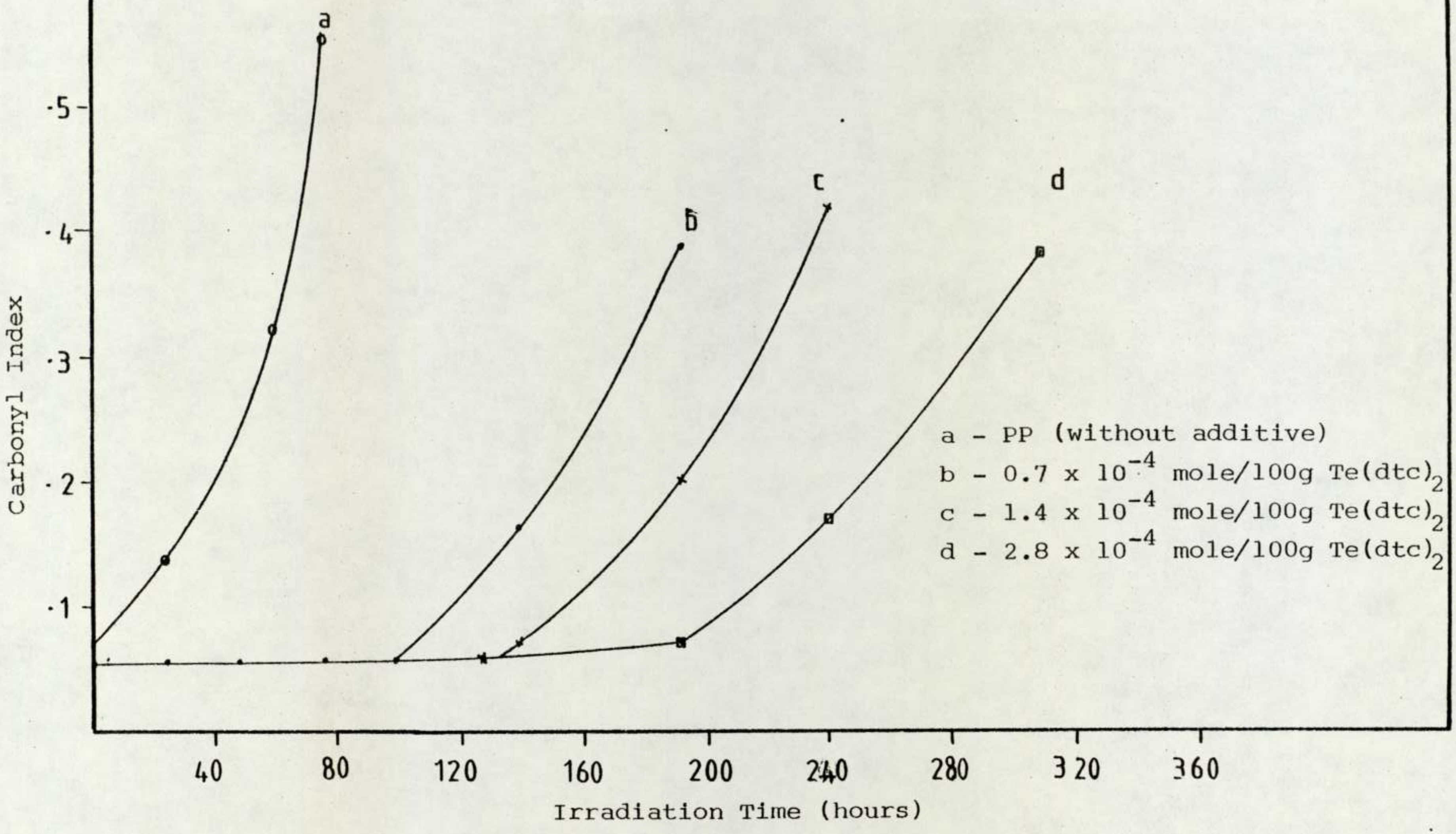


Fig 5.22 Effect of Te(dtc)$_2$ at various concentrations on the photo-oxidation of PP processed for 5 minutes at 180°C (closed mixer)

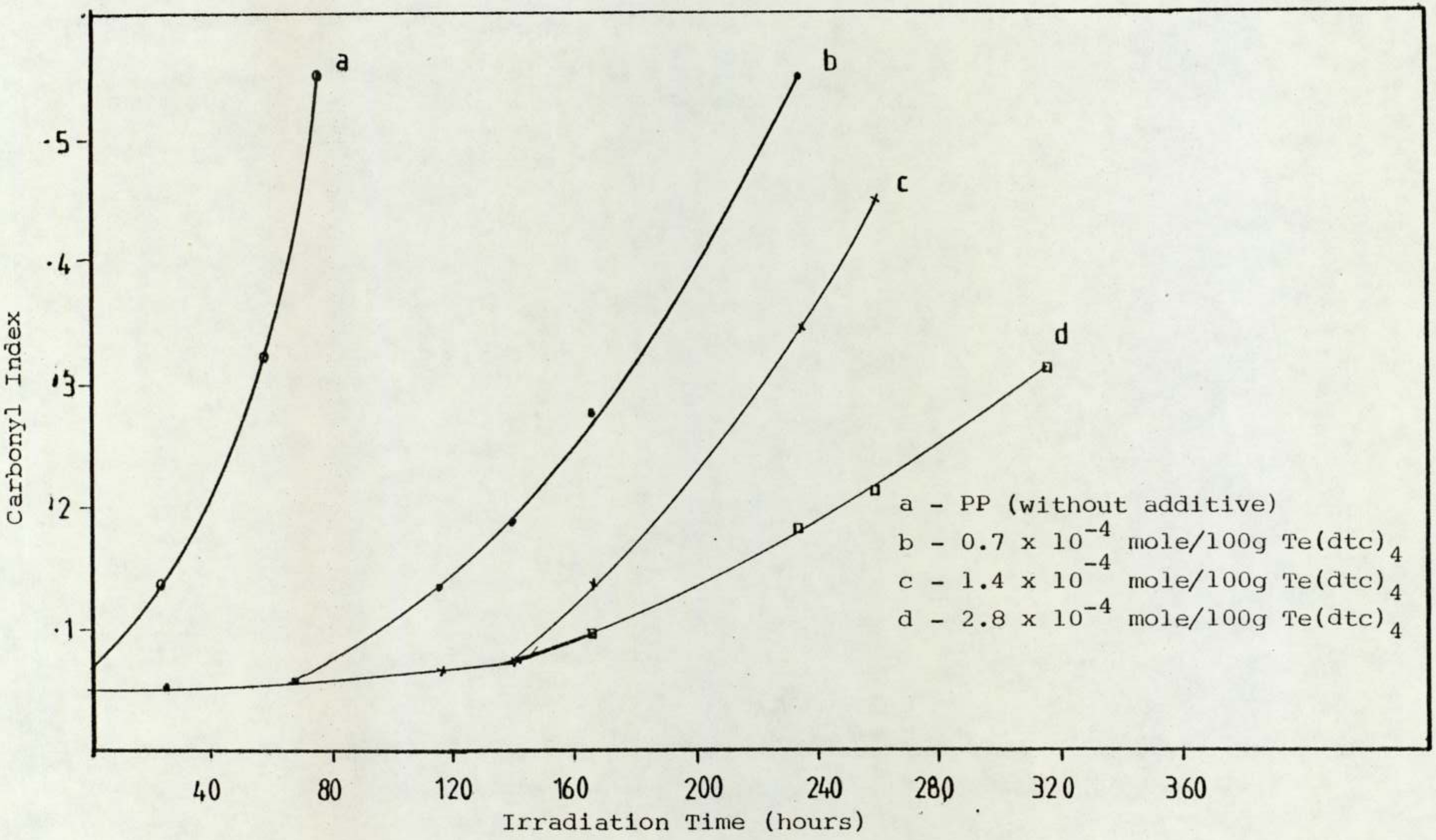


Fig 5.23 Effect of $Te(dtc)_4$ at various concentrations on photo-oxidation of PP processed for 5 minutes at 180°C (closed mixer)

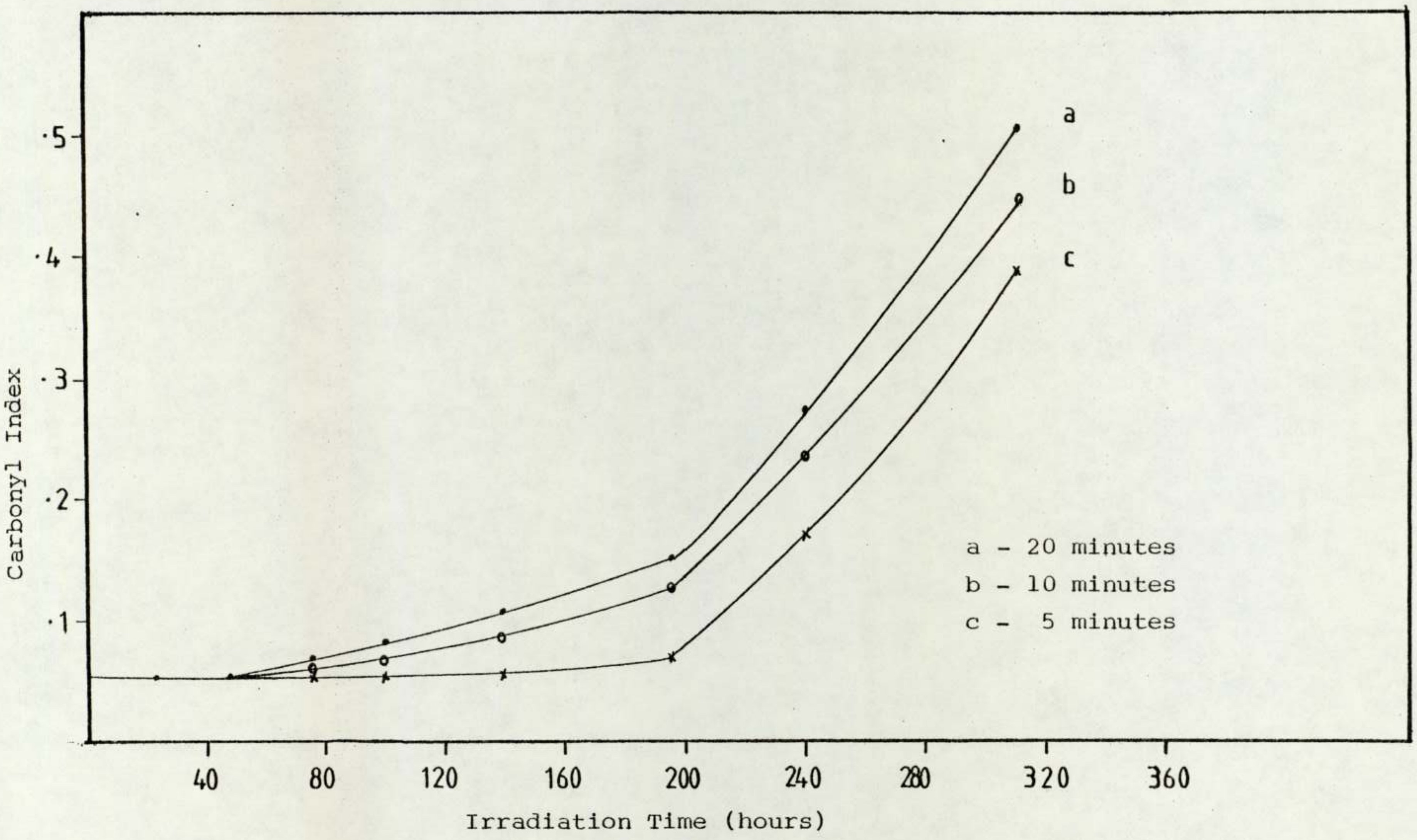


Fig 5.24 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 2.8×10^{-4} mole/100g $Te(dtc)_2$

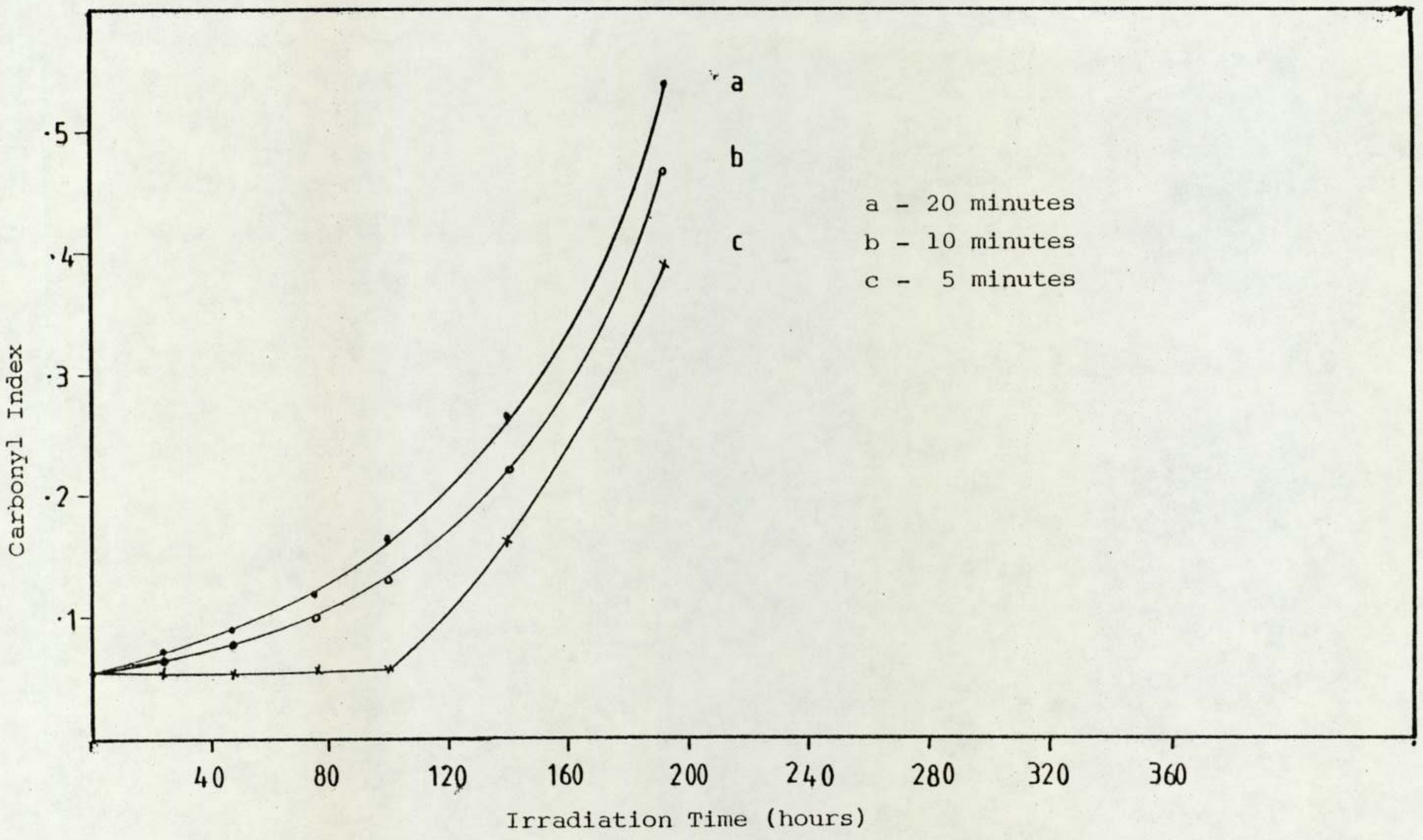


Fig 5.25 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 0.7×10^{-4} mole/100g $Te(dtc)_2$

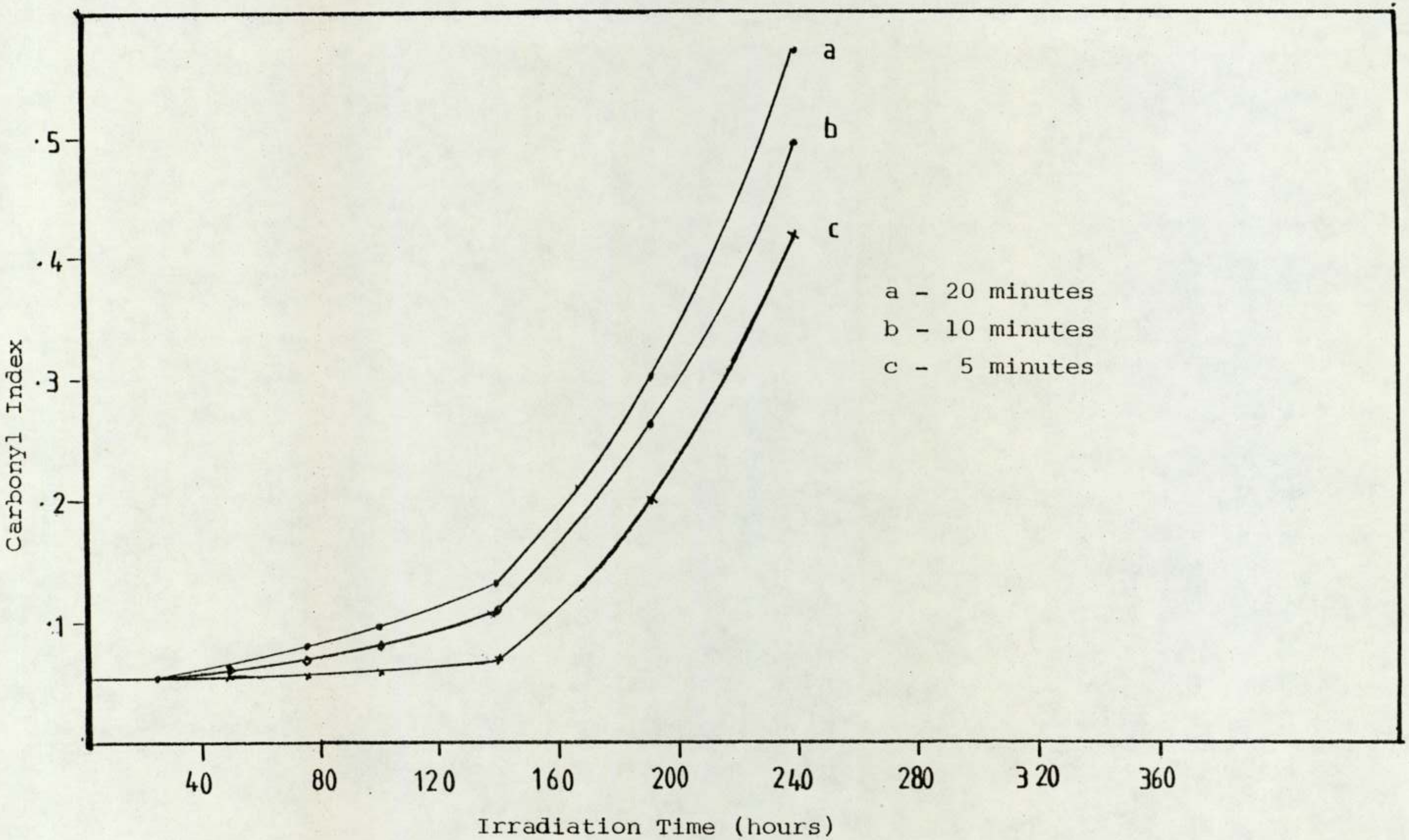


Fig 5.26 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP conatining 1.4×10^{-4} mole/100g $Te(dtc)_2$

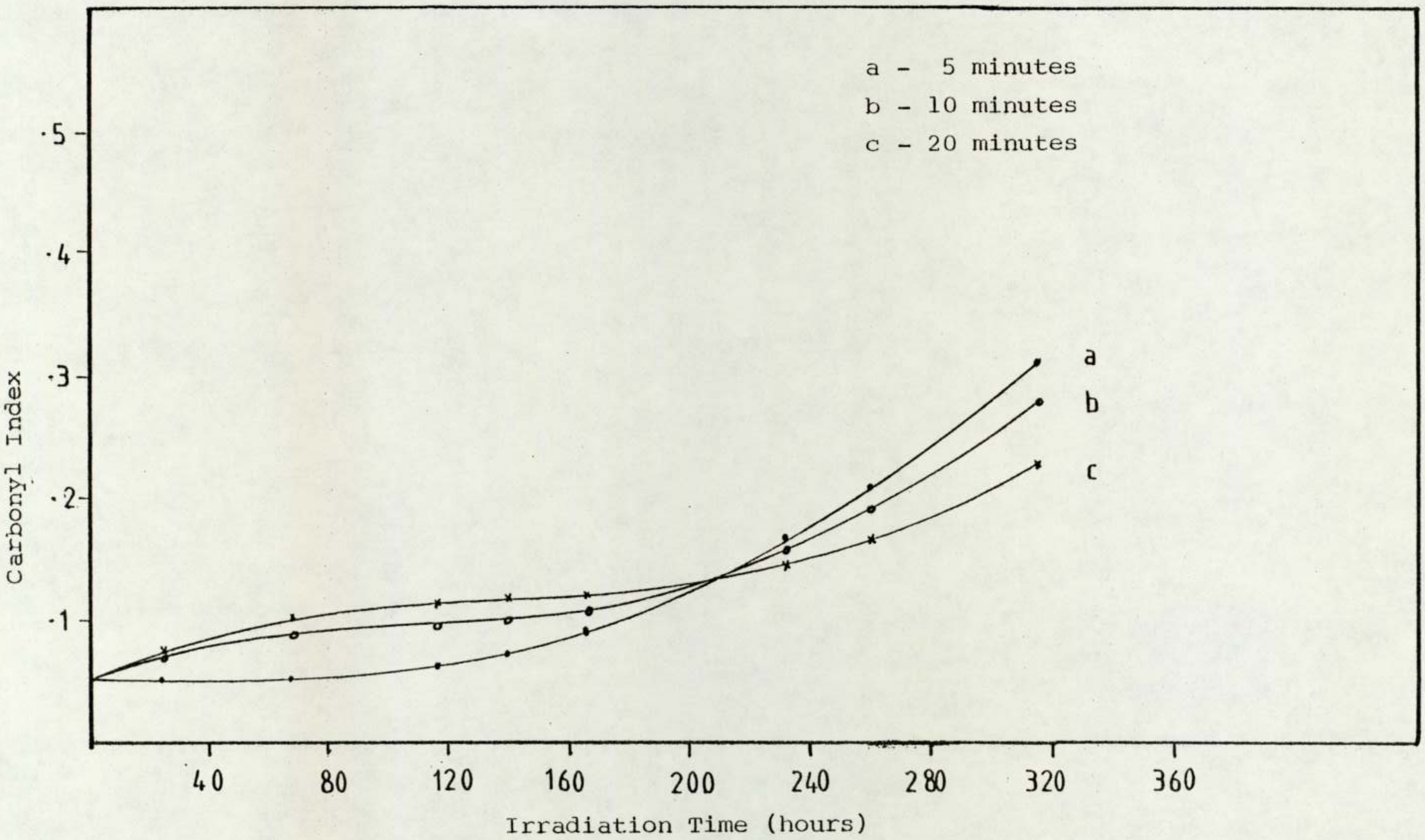


Fig 5.27 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 2.8×10^{-4} mole/100g $Te(dtc)_4$

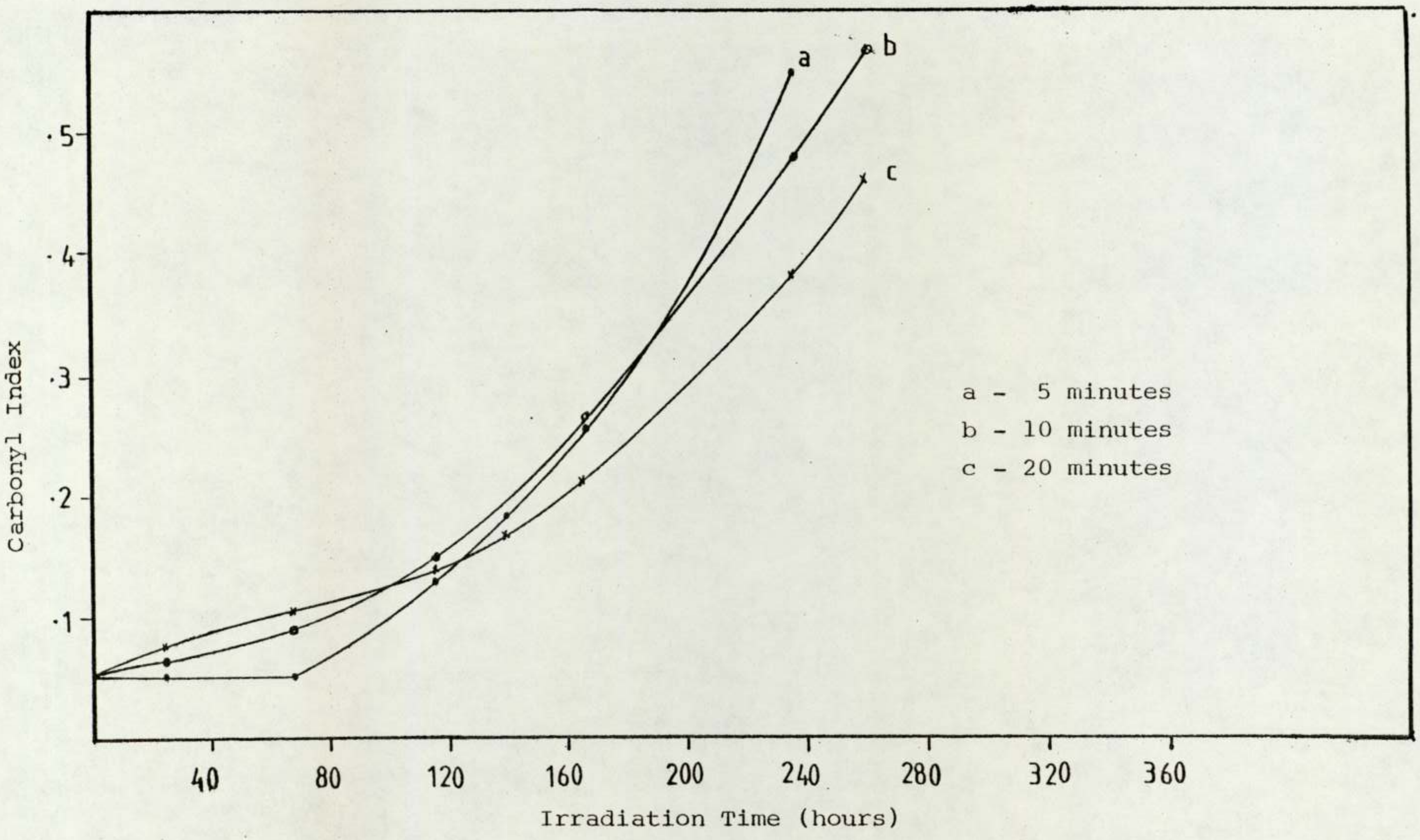


Fig 5.28 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP containing 0.7 x 10^{-4} mole/100g $Te(dtc)_4$

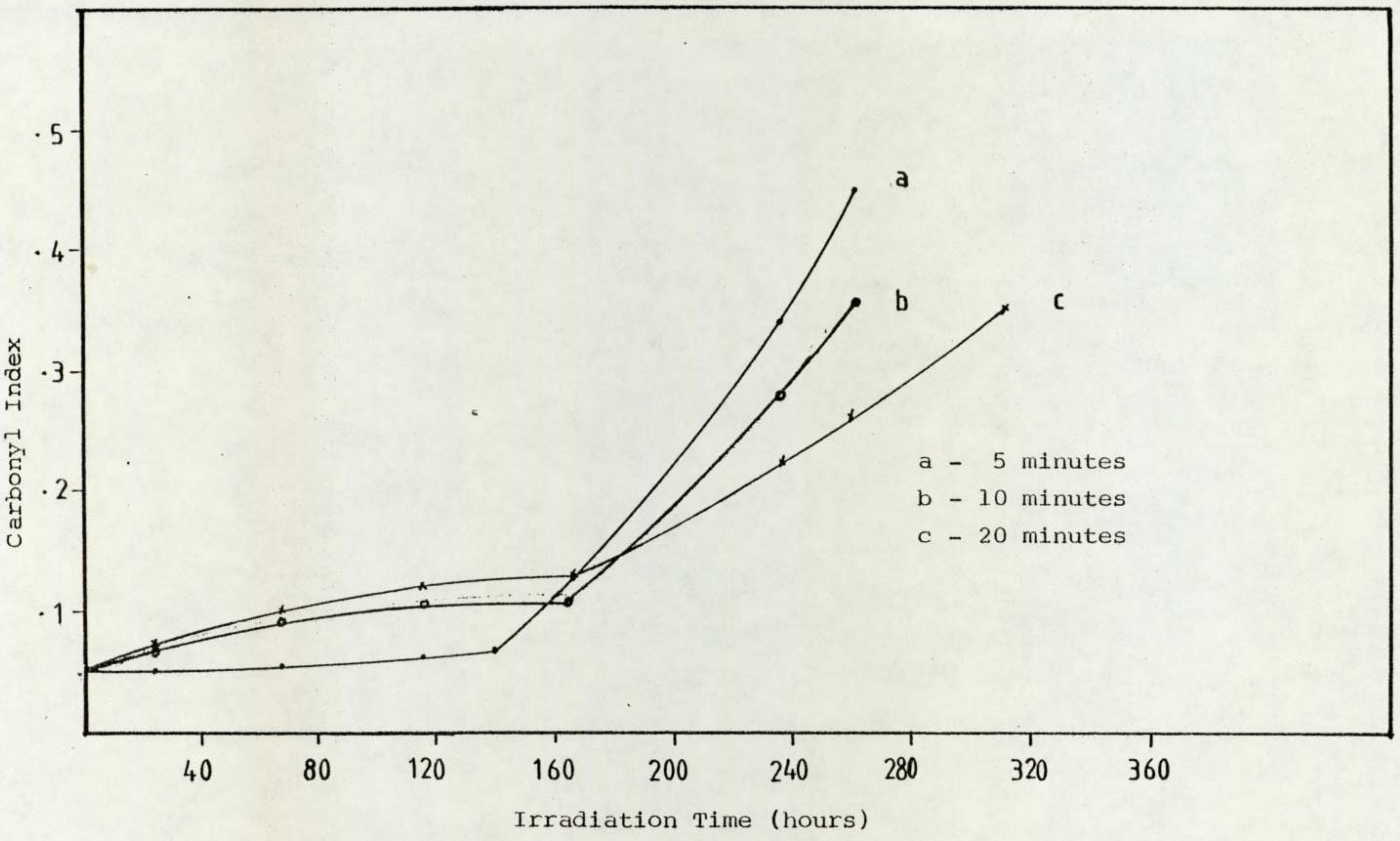


Fig 5.29 Effect of processing at 180^{o}C (closed mixer) on photo-oxidation of PP containing 1.4 x 10^{-4} mole/100g Te(dtc)$_4$

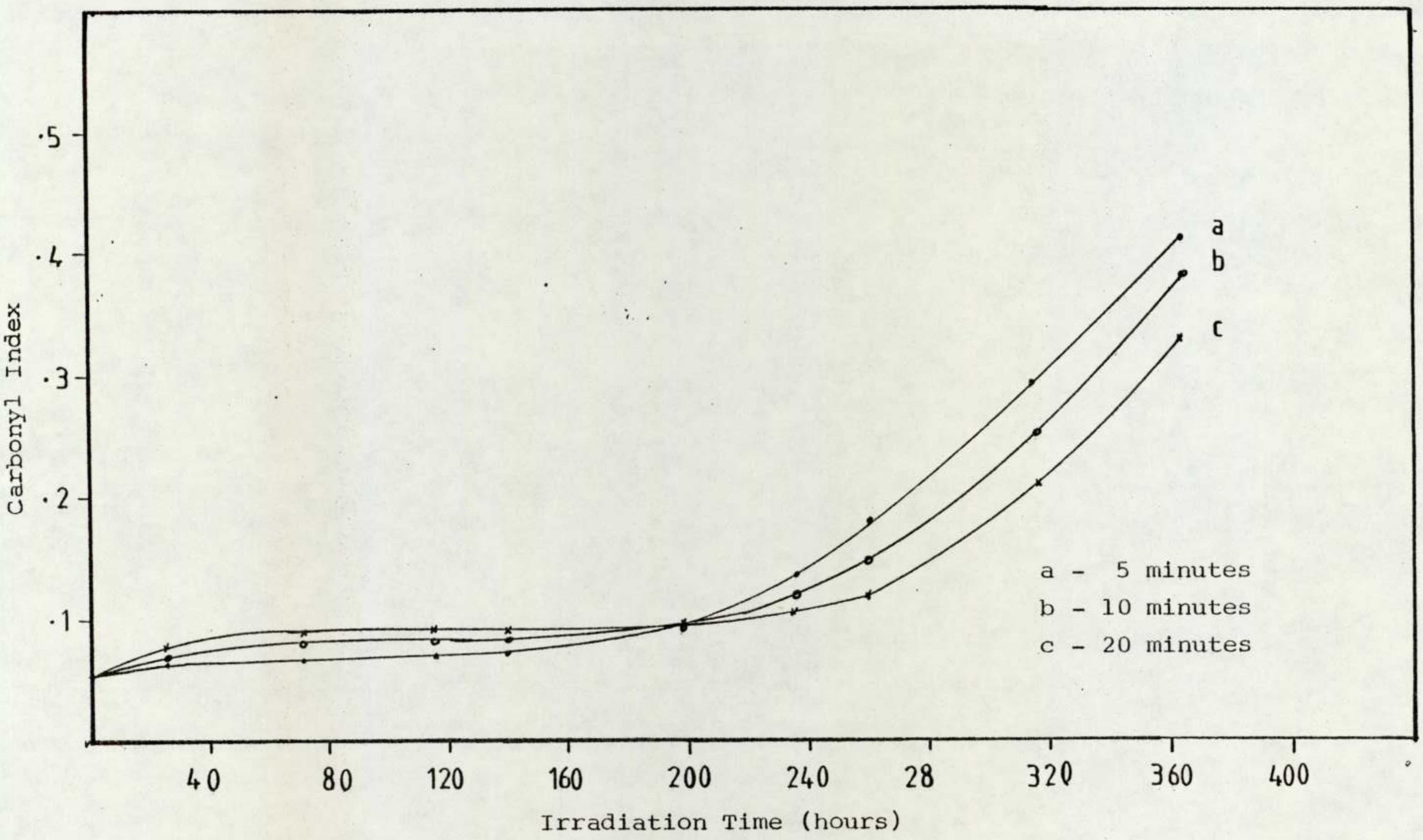


Fig 5.30 Effect of processing at 180°C (closed mixer) on photo-oxidation of PP conatining 1.4 x 10^{-4} mole/100g Te$(dtc)_2$+1.4 x 10^{-4} mole/100g TETD

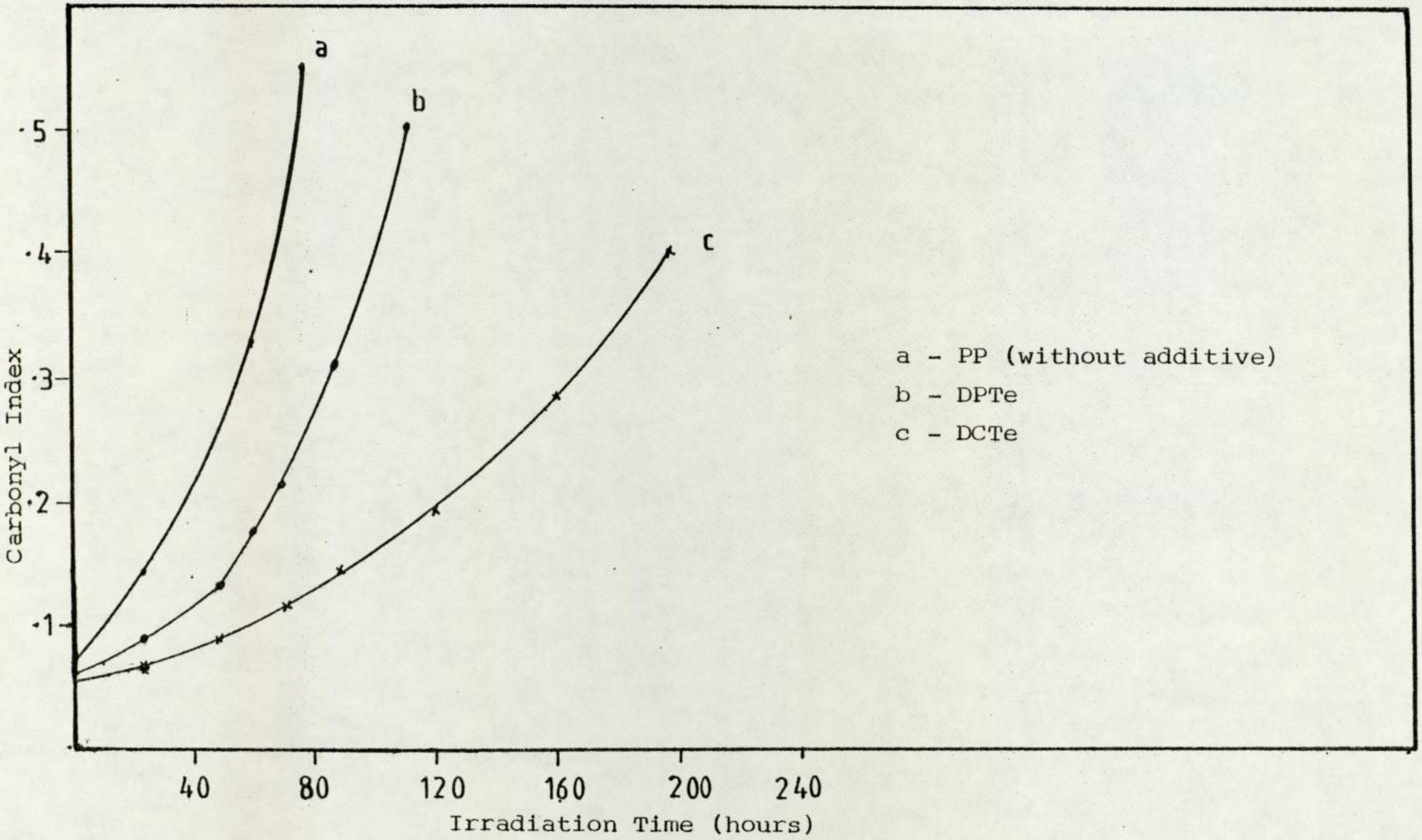


Fig 5.31 Effect of organotelluride (2.8 x 10^{-4}mole/100g) on photo-oxidation of PP processed at 180^{o}C (closed mixer)

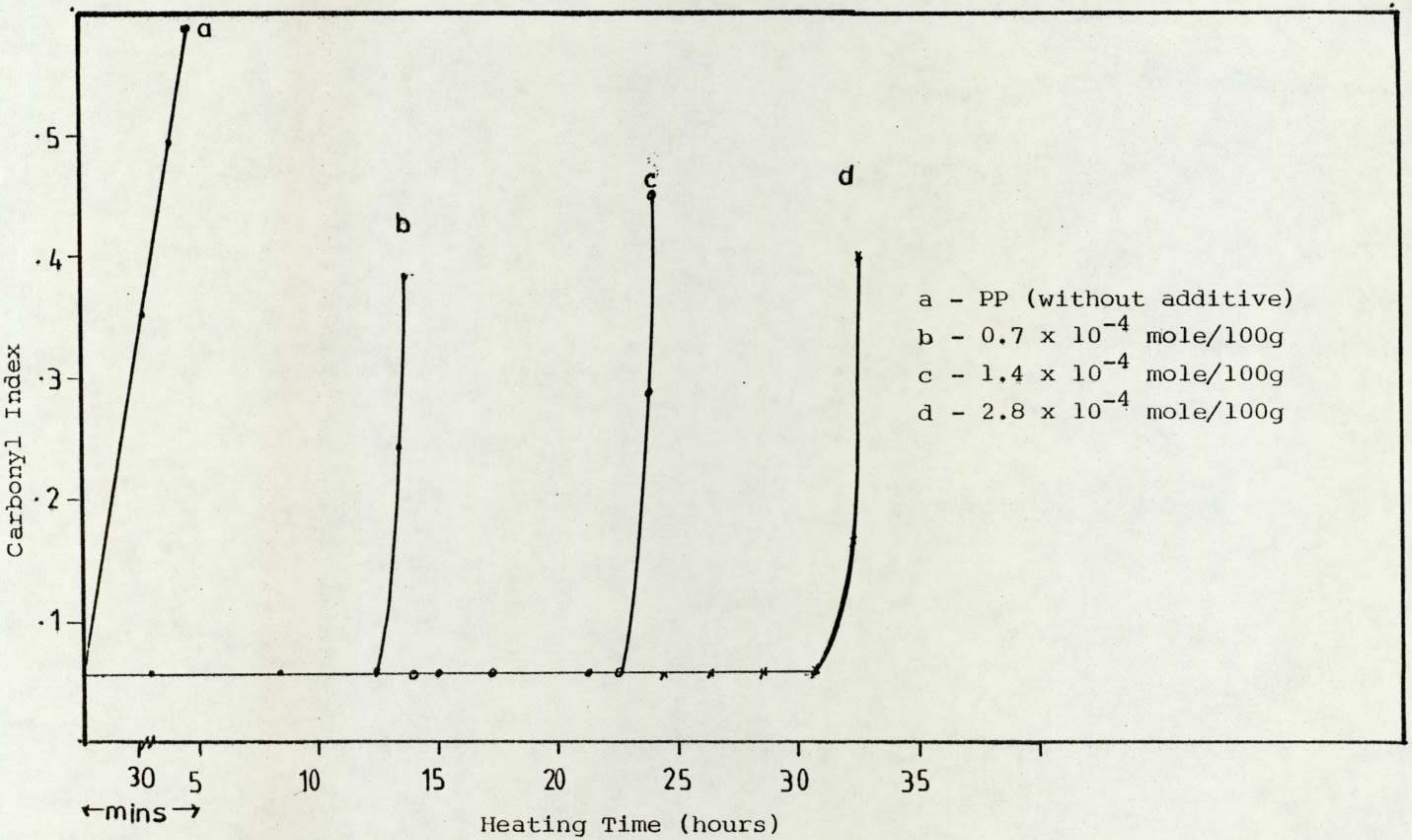


Fig 5.32 Effect of $Te(dtc)_2$ at various concentrations on thermal-oxidation of PP at 140°C processed for 5 minutes (closed mixer)

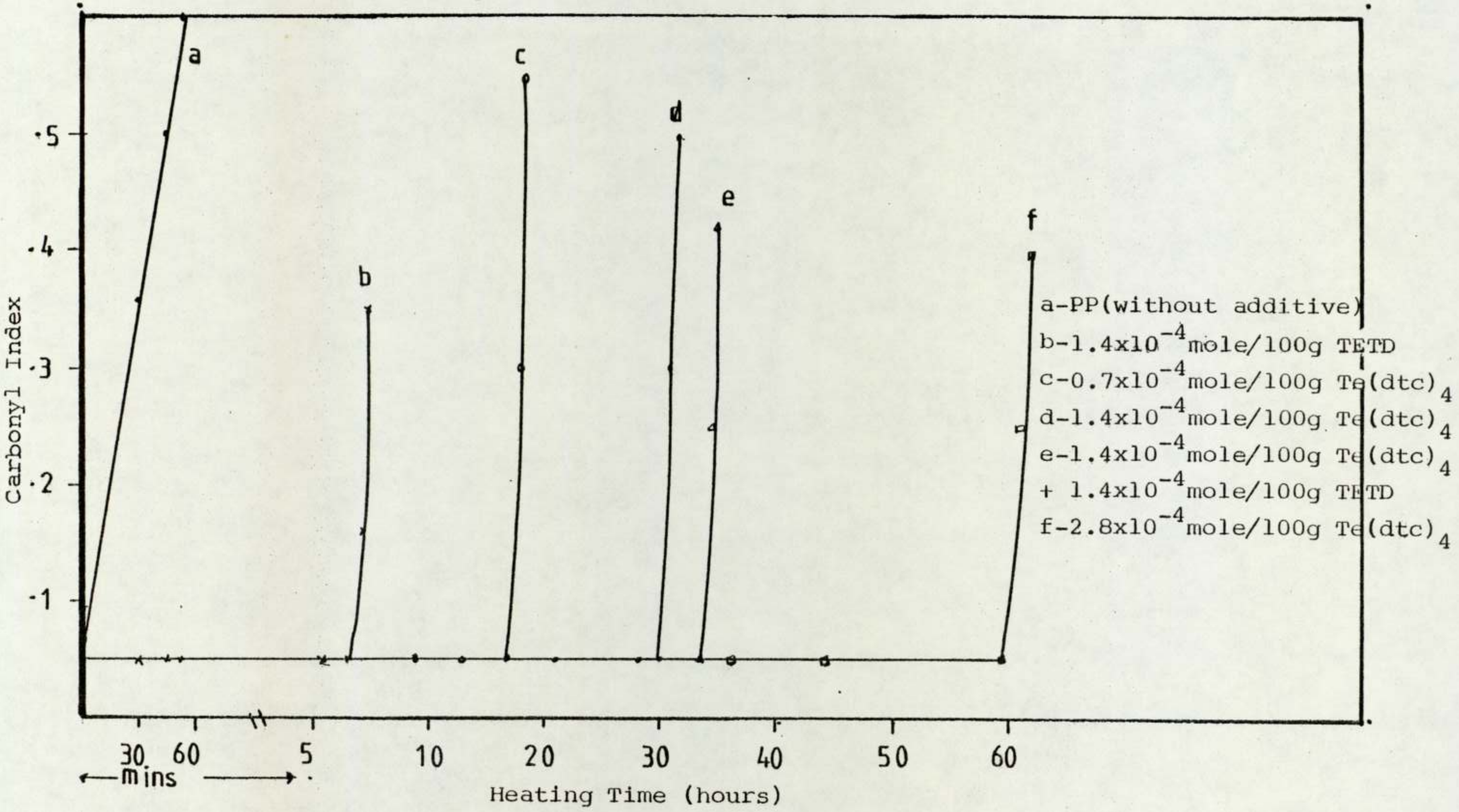


Fig 5.33 Effect of Te(dtc)$_4$ at various concentrations on thermal-oxidation of PP at 140°C processed for 5 minutes (closed mixer)

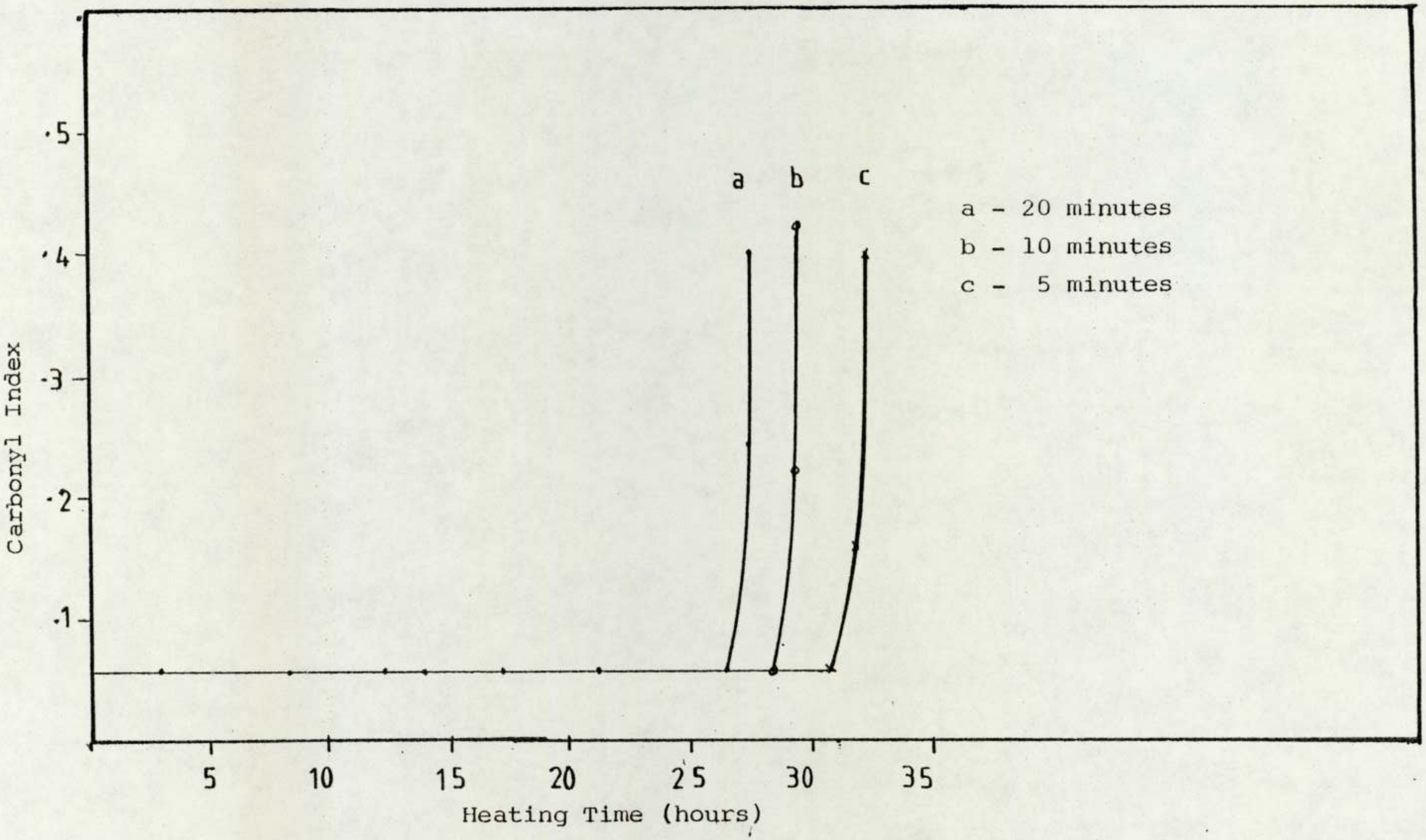


Fig 5.34 Effect of processing at 180^{o}C (closed mixer) on thermal-oxidation of PP at 140^{o}C containing $Te(dtc)_2$ 2.8×10^{-4} mole/100g

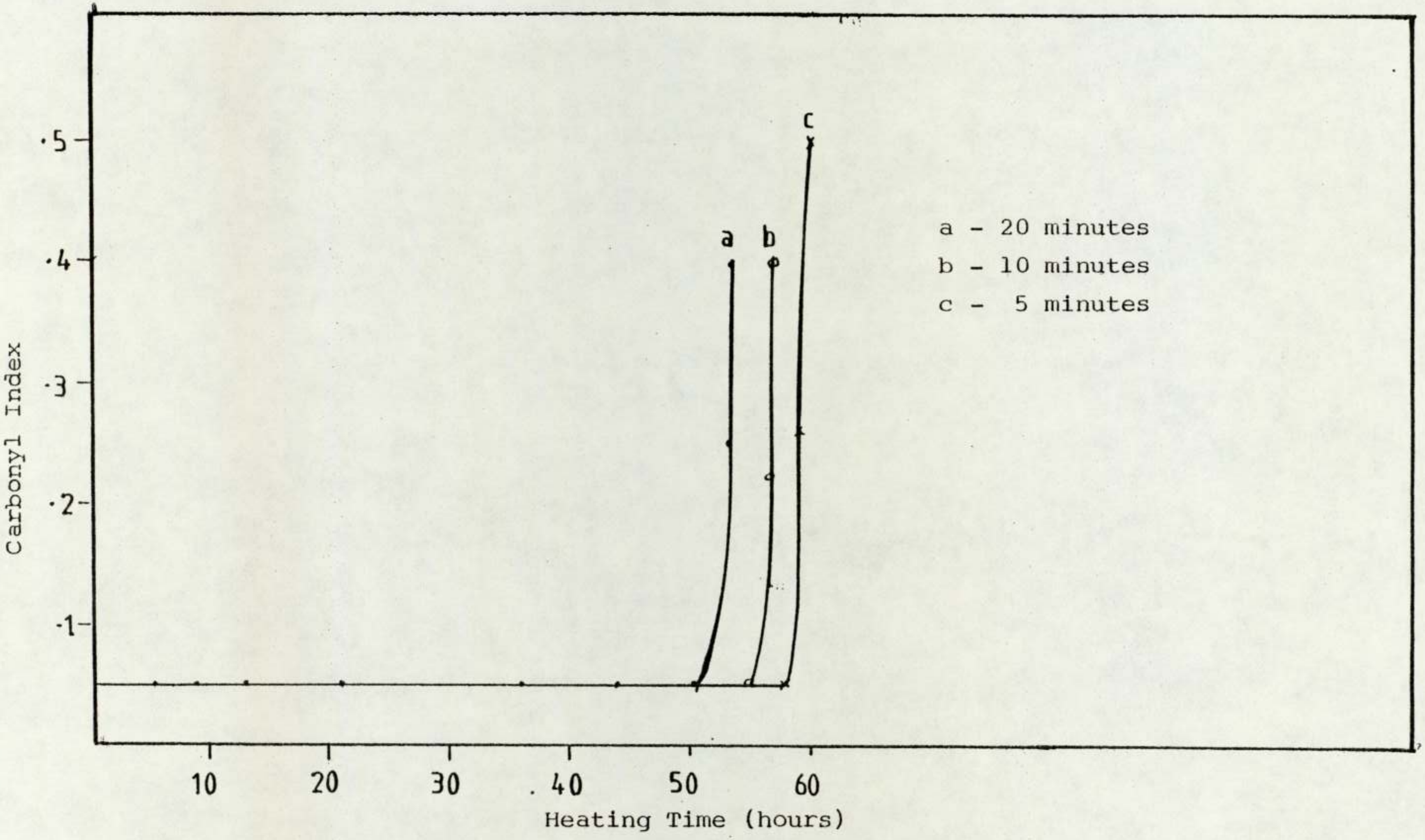


Fig 5.35 Effect of processing at 180°C (closed mixer) on thermal-oxidation of PP at 140°C containing $Te(dtc)_4$ 2.8×10^{-4} mole/100g

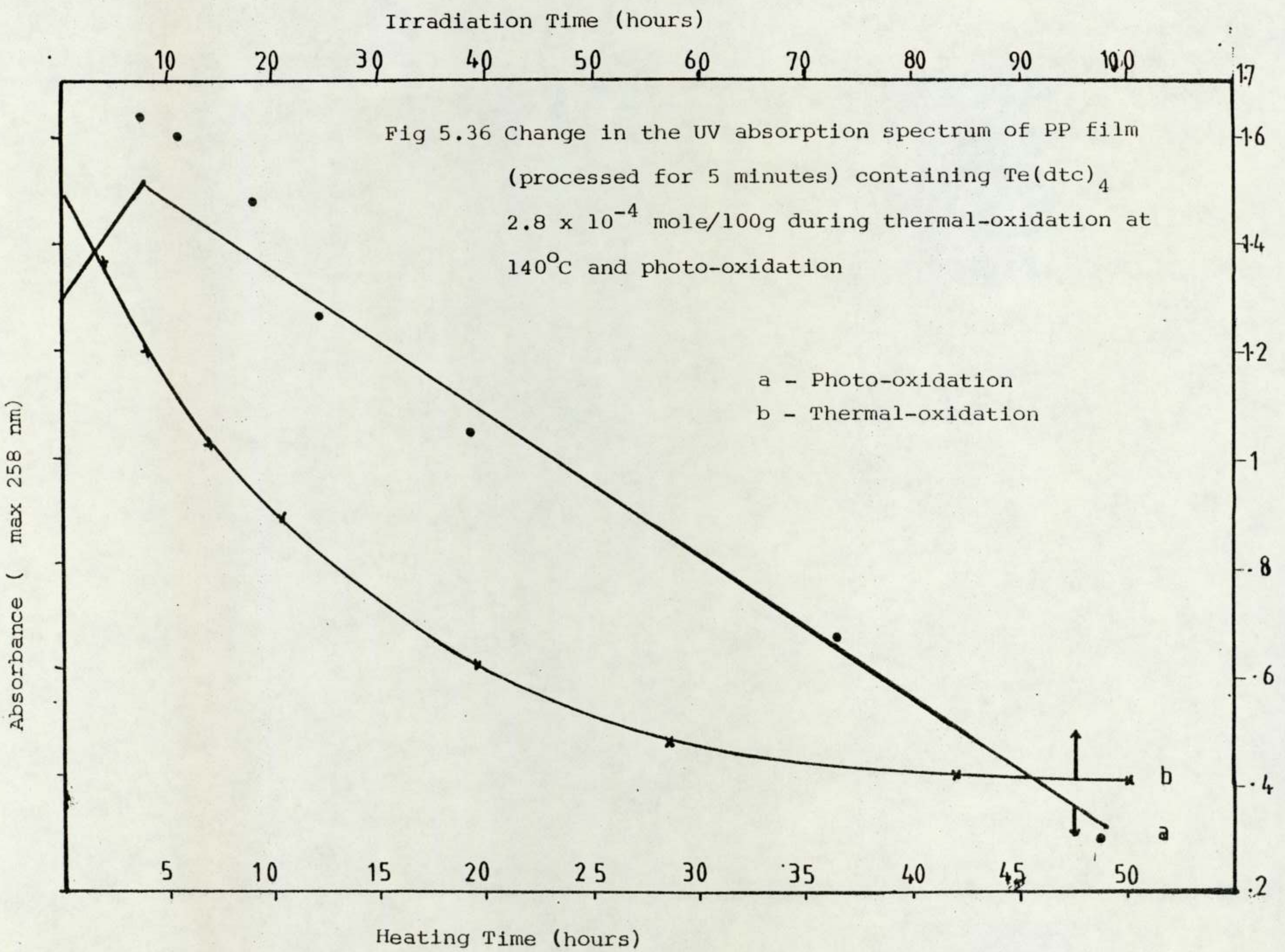


Fig 5.36 Change in the UV absorption spectrum of PP film (processed for 5 minutes) containing $Te(dtc)_4$ 2.8×10^{-4} mole/100g during thermal-oxidation at 140°C and photo-oxidation

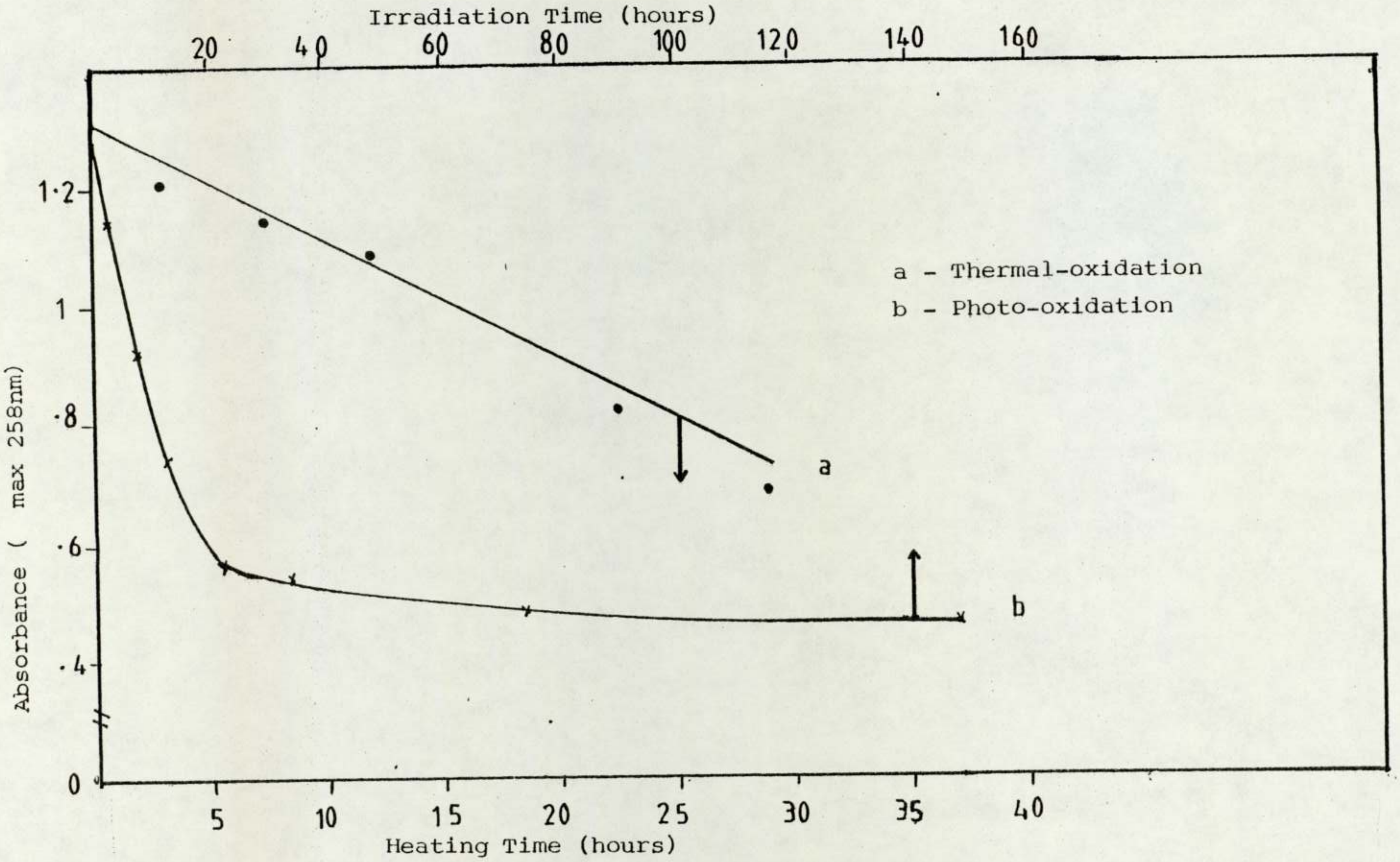


Fig 5.37 Change in the UV absorption spectrum of PP film (processed for 5 minutes) containing Te(dtc)$_2$ 2.8 x 10^{-4} mole/100g during thermal oxidation at 140^{O}C and photo-oxidation

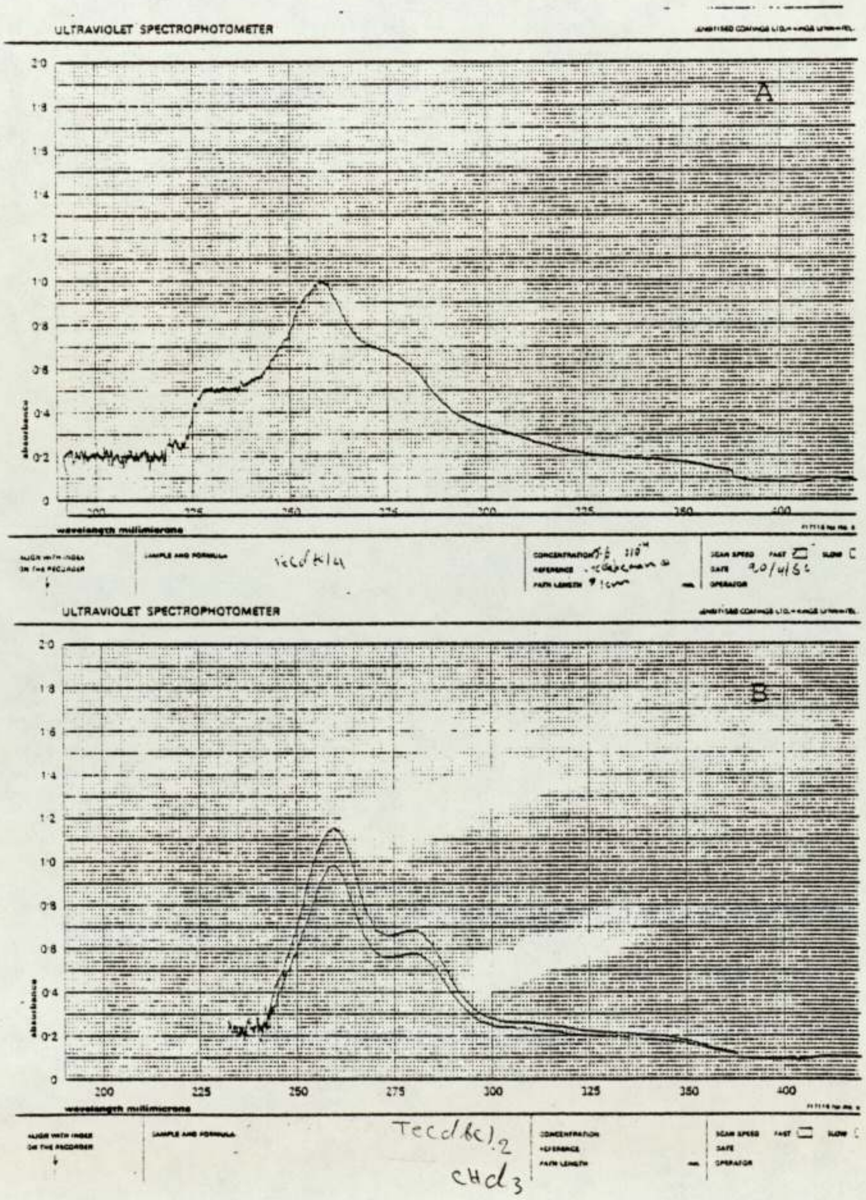


Fig 5.38 A-UV Spectrum of Te(dtc)$_4$

B-UV Spectrum of Te(dtc)$_2$

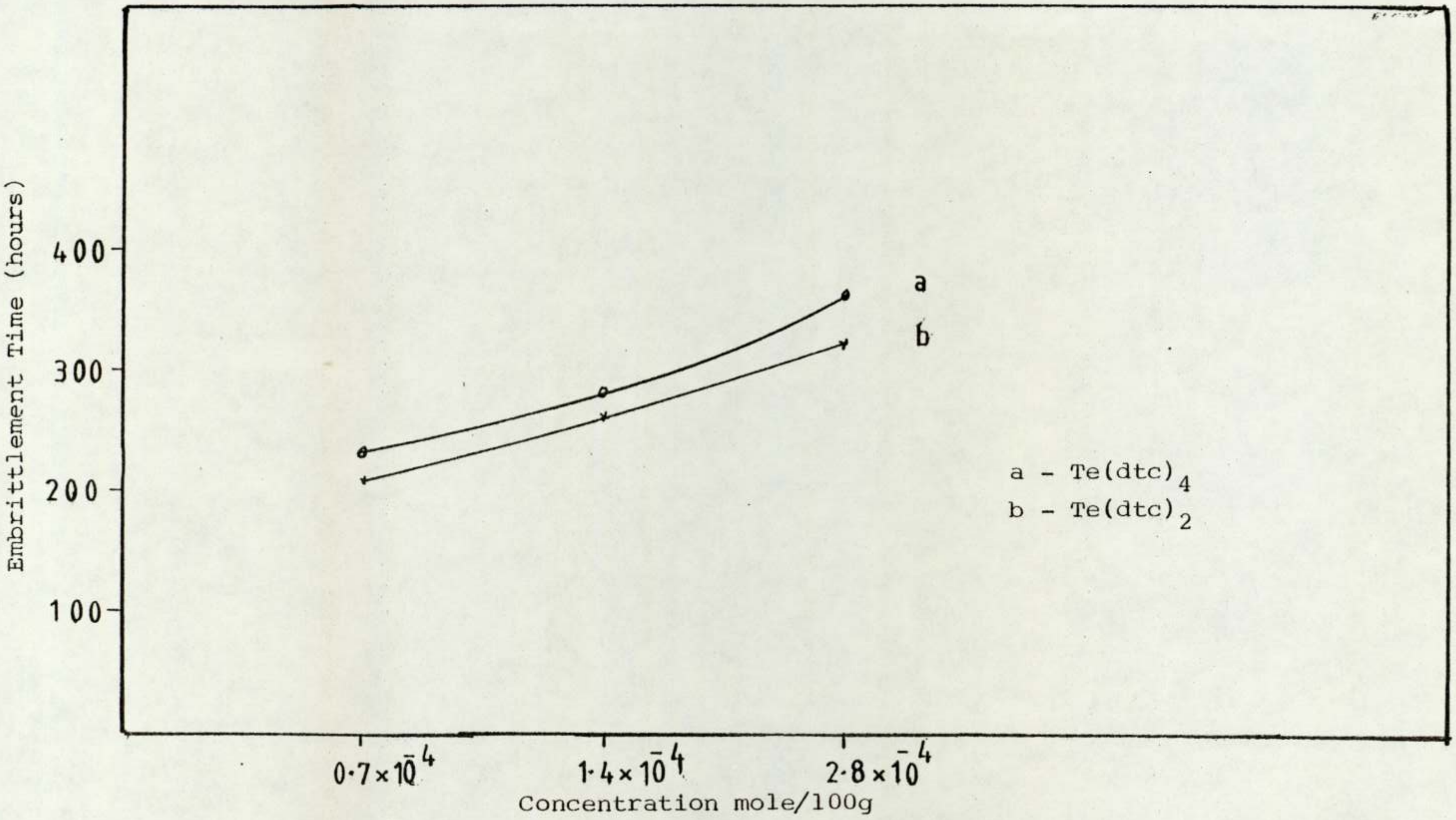
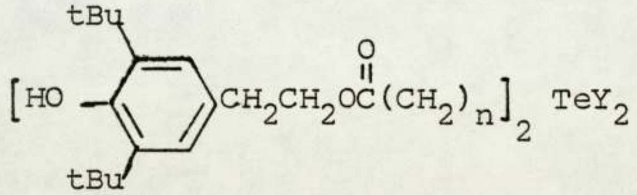
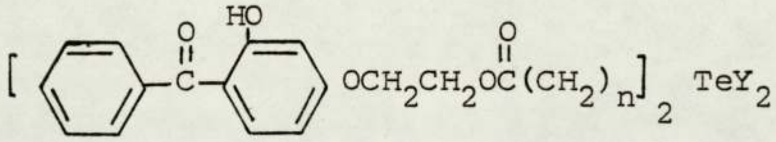


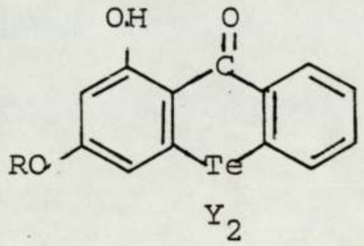
Fig 5.39 Effect of Te(dtc)$_4$ and Te(dtc)$_2$ concentration on their photo-stability activity in PP processed for 5 minutes at 180^{o}C (closed mixer)

SUGGESTIONS FOR FURTHER WORK

1 - To improve the thermal and UV stability of organotellurium compounds in PVC, the following compounds could be synthesised:







Where Y is either mercaptide or maleate.

2 - To facilitate our understanding of the stabilisation action of tellurium dialkyldithiocarbamate. It is necessary to study model compounds. This includes, both the hydroperoxide decomposition and free radical scavenging mechanisms.

3 - The nature of the alkyl group in tellurium dialkyldithiocarbamate may have a profound influence

on the stabilising action of these compounds in PP. It is, therefore, desirable to adjust the size of the alkyl groups (ie. R=CH_3, C_2H_5, C_4H_9, C_6H_{13},C_8H_{17}) to improve the stabilising efficiency of these compounds.

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