STUDIES WITH DITHIZONE :

THE EXTRACTION OF THALLIUM(III)

A thesis submitted to the

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MASTER OF SCIENCE

by

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ABSTRACT

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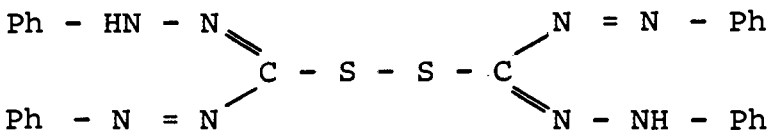
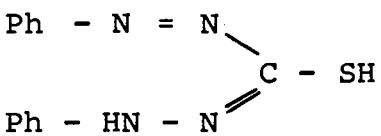
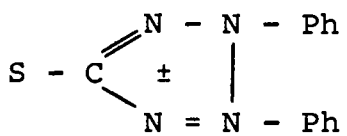
Thallium(III) reacts with dithizone(I) in a complicated way through a number of intermediate products which depend on the relative proportions of reactants, the pH of the aqueous phase, the order of mixing of reactants, the time of phase equilibrium and the nature of the organic solvent used.



(III); disulphide



(I); dithizone



(IV); mesoionic compound

The reaction between thallium(III) and dithizone is essentially oxidative in character. In the present work the complete reaction scheme is proposed: Thallium(III) reacts with dithizone to give a thallic-dithizonate complex, $[Tl^{III}(HDz)_3]$, which spontaneously and oxidatively disproportionates to the disulphide (III) and a thallium(I)-dithizonate complex, [Tl(HDz)]. The disulphide(III) decomposes by first-order heterolytic fission to give equimolar amounts of dithizone and the mesoionic compound (IV). The Tl(HDz) complex undergoes reversion to give Tl^+ in the aqueous phase and dithizone in the organic phase. In the presence of excess thallium(III) the regenerated dithizone

is oxidized to the mesoionic compound (IV): the mesoionic compound (IV), partitions between the two phases and appears to react with excess thallium(III) to give possibly a mesoionic compound (IV)-thallium(III) complex and an unspecified oxidation product.

The molecular structure of the 1 : 1 adduct formed between diphenylthallium(III) and dithizone has been shown by single crystal X-ray diffraction, to be a five co-ordinate diphenylthallium(III) complex: the dithizone acts as a bidentate chelating ligand co-ordinating through the nitrogen and sulphur atoms. Ethanol (solvent of recrystallisation) co-ordinates in the fifth position.

CHAPTER 1

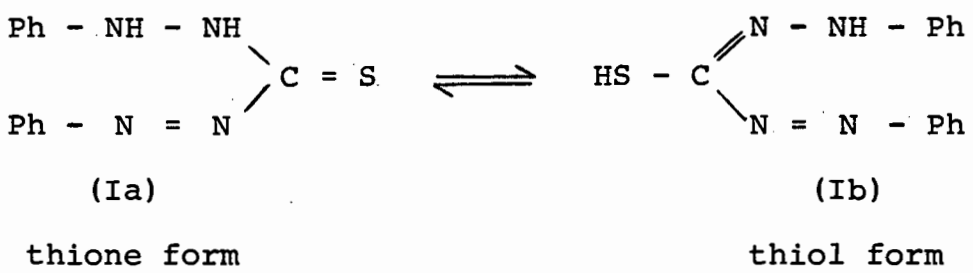
INTRODUCTION

Dithizone (Ia, Ib) or diphenylthiocarbazone (systematically named as 3-mercapto-1,5-diphenyl-formazan, or in Chemical Abstracts as diazenecarbo thioic acid, phenyl-, 2-phenylhydrazide) was first synthesised in 1878 by Emil Fischer [1] during his investigation of the series of compounds resulting from the reactions of phenylhydrazine with carbon disulphide. With Besthorn [2] he also noted its reaction with certain heavy metals to form brilliantly coloured compounds. Some years later Bamberger *et al.* [3] prepared dithizone by a different route and reported the synthesis of a few of its metal complexes. However, it was not until 1925 that Hellmuth Fischer [4] showed its great potential for the detection and determination of many heavy metal ions. It has now become more or less indispensible in trace metal analysis and there is extensive literature concerning dithizone and its analytical applications [5]. Irving [6,7] has recently reviewed the whole subject.

Dithizone is a violet-black solid, very sparingly soluble in water but readily soluble in most organic solvents to give strongly coloured solutions. Dilute solutions of dithizone in carbon tetrachloride (CCl_4) and chloroform ($CHCl_3$) are green, but more concentrated solutions are dichroic (red in transmitted light, green in reflected light). The visible spectrum of dithizone in an organic solvent exhibits two well-defined bands (Figure 1). Although the positions of $\lambda_{max,1}$ and $\lambda_{max,2}$ vary comparatively little with change of solvent, there are striking changes in the relative magnitudes of the extinction coefficients $\varepsilon_{max,1}$ and $\varepsilon_{max,2}$. The subscripts 1 and 2 are used to distinguish

the longer and shorter wavelength, respectively [6].

The presence of these two widely separated peaks gave rise to the hypothesis that in organic solvents dithizone exists as a tautomeric equilibrium mixture of the thione (Ia) and the thiol (Ib) forms.



(Ia) thione form

(Ib) thiol form

FIGURE 1: Absorption spectrum of dithizone in chloroform.

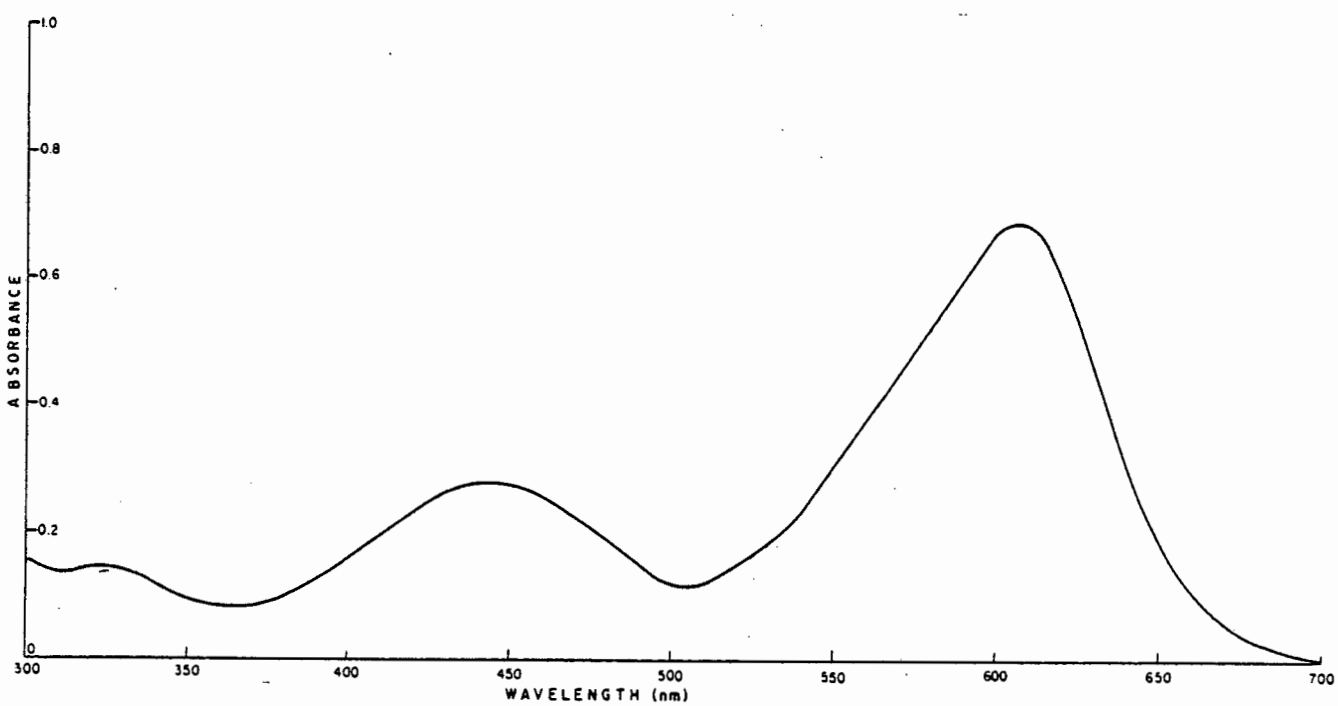
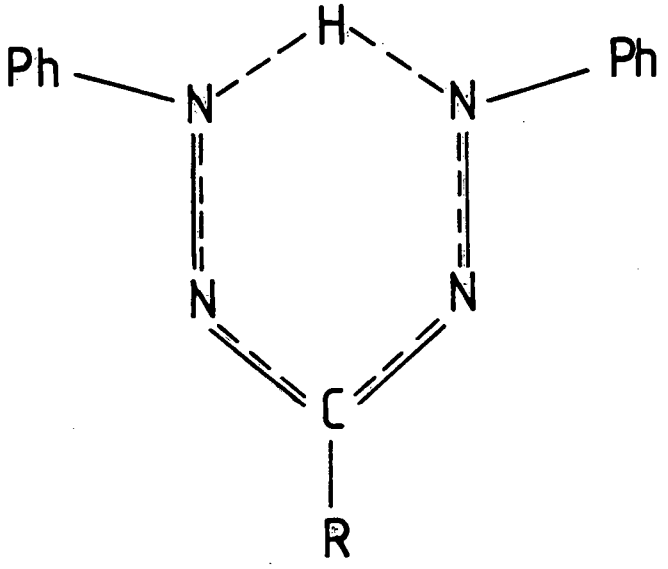


FIGURE 2: Internal hydrogen-bonding in formazans.



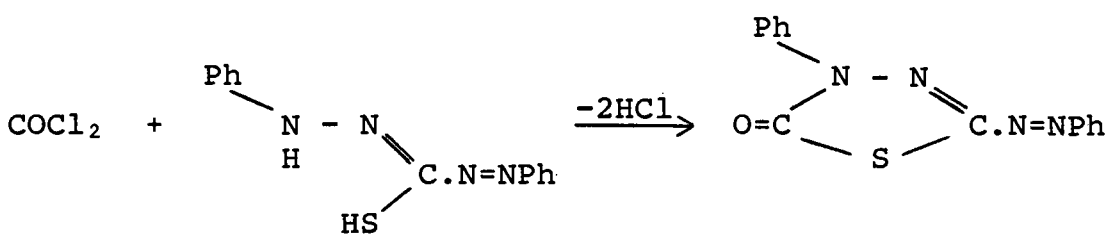
[H_2Dz: R=SH]

The tautomerism indicated by (Ia) $\rightleftharpoons$ (Ib) is an oversimplification since cis-trans isomerism about the azo-bond, -N=N-, and syn-anti isomerism about the bond -N=C< will increase the number of possible forms, in addition to which internal hydrogen bonding in the formazans (Figure 2) has been thoroughly established experimentally. The resolution of these problems by e.g. NMR studies has been reviewed [6,8].

As an analytical reagent dithizone suffers from certain disadvantages. It is difficult to obtain absolutely pure dithizone in the solid state and its solutions in organic solvents tend to deteriorate on keeping, especially in the presence of alkalies, oxidising agents and light. In view of this, the so-called 'mono-colour methods' [6] which depend on the constancy of the concentration of standard solutions of dithizone, are always open to question and a variety of procedures, more or less elaborate, have been designed (e.g. mixed colour method) to circumvent the difficulties. One particularly elegant method, namely the 'reversion procedure' was suggested by Irving *et al.* [9].

Although some of the disadvantages arising from the instability of dithizone solutions can be mitigated as mentioned above, the actual causes of the deterioration of its solution have never clearly been defined, but it is generally regarded as an oxidation process probably catalysed by light [10]. It is clearly of significance that solutions of dithizone in chloroform undergo a photochemical reaction, with a colour change from green to pale yellow as 5-phenylazo-3-phenyl-1,3,4-thiadiazol-2-one (II) [λ_{max} 375 nm; ε_{max} = 19 300 cm^2 mol^{-1}] is formed by a reaction with phosgene [11].

$$CHCl_3 \xrightarrow[h\nu]{[O]} COCl_2 + HCl$$



(II)

The most remarkable mode of decomposition is that produced by iodine and a whole range of other oxidising agents. In the presence of water, iodine brings about the expected oxidation of dithizone to the disulphide, bis-1,5-diphenylformazan-3-yl-disulphide (III), which decomposes spontaneously by first order kinetics to give an equimolar mixture of dithizone and a mesoionic compound (IV) previously prepared and commonly known under the name dehydrodithizone [10].

Dehydrodithizone (IV) has been prepared by oxidising dithizone with potassium hexacyanoferrate (III) and correctly formulated

by Ogilvie and Corwin [12] as a mesoionic compound. The structure of this orange-red compound, m.p. 173°C (decomp.), systematically named 2,3-diphenyl-2H-tetrazolium-5-thiolate, has been confirmed by X-ray crystallography [13].

With stronger oxidants, e.g. concentrated hydrogen peroxide in 0.5 M alkali, the sulphonic acid (V) is formed [14].

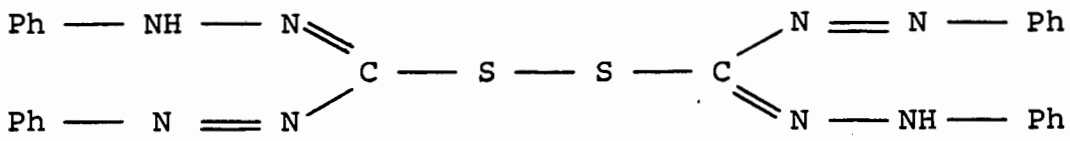
Yet another oxidation product is obtained when solutions of dithizone are left in contact with concentrated mineral acids or where a solution in glacial acetic acid is heated [15]. This is a bicyclic compound, 3-phenylazobenzo-1,3,4 (4H) - thiadiazole (VI). The structure has been confirmed by X-ray crystallography [16].

Each of these oxidation products (Figure 3, (III - VI)) may occur in deteriorated solutions of dithizone together with the photochemically produced thiadiazoline (II).

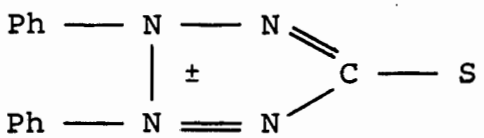
However, the deterioration of dithizone solutions can be effectively eliminated by paying special attention to the purity of the solvents and the conditions of storage.

Since dithizone has two potentially dissociable hydrogen atoms it has been convenient to abbreviate its formula as H_2Dz. When a solution of dithizone in an organic solvent is shaken with an alkaline aqueous solution some of the dithizone is transferred to the aqueous phase as a consequence of the formation of dithizonate anions (HDz^-). Dithizone behaves as a weak monobasic acid under these conditions. In the aqueous phase the

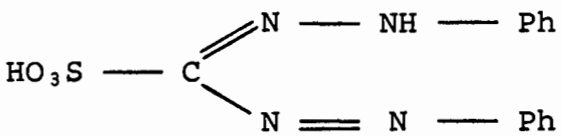
FIGURE 3: The various oxidation products of dithizone.



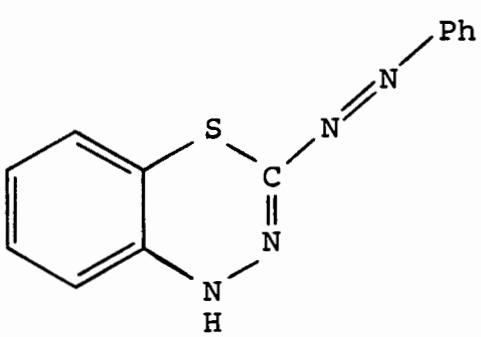
(III), Di-(1,5 diphenyl formazyl) disulphide



(IV), Anhydro-5-mercapto, 2,3-diphenyl tetrazolium hydroxide; the mesoionic compound



(V), 1,5 Diphenyl formazan-3-disulphonic acid



(VI), 2-phenylazobenzo-1,3,4(4H) thiadiazine; "The purple compound".

following equilibrium is assumed to exist

$$H_2Dz \overset{K_r}{\rightleftharpoons} HDz^- + H^+$$

and pK_r for this dissociation is ~ 4.5 [6].

The ability to extract certain metals from aqueous solutions as their dithizonates into a solvent such as $CHCl_3$ or CCl_4 was discovered by Hellmuth Fischer and exploited by him and other workers for a wide variety of analytical procedures [5,6].

Two classes of stoicheiometric metal-dithizonate complexes can be distinguished:

(a) those derived from the anion (HDz^-) and a cation M^{n+}, which have the formula $M(HDz)_n$, and

(b) those richer in metal and derived from the dinegatively charged anion Dz^{2-} and the metal M^{n+} and having the formula $M_{2/n}Dz$.

Nowadays the former are invariably termed primary dithizonates and the latter, secondary dithizonates.

The formation of a metal dithizonate is a two-phase reaction. The various equilibria governing the extraction of metal (primary) dithizonates is shown diagrammatically in Figure 4, which represents the simplified system in which no auxillary complexing agents are present, and where no complexes between the cation M^{n+} and hydroxyl ions need be considered. K_r and p_r are the (first) acid dissociation constant and partition coefficient of the reagent dithizone, respectively; while $\beta_n = [M(HDz)_n]/[M^n][HDz^-]^n$ is the overall stability constant of the metal dithizonate,

FIGURE 4: Equilibria in a two-phase system involving cations, M^{n+}, dithizone, H_2Dz, and a primary metal dithizonate, $M(HDz)_n$, in the absence of auxillary complexing agents.

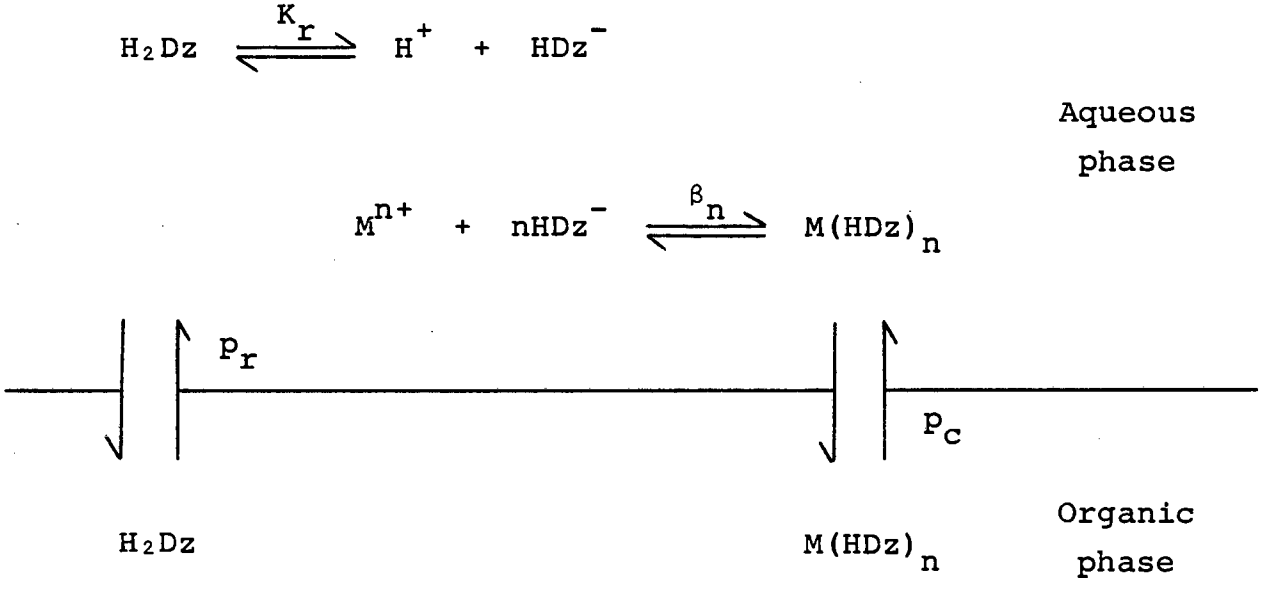


TABLE 1.1: Metals forming complexes with dithizone

Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se
-	-	-	Pd	Ag	Cd	In	Sn	Sb	Te
-	-	-	Pt	Su	Hg	Tl	Pb	Bi	Po

$M(HDz)_n$, and $P_c = [M(HDz)_n]_O/[M(HDz)_n]$ is its partition coefficient. Where the subscript 'O' or the superscript bar distinguishes the organic from the aqueous phase.

The fundamental equation for the extraction is:

$$M^{n+} + \overline{nH_2Dz} \overset{K_{ex}}{\rightleftharpoons} \overline{M(HDz)_n} + nH^+ \qquad (1\text{-}1)$$

The position of equilibrium is governed by the magnitude of the extraction constant,

$$K_{ex} = [M(HDz)_n]_O[H^+]^n/[M^{n+}][H_2Dz]_O^n$$

Assuming that the concentration of uncharged complex in the aqueous phase will be negligible, the distribution ratio, D, will be given by:

$$D = [M(HDz)_n]_O/[M^{n+}] = K_{ex}[H_2Dz]_O^n/[H^+]^n$$

whence

$$\log D = \log K_{ex} + n(pH + \log [H_2Dz]_O)$$

Since variations in the concentration of dithizone are bound by the solubility of the reagent in the organic solvent, whereas $[H^+]$ can be varied by a factor of at least 10^{15}, it will be obvious that control of pH will be of importance.

When a solution of dithizone in an immiscible organic liquid is shaken with an aqueous solution of a metal ion [5] or organometallic ion [17], dithizone behaves as a weak monobasic acid of pK_r ~4.5 [18, 19] and forms strongly coloured complexes

which are extracted into the organic phase. The colour of the metal complexes depend upon the metal involved. With the exception of Pd, Pt and Ni, which show several absorption bands, all metal dithizonates possess a single absorption band in the region 450-550 nm (Figure 5). The change in the spectrum on forming a metal complex can be explained by the disappearance of the thione band at ~ 620 nm and a bathochromic shift of the thiol band from ~ 420 nm. A most valuable feature is that their absorbance at 620 nm is often negligible.

Although dithizone is an extremely sensitive reagent (usually requiring only a few micrograms of metal ions and operating at concentrations around 10^{-5} Molar), it is not specific since it forms complexes with a variety of cations derived from metals grouped in the centre of the Periodic Table (See Table 1.1). These are predominantly those metals which can be precipitated as sulphides from aqueous solutions. Many complexes of organometallic cations such as $C_6H_5Hg^+$, $(CH_3)_2Tl^+$ and $(C_2H_5)_3Pb^+$ are also known [17]. It has also been reported that in 50% (v/v) aqueous ethanol, dithizone gives 1:1 complexes with all the lanthanons, the stability constants ranging from $10^{1.40}$ (lanthanum) to $10^{2.30}$ (lutetium) [7].

However, this reagent can be made more selective by suitable adjustment of the pH of the aqueous phase or by the use of the appropriate masking agents to produce competitive complex formation in the aqueous phase.

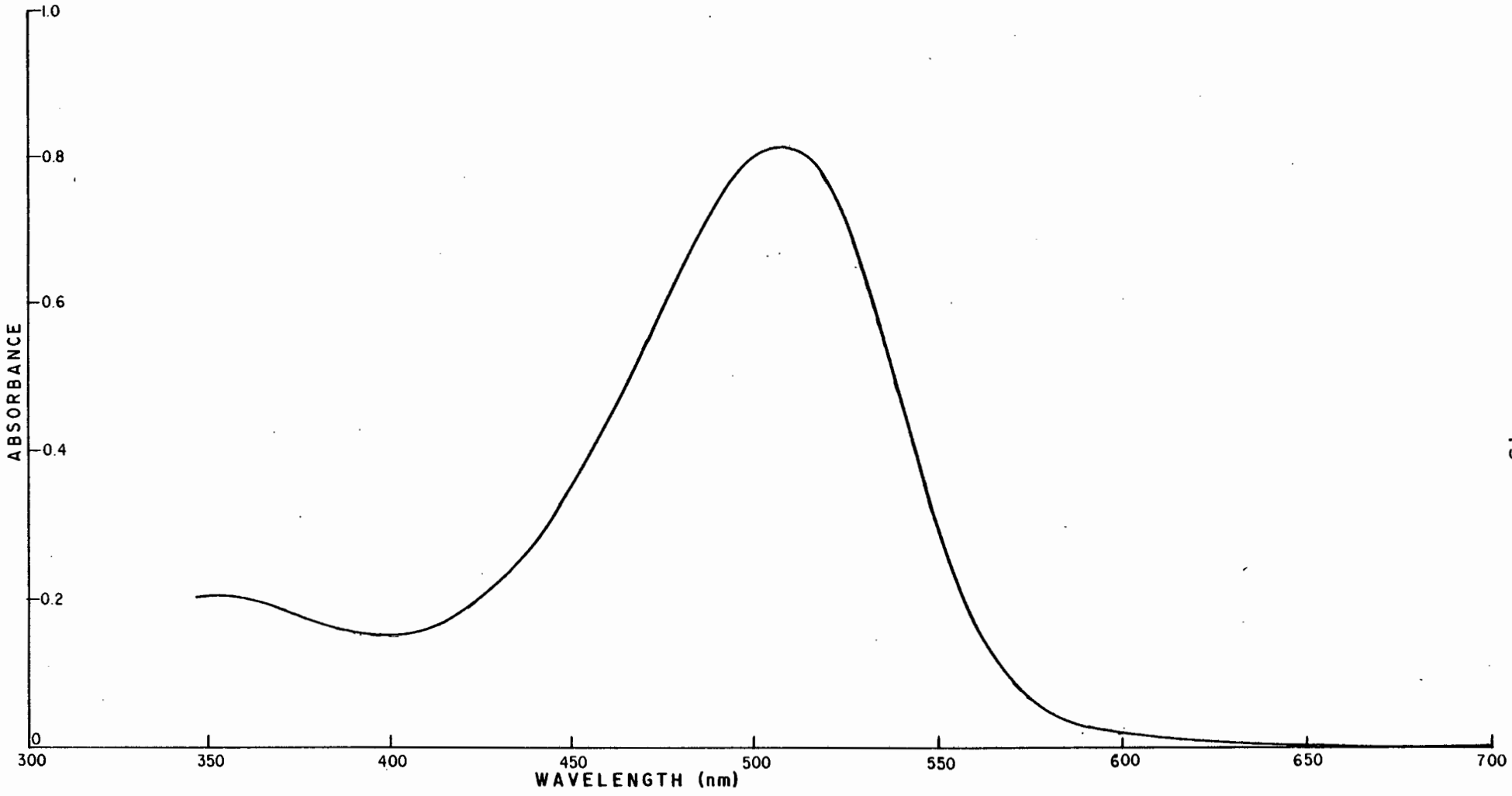


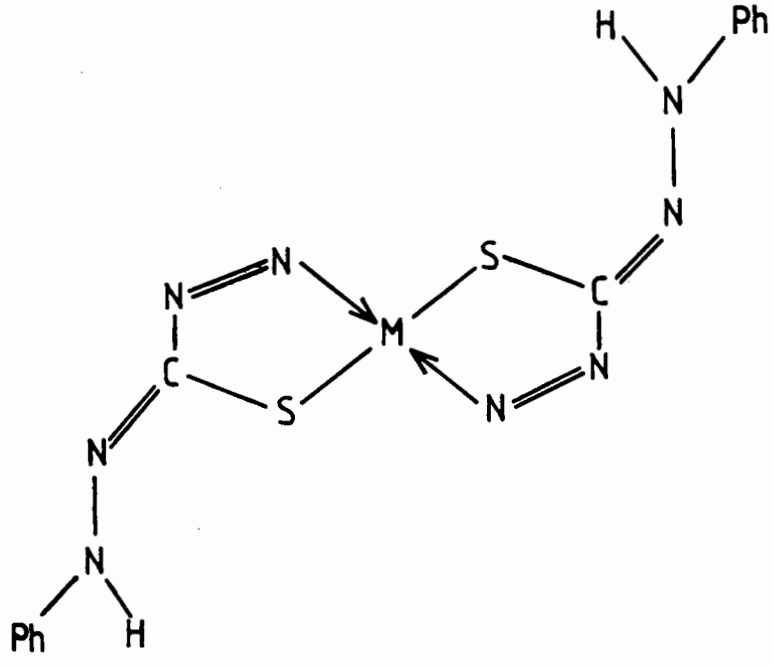
FIGURE 5: Absorption spectrum of thallium(I)-dithizonate [Tl(HDz)] complex in chloroform (λ_{max} 508 nm; ε = 33000 cm^2 mol^{-1})

The extraction of univalent and divalent metal ions with H_2Dz has been thoroughly studied and found under the correct conditions to be relatively straightforward [5]. The structures of several of these metal dithizonates have been determined by X-ray crystallography. In each case the dithizone has been found to behave as a bidentate chelating agent co-ordinating through both nitrogen and sulphur to give a five-membered chelate ring of the type in Figure 6 [20-25].

On the otherhand, with ions of large size and charge, such as Ga^{3+}, Ge^{4+} and Sn^{4+} and especially with powerfully oxidising cations, namely, Au(III), Se(IV), Te(IV), Fe(III) and Tl(III), reactions with dithizone are very complicated. Many of these reactions have as yet not been clearly explained [6].

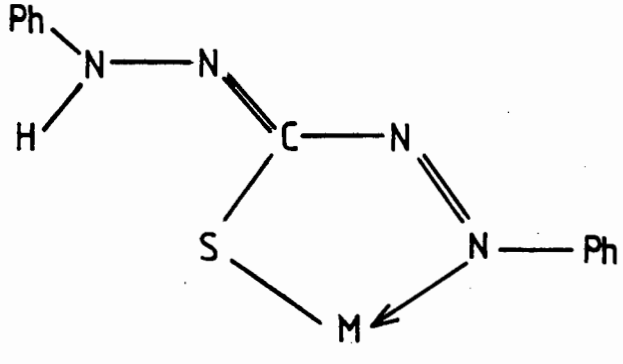
Cox and Servant [26] made a thorough study of the gold-dithizone system. They first showed that the reaction was essentially oxidative in character, the mixture of products depending upon the concentration in the aqueous phase of Au(III), of halide ion, of hydrogen ion, and on the duration and vigour of extraction. The interaction of gold(III) with dithizone under weakly acid conditions can be summarised as follows:

FIGURE 6: Some modes of co-ordination of dithizone to metallic cations.



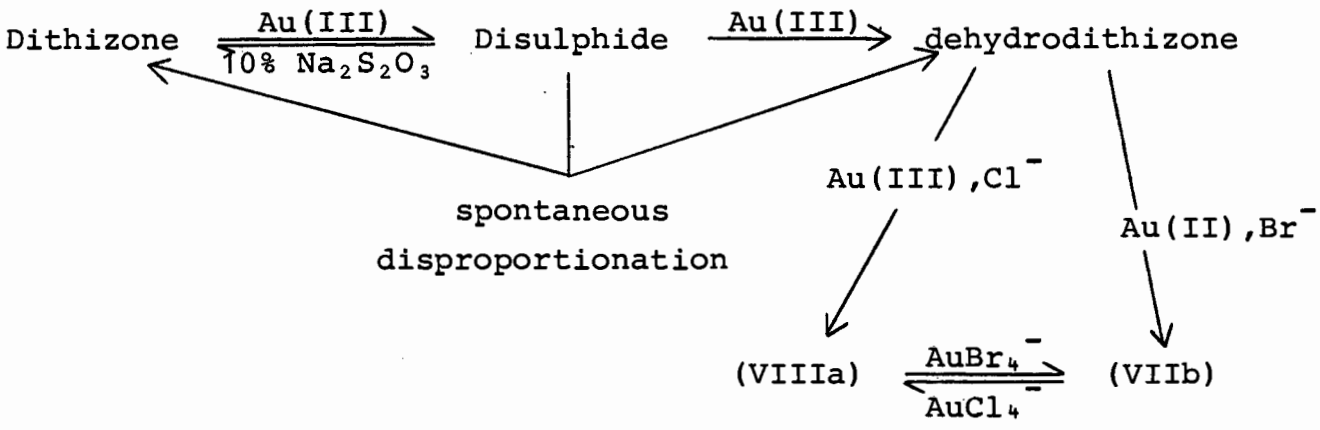
M = Ni^{2+}, Cu^{2+}, Pt^{2+}, Pd^{2+} (square planar)

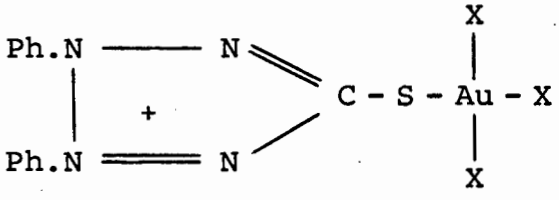
M = Zn^{2+}, Hg^{2+} (tetrahedral)



M = Ag^{+}, Cu^{+}, RHg^{+}

(R = alkyl or aryl)





(VIIa; X = Cl
VIIb; X = Br)

Whereas Stary has given convincing radiometric evidence that Se(IV) reacts with four molecules of dithizone to give a yellow dithizonate, Irving and Ramakrishna only observed oxidation to the yellow disulphide under what appear to be the same conditions [6]. It may well be that, as in the case of Te(IV), the formation of a bis-dithizonate is accompanied by an oxidation product of dithizone [6]. However, no final conclusions have been drawn concerning these two metal ions.

Fe(III) does not form a dithizonate but oxidizes dithizone in alkaline medium, especially in the presence of cyanide [40].

The reaction of thallium(I) with dithizone has been thoroughly studied [5-7, 27-29] and found to lead to a red stable 1:1 complex (pH range 9-12) extractable from CCl_4 or $CHCl_3$;

$$Tl(I)^+ + \overline{H_2Dz} \rightleftharpoons \overline{TlHDz} + H^+ \qquad (1-2)$$

On the otherhand, thallium(III) [like gold(III)] reacts in a most complicated way and the complete reaction scheme has yet to be established [30].

Objectives of Research

The object of the present work was to investigate the interaction between thallium(III) and dithizone by liquid-liquid extraction and absorptiometry in order to establish a complete reaction scheme.

Preliminary studies carried out confirmed the previous work by Irving *et al.* [30]. The reaction was found to be essentially oxidative in character, as well as involving a series of intermediate reactions taking place successively to give a number of reaction products in the organic phase. The initial reaction, leading to the postulated formation of a wine-red $Tl(HDz)_3$ complex, is extremely rapid. This is followed by its spontaneous disproportionation to give Tl(HDz) and the oxidation products, disulphide(III) and mesoionic compound(IV). The course of the reactions involved appear to depend upon the pH of the aqueous phase, the concentration and order of mixing of the reactants, the time of equilibration and on the nature of the organic solvent used.

The study of the interaction between thallium(III) and dithizone was conducted in three stages. Firstly, a detailed investigation of the interaction using chloroform as the organic solvent was undertaken. Secondly, studies were carried out to examine

the effects of the pH of the aqueous phase, the concentration and order of mixing of reactants, and the time of equilibration on the course of the reaction between Tl(III) and dithizone in chloroform. Finally, the results obtained during the study of the reaction in chloroform suggest that the nature of the organic solvent would have a significant effect on the course of the intermediate reactions. Hence, the matter was pursued and the interaction between thallium(III) and dithizone using carbon tetrachloride as the organic solvent was investigated.

Although the stoicheiometries of the previously studied thallium-dithizonates, viz., thallium(I)-dithizonate [5, 6, 27-29]; dimethylthallium(III)-dithizonate and diphenylthallium(III)-dithizonate [17], have been established, their structures are still unknown. This motivated a study of the molecular structure of the diphenylthallium(III)-dithizone [$Ph_2Tl(HDz)$] complex. The complex was prepared and suitable crystals were submitted for structural analysis. A general description of the molecular structure is given in Chapter 8.

CHAPTER 2

OXIDATION OF DITHIZONE: THE PROPERTIES AND REACTIONS OF THE MESOIONIC COMPOUND (IV) AND THE DISULPHIDE(III)

Since the reaction between thallium(III) and dithizone is essentially oxidative in character it is evident that the study of the reaction and its subsequent interpretation would demand a clear knowledge about the oxidation of dithizone. Systematic experimental studies have been carried out by a number of workers [10-12, 14, 15] to investigate and elucidate the processes involved in the oxidation of dithizone. In these studies dithizone was oxidized under various controlled conditions using a number of oxidizing agents including the heavy metal cations Fe(III) and Tl(III). When Tl(III) was used as the oxidant it was found that one major oxidation product was formed, the mesoionic compound (IV).

In the present work, preliminary studies confirmed that Tl(III) reacts with dithizone in chloroform to give the mesoionic compound as the final product. In addition, the formation of the disulphide as an intermediate product was postulated.

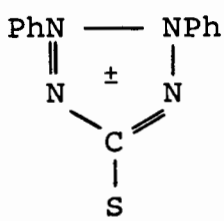
This chapter summarizes the properties and reactions of the mesoionic compound (IV) and the disulphide(III).

2.1 THE MESOIONIC COMPOUND (IV)

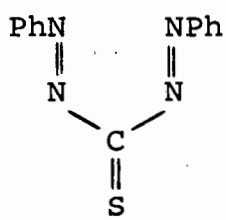
Ogilvie and Corwin [12] were the first to suggest the mesoionic structure (Figure 7 - (IV)) for the orange crystalline "dehydrodithizone" obtained by oxidizing dithizone with potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$). This superseded the thiacarbazone structure (Figure 7 - (VIII)) ascribed by Fischer and Besthorn [2] to the product obtained by treating a dithizone

solution in potassium hydroxide with manganese dioxide, as well as the tetrazolium betaine structure (Figure 7 - (IX)) proposed by Bamberger *et al.* [3] for the product obtained by aerial oxidation or by the oxidation of dithizone with amyl nitrite. Both these compounds (formulated as (VIII)and (IX)) have been shown by Irving *et al.* [10] to be identical with the 'dehydrodithizone' obtained by oxidizing dithizone with $K_3Fe(CN)_6$, which has been correctly formulated by Ogilvie and Corwin as the mesoionic compound (IV). According to Baker *et al.* [31], (IV) is the accepted symbolism for mesoionic compounds and does not imply that a unit negative charge is associated with the exocyclic sulphur atom.

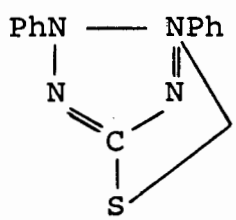
Figure 7



(IV)



(VIII)



(IX)

The structure of this orange-red compound, systematically named 2,3-diphenyl-2H-tetrazolium-5-thiolate, has been confirmed by X-ray crystallography. The phenyl groups are co-planar, with the dihedral angle between the plane of each phenyl ring and the tetrazolium ring being 45°. The tetrazolium ring and exocyclic sulphur atom are coplanar and exhibit extensive electron delocalisation [13].

The mesoionic compound (IV) for convenience will be referred to hereafter by the trivial name 'meso'.

'Meso' is also formed from dithizone by other oxidizing agents e.g. I_2 in aqueous solution, H_2O_2 in dilute NH_3, Fe(III) and Tl(III). In several cases it is accompanied by the disulphide (III) [10].

As a consequence of its more polar nature, meso is more soluble than dithizone in polar solvents and gives orange-yellow coloured solutions. The electronic spectrum of the meso (Figure 8) shows a major peak in the UV region (λ_{max} 266 nm) and a weak band in the visible region (λ_{max} 430 nm).

The electronic spectrum of meso has been found to be unusually sensitive to the solvent used. This phenomenon which can be correlated systematically with the polarity of the solvent has been thoroughly studied by Kiwan and Irving [32]. The authors suggest that the extreme sensitivity is due to the greater charge separation or the presence of the more polarisable negatively charged sulphur atom.

Ogilvie and Corwin noted that meso could undergo nucleophilic displacement reactions as a result of the nucleophilic nature of the sulphur atom. The nucleophilic displacement of halogens from methyl iodide and chloroacetic acid gave rise to the corresponding tetrazolium salts.

The mesoionic compound is a neutral substance and can act as a base and accept a proton as shown below:

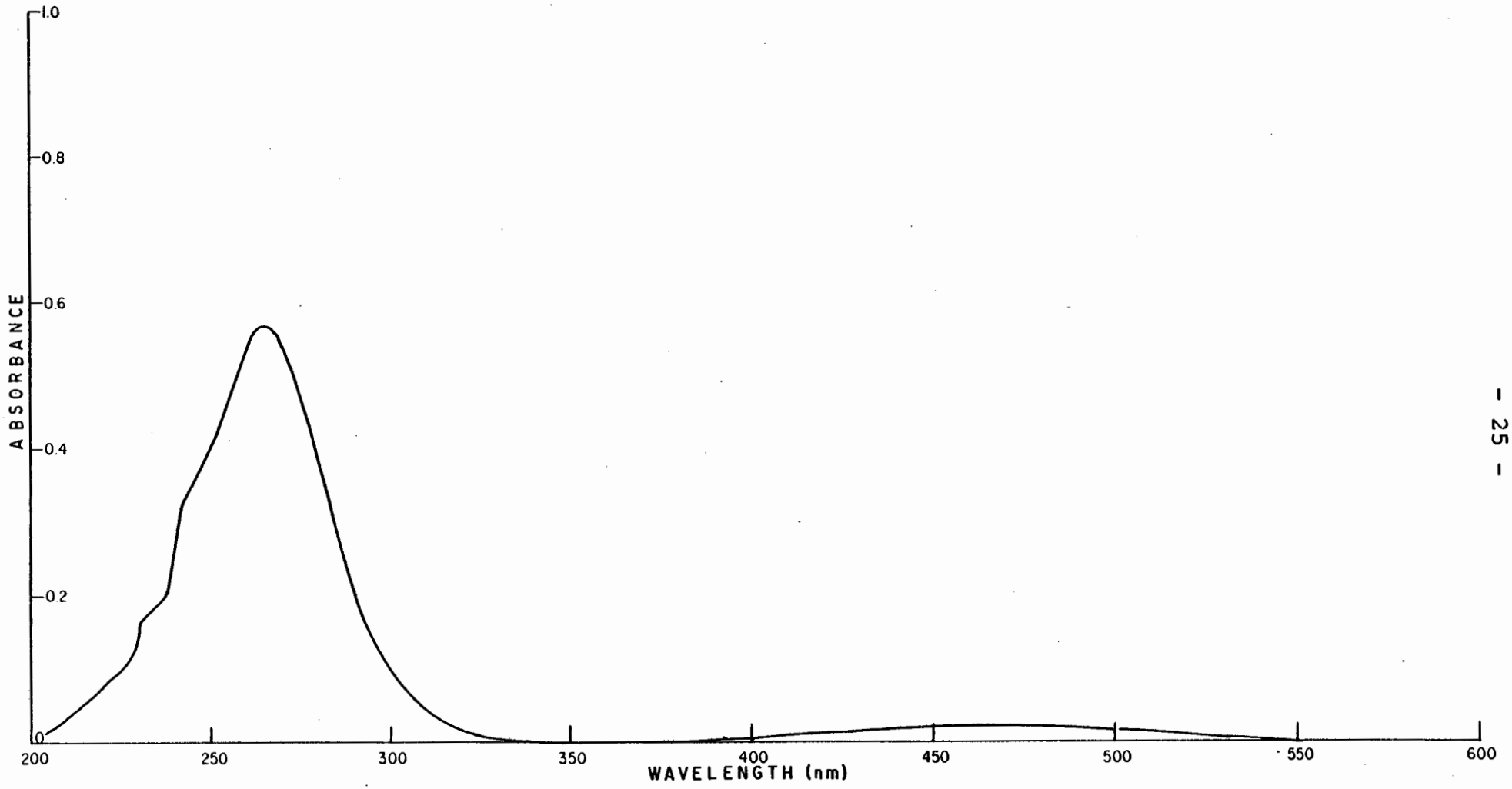
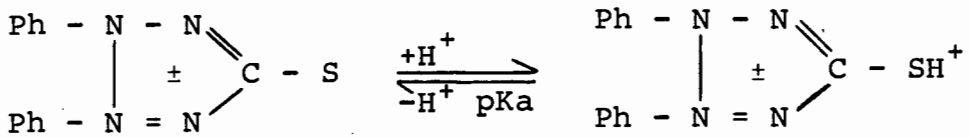


FIGURE 8: Absorption spectrum of the mesoionic compound (IV) in chloroform.



(IV) (IVa)

The protonated meso (IVa) was found to be a strong acid. The acid dissociation constants (pKa) determined in aqueous HCl [12] and $HClO_4$ [33] solutions are -1.57 and -1.59, respectively.

In view of the extensive electron delocalisation in the tetrazole ring and the exocyclic sulphur atom meso has been found to have some interesting metal complexing properties. Kushi and Fernando [34] have shown that the reaction between mercury(II) chloride ($HgCl_2$) and meso gives a 1:1 adduct with an empirical formula $C_{13}H_{10}N_4S \cdot HgCl_2$. The structure of this 1:1 adduct has been shown by X-ray crystallography to be a sulphur bridged polymer containing five co-ordinate Hg atoms. Each Hg atom is co-ordinated to three sulphur and two chlorine atoms. The co-ordination polyhedron around the Hg atom being a distorted trigonal bipyramid [35].

Sahota [10] also found that Hg^{2+} forms a water-soluble complex with meso. The stoicheiometry of the complex was shown to be $[Hg(meso)]^{2+}$. Analogous complexes have been established by Cox and Servant [26] during their study of the reaction between gold(III) and dithizone. The authors showed that Au(III) reacts with meso to give tribromo- and trichlorodehydrodithizone gold(III) complexes which are extractable into the organic phase.

2.2 THE DISULPHIDE(III)

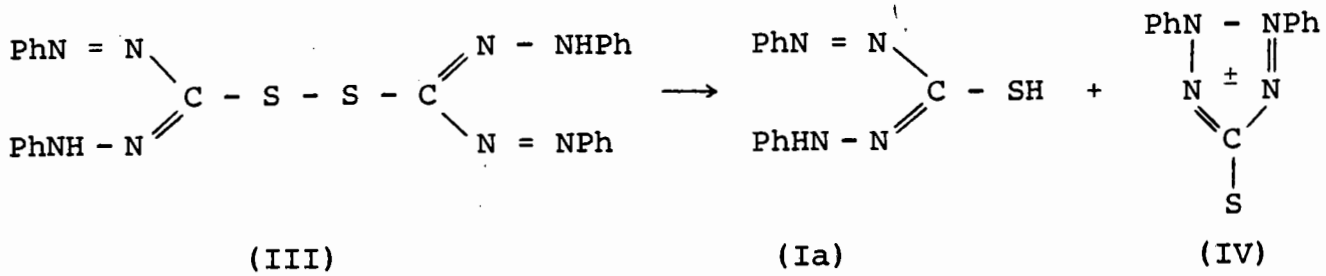
According to the literature [10], dithizone can exist both as a thioketone(Ia) and in the tautomeric thiol form (Ib), therefore mild oxidation should yield the disulphide(III) as this is a characteristic reaction of thiols - especially oxidation with iodine which is commonly used to oxidize thiols to the corresponding disulphides according to the following equation:

$$\overline{2H_2Dz} + \overline{I_2} \longrightarrow 2HI + \overline{(HDz)_2} \qquad (2\text{-}1)$$

The authors in fact found that when solutions of iodine and dithizone in chloroform were shaken in the presence of water, the green colour of the dithizone immediately changed to red and hydriodic acid appeared in the aqueous phase in stoicheiometric agreement with equation (2-1).

The disulphide(III), systematically named bis-1,5-diphenylformazan-3-yl-disulphide, gives yellow to red coloured solutions depending on the concentration and also on the organic solvent used. The electronic spectrum of the disulphide shows one strong absorption band in the region 410 - 428 nm and two in the ultra-violet region: one at *ca.* 303 nm attributable to the S-S bond and another at a still shorter wavelength due to the aromatic rings. The molecular extinction coefficient varies with the solvent used.

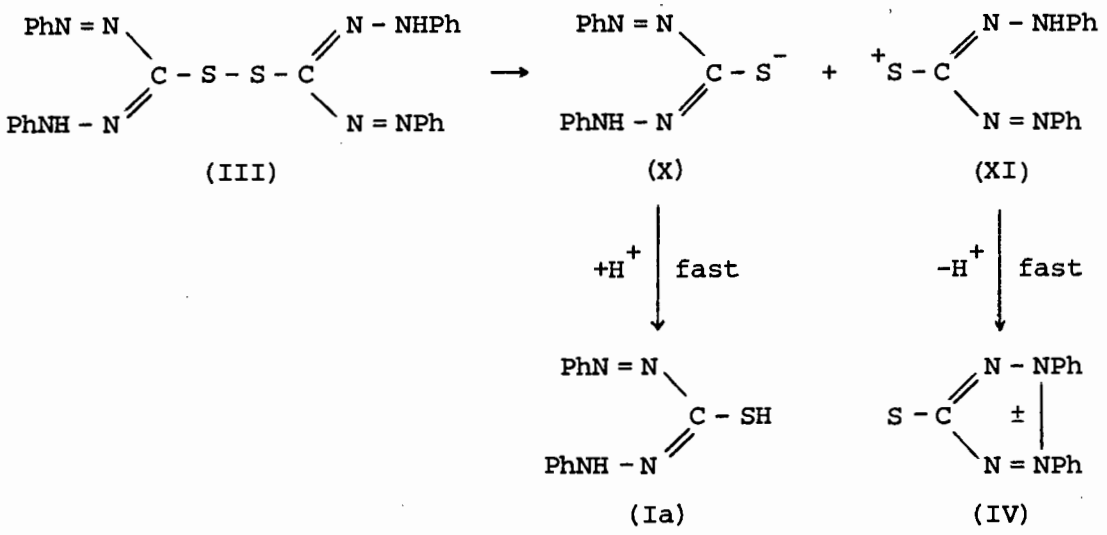
The disulphide was found to undergo spontaneous thermal fission to give equimolar amounts of dithizonate(Ia) and meso(IV) according to the following scheme:



(III) (Ia) (IV)

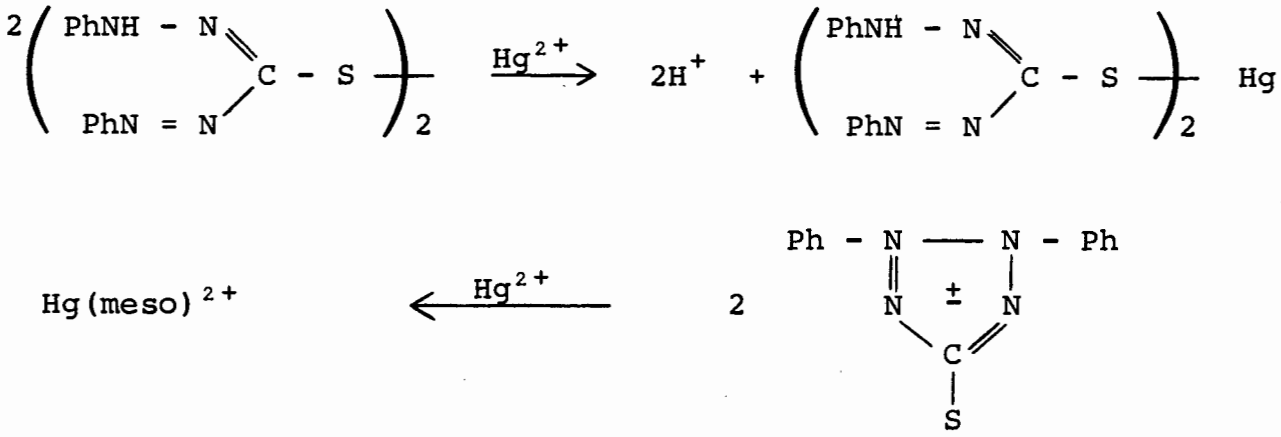
The band at 420 nm (for the disulphide in $CHCl_3$) decreases with a corresponding increase in absorbance at 620 nm and 266 nm, for dithizone and meso, respectively.

The kinetics of the reaction (III) → (Ia) + (IV) has been studied by Kiwan and Irving [36, 37] in a variety of solvents and it was shown to provide a unique example of first-order heterolytic fission. The results suggested that the rate determining stage in the thermal fission of the disulphide(III) is a slow heterolytic fission of the sulphur-sulphur bond to give a dithizonate anion (X) and a sulphenium cation (XI). The latter rapidly releases a proton and rearranges to form the mesoionic compound (IV). The dithizonate ion rapidly accepts a proton to give the conjugate acid shown in (Ia) in the thiol form although equilibrium with the tautomeric thione form is known to be established very rapidly.



Kiwan and Irving also found that the effect of solvent polarity is marked. The rate of fission decreasing in the order ethanol << acetonitrile < acetone < chloroform < 1,2-dichloroethane << carbon tetrachloride < diethylether < cyclohexane $\lesssim$ n-hexane $\lesssim$ isooctane, which parallels the order of their respective polarity parameters. This trend may be expected, since the mesoionic compound is strongly polar and therefore polar solvents would favour the decomposition of the disulphide presumably by stabilising the more polar charge separate transition state by solvation and so lowering the free enthalphies of activation ΔH_{+}^{+}.

Cleavage of the disulphide sulphur-sulphur bond by cations (e.g. Zn^{2+}, Cd^{2+}, Cu^{2+}, Pd^{2+} and $PhHg^{+}$) to give the corresponding metal dithizonate and an equivalent amount of the mesoionic compound, as well as cleavage of the sulphur-sulphur bond according to the following reaction:



have been reported [10]. An analogous type of reaction has also been established for gold(III) (refer to p. 18) except that the final reaction products are the trichloro- and tribromo-dehydrodithizone gold(III) square planar complexes [26].

CHAPTER 3

EXPERIMENTAL APPROACH

3.1 METHODS USED TO STUDY THE INTERACTION BETWEEN THALLIUM(III) AND DITHIZONE

The interaction between thallium(III) and dithizone involves a two phase extraction procedure: Tl(III) in an aqueous acidic layer (pH = 1) and H_2Dz in an organic layer - chloroform as the organic solvent. The various equilibria governing the extraction of primary metal-dithizonates have been discussed in Chapter 1.

Dithizone and all its strictly stoicheiometric metal complexes are characteristically and intensely coloured. They are almost entirely insoluble in water while soluble in a range of organic solvents, such as chloroform and to a lesser extent carbon tetrachloride. Furthermore, the solutions of dithizone and metal dithizonates obey the Beer-Lambert Law over the entire range of analytical concentrations. In addition, the oxidation products of dithizone which have been studied and well-characterized usually tend to favour the organic phase [10]. Hence, the most obvious methods for studying the interaction between Tl(III) and H_2Dz would be liquid-liquid extraction followed by absorptiometry to record the changes undergone in the organic layer.

Spectrophotometric determination of metals using dithizone can be carried out according to three methods as described in the literature [6, 29]. The 'mono-colour' method is where the extraction of the metal is carried out with excess dithizone which is then removed after extraction by washing the organic phase with aqueous alkali. This method is, however, always

open to question as it depends greatly on the constancy of the concentrations of the standard solutions of dithizone, which are known to deteriorate fairly rapidly in $CHCl_3$ when in contact with buffers of higher pH values. The mono-colour method also involves other sources of error, namely, if the alkalinity of the wash solution is too high some of the metal dithizonate may decompose, or if the alkalinity is not high enough, an appreciable amount of free dithizone may be left in the organic layer. Although with some metals good results can be obtained by this method it is not sound in principle and the 'mixed-colour' method which was developed to circumvent the difficulties encountered in the mono-colour method is much to be preferred.

In the mixed-colour method the excess dithizone is allowed to remain in the organic solvent with the metal dithizonate. The absorbances (A_1, A_2) of the dithizone and metal-dithizonate in the mixture are then measured at the wavelengths (λ_1, λ_2) chosen so that the differences in the extinction coefficient, ε, for each are maximal. The concentration, c, of the metal dithizonate complex will be given by:

$$A_1 = (c_d\varepsilon_{d,1} + c_c\varepsilon_{c,1})\ell \quad \text{at } \lambda_1$$

$$A_2 = (c_d\varepsilon_d + c_c\varepsilon_{c,2})\ell \quad \text{at } \lambda_2$$

whence

$$c_c = (A_1\varepsilon_{d,2} - A_2\varepsilon_{d,1})/(\varepsilon_{c,1}\varepsilon_{d,2} - \varepsilon_{c,2}\varepsilon_{d,1})$$

where the subscripts d and c represent the dithizone and metal complex, respectively.

Although this method circumvents the possible errors involved in the mono-colour method, both methods still have the drawback of not being able to account for any adventitious light absorbing species present in the organic phase. These may be derived from dithizone as oxidation products or traces of other metal dithizonates which are present as impurities. Nevertheless, under properly controlled conditions the mixed-colour method has been found to be valuable in obtaining good reproducible results as was reported by Clarke and Cuttita [38] for the determination of thallium(I) by dithizone.

An alternative procedure, using the mixed colour method, would be to measure the mixture against a portion of the original dithizone solution instead of the solvent blank. If the dithizone solution to be used in the reference cell is then subjected to a partition stage involving precisely the same aqueous medium as that used in the extraction stage, the desired metal component being absent, then this will take into account the loss of any dithizone to the aqueous phase, as dithizonate anions. It will also take into account the presence of any coloured impurities. The difference in absorbance would then give the concentration of the extracted metal complex only.

One particular method, the reversion procedure, introduced by Irving *et al.* [9] takes into account the drawbacks of the two above-mentioned methods and also allows for the presence of coloured impurities in the organic phase.

If the concentration of each individual impurity is denoted by

c_i with the extinction coefficient ε_i then the absorbance of the mixed solution can be given by:

$$A_{(mixture)} = (c_d\varepsilon_d + c_c\varepsilon_c + \Sigma c_i\varepsilon_i)\ell$$

It is now possible to treat the organic phase with a 'reversion agent' chosen so that only the desired metal dithizonate is reverted according to equation (3-1),

$$nH^+ + \overline{M(HDz)_n} \longrightarrow M^{n+} + \overline{n(H_2Dz)} \qquad (3\text{-}1)$$

an equivalent amount of pure dithizone will be liberated and the absorbance of the reversion mixture will be:

$$A_{(reversion)} = (c_d\varepsilon_d + nc_c\varepsilon_d + \Sigma c_i\varepsilon_i)\ell$$

So the difference (the 'reversion value') becomes:

$$A_R = A_{(reversion)} - A_{(mixture)}$$

$$= c_c(n\varepsilon_d - \varepsilon_c)\ell$$

It is a condition that the measurements are made at λ_{max} for dithizone, where $\varepsilon_d >> \varepsilon_c$ for the majority of metals. Under these circumstances the calibration curve will be linear and pass through the origin and is independent of the actual concentration of the dithizone used.

Rupainwar and Kakkar [39] developed a modified reversion procedure for the determination of microgram quantities of thallium(I)

using dithizone. This method with further modification (described later) was used in the present study to determine the exact amounts of Tl(I) extracted by dithizone. In addition, this method was also particularly useful for determining the stoicheiometry of the metal-dithizonate complexes as well as a means for standardizing solutions of Tl(I) and Tl(III) utilized.

The three above-mentioned methods involve the use of excess reagent. However, in the present study the procedure of total conversion was employed, i.e. where the metal ions were in far greater excess than the dithizone. In cases where there were mixtures of dithizone and reaction products in the organic phase the mixed-colour method was used.

It was soon realised that the interaction between Tl(III) and H_2Dz involved a series of rapid reactions taking place successively. The initial stage of the reaction proceeding far too rapidly to allow for detailed examination. It was therefore considered worthwhile to study the interaction in a single phase rather than the usual two-phase system so that direct spectrophotometric measurements could be made immediately after mixing the reactants, thus avoiding the inevitable time delay between solvent extraction and spectrophotometric measurements. Furthermore, by studying the interaction between Tl(III) and H_2Dz in a single phase stopped-flow methods, which are specially designed for the study of fast reactions, could be employed.

It was found that in the ratios 1 : 3 : 1 ($CHCl_3$: MeOH : $HClO_4$) the three solvents were miscible thus constituting a single phase. However, this monophase was found to be unsuitable for investigating the interaction between Tl(III) and H_2Dz because:

(i) Dithizone was found to be unstable in this medium.

(ii) Methanol increases the polarity of the monophase. Consequently, this would increase the rates of the reactions involved owing to the nature of the reaction products formed.

The reason why dithizone is unstable in this medium could not be explained. The purity of the materials were rechecked and hydroxylamine hydrochloride was added to freshly prepared dithizone solutions to reduce any oxidant that may be present. However, the solutions still remained unstable. The same effect was observed even when water or HCl were used instead of $HClO_4$.

Unfortunately, further attempts to find a suitable single phase proved to be unsuccessful.

CHAPTER 4

PRELIMINARY INVESTIGATION

In a preliminary experiment in which a solution of dithizone in chloroform (Figure 9, spectrum 1) was added to an aqueous acidic solution (pH = 1) containing excess Tl(III) in a separating funnel, an immediate colour change in the organic phase from green to a wine-red (Figure 9, spectrum 2) was observed. After shaking the two phases for one minute there was a further change in colour in the organic phase to a pink-red (Figure 9, spectrum 3). On standing (3 - 4 hours) the organic layer underwent a series of further colour changes from pink-red, orange and finally to a yellow (Figure 9, spectrum 4).

From the foregoing observations it is evident that the interaction between thallium(III) and dithizone in chloroform is complex in that a number of reactions take place successively.

At this stage it was only possible to speculate that the initial wine-red extract was due to the formation of a transient thallic-dithizonate, $Tl(HDz)_3$. The $Tl(HDz)_3$ spontaneously disproportionating to give various reaction products in the organic phase (Figure 9, spectrum 2).

Since Tl(III) is a powerful oxidant (standard reduction potential, $E^{\ominus} = +1.33$ V [40]), one might anticipate that there would be a simultaneous oxidation of dithizone and reduction of Tl(III) to Tl(I). Previous studies [10] have shown that Tl(III) oxidizes dithizone to give the mesoionic compound (IV) as the major oxidation product. Referring to Figure 9, the spectrum representing the yellow extract (λ_{max} 266 nm) is identical to the spectrum representing the authentic meso in $CHCl_3$ (Figure 8). This

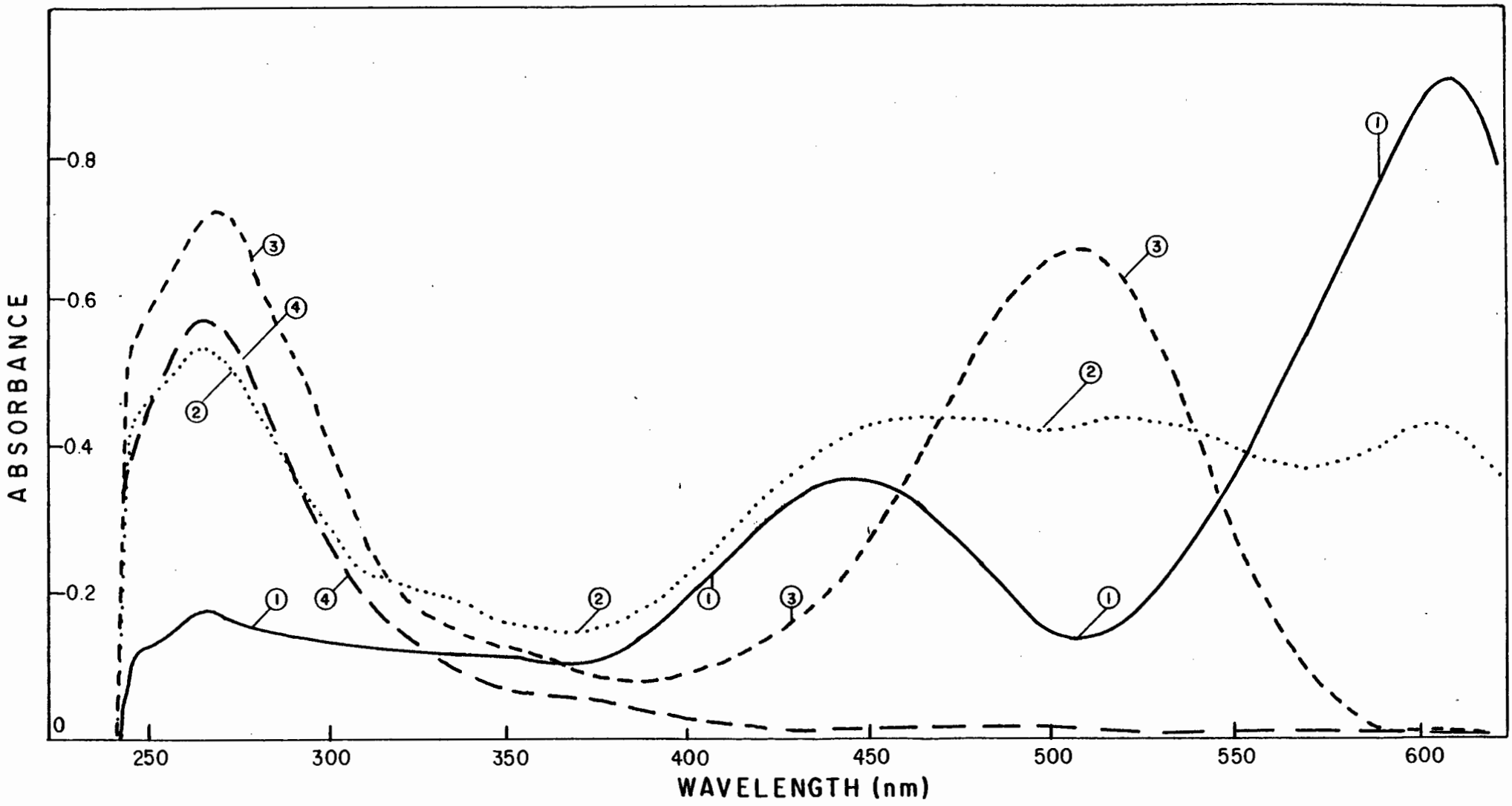


FIGURE 9: Interaction between thallium(III) (4×10^{-3} M) and dithizone in chloroform (2×10^{-5} M). The absorption spectra of the:

1: dithizone solution in chloroform
2: wine-red organic extract
3: pink-red organic extract
4: yellow organic extract.

confirms that the reaction between Tl(III) and H_2Dz is oxidative in character and gives meso as the final reaction product.

In spectrum 3, the disappearance of the absorbance at 605 nm (due to dithizone) suggests that dithizone is being consumed during the reaction in forming possibly a dithizonate complex that absorbs at 508 nm, as this peak has now become predominant. At the same time the broad absorption band below 508 nm has also disappeared. Since it has been established that thallium(III) oxidizes dithizone it is possible that the resulting Tl(I) formed may complex with the dithizone to give a thallium(I)-dithizonate complex, Tl(HDz). According to the literature [5, 6] the Tl(HDZ) does absorb strongly in this region. This may well explain the presence of the well-characterized peak at 508 nm.

It is evident from the spectrum 2 that the absorbance at $\sim$ 450 nm is far greater than would be expected if H_2Dz, Tl(HDz) and meso were the only absorbing species present in the organic phase. This implies that another product, contributing to the absorption of dithizone at 450 nm, must also be present in the organic phase. Since the disulphide(III) is known to absorb strongly in this region [10], this suggested that it also formed during the reaction.

The foregoing observations gave rise to the following hypothesis based on the assumption that a thallic-dithizonate is formed initially: Thallium(III) reacts with dithizone to give a transient thallic-dithizonate which oxidatively disproportionates to give Tl(HDz) and the disulphide. The disulphide spontaneously

decomposes to give equimolar amounts of dithizone and meso. The Tl(HDz) undergoes reversion to give dithizone in the organic phase and Tl^+ in the aqueous phase. The regenerated dithizone being further oxidized by the excess Tl(III) to give meso as the final reaction product.

Detailed experiments described in Chapter 5, Part 1 were carried out to test these hypotheses.

Since the interaction between Tl(III) and dithizone involves a two-phase extraction procedure, which is determined by a number of parameters (Figure 4), one might anticipate that the course of the reactions involved would depend on the pH of the aqueous phase, the concentration and order of mixing of reactants, the time of equilibration and on the nature of the organic solvent used. Studies to examine the effects of the above-mentioned variables on the course of the reaction are described in Chapter 5, Part II and Chapter 6.

Before any detailed spectrophotometric measurements were undertaken it was necessary to check whether dithizone and meso interact in solution. A binary mixture of the two solutions was prepared and its absorbance spectrum recorded. The absorbance of each component was measured and found to be strictly additive. Therefore it should be possible to calculate the individual concentrations of dithizone and meso in solution, during the study of the interaction between Tl(III) and dithizone.

PART I

CHAPTER 5

INVESTIGATION OF THE INTERACTION BETWEEN THALLIUM(III) AND DITHIZONE IN CHLOROFORM

5.1 FORMATION OF THALLIUM(I)-DITHIZONATE

In the preliminary experiment, described in the previous chapter, it was postulated that the pink extract (Figure 9, spectrum 3), which gives rise to the well-characterized peak at 508 nm, is due to the formation of a Tl(HDz) complex. To test this hypothesis the extraction of Tl(I) by dithizone was carried out. In agreement with the literature [5-7, 27-29], experiments showed that Tl(I) is quantitatively extracted by dithizone in the pH range 10 - 12 to give a stable pink-red complex in the organic phase (refer to p. 15, Figure 5: λ_{max} 508 nm, ε = 33 000 cm^2 mol^{-1}), according to the following equation:

$$Tl^+ + HDz^- \longrightarrow \overline{Tl(HDz)} \qquad (5\text{-}1)$$

No extraction occurred under acidic conditions (pH < 6).

On the basis of the foregoing results, it is evident that Tl(III) also reacts with dithizone at pH = 1 to give a product extractable into the organic phase which absorbs at the same λ_{max} as the authentic Tl(HDz) complex. This strongly supports the hypothesis that a Tl(HDz) complex is formed by the reaction between Tl(III) and H_2Dz. Further experiments were carried out to verify this.

A solution of dithizone in chloroform (1.7×10^{-5} M) was added to an aqueous solution of Tl(III) (2×10^{-5} M) in a separating funnel and shaken for 1 minute. When the layers had separated, the organic layer containing the pink extract was transferred into another separating funnel. A portion of this solution was

used to record an absorption spectrum (Figure 10, spectrum 1), and then returned to the separating funnel containing the remaining solution. This solution was reverted with 1M $HClO_4$ whereupon the green dithizone solution was regenerated in the organic phase (Figure 10, spectrum 2).

From the spectra 1 and 2 in Figure 10 the composition of the metal-dithizone complex could be calculated:

Concentration of the dithizone solution taken

$= 1.7 \times 10^{-5}$ M

The concentration of the complex formed (λ_{max} 508 nm):

Spectrum 1 shows that some unreacted dithizone is also present in the organic solution. The extinction coefficient for dithizone at 508 nm, calculated from the spectrum of the pure reagent, is 5 900 cm^2 mol^{-1}. Therefore, the amount of absorption interference at 508 nm from the unreacted dithizone is:

5 900/41 400 x 0.070 = 0.012

Based on the assumption that the complex is Tl(HDz) - the concentration of the complex is:

A = 0.196 - 0.012 = 0.184 (ε = 33 000)

Concentration = 0.184/33 000

$= 0.56 \times 10^{-5}$ M

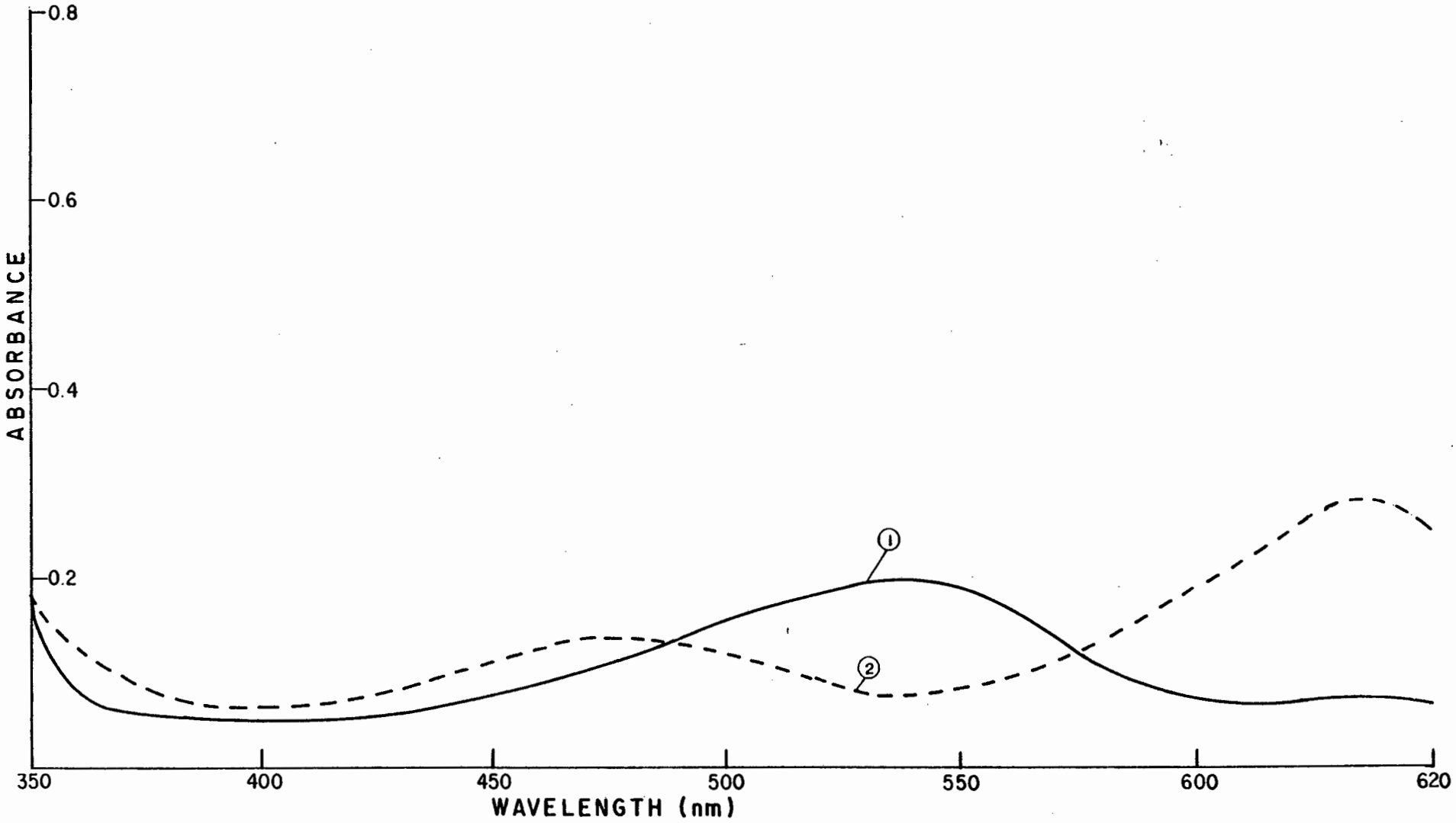


FIGURE 10: Interaction between thallium(III) (2×10^{-5} M) and dithizone in chloroform (1.7×10^{-5} M): Reversion of the Tl(HDz) complex. Absorption spectra of:

1: Tl(HDz) complex 2: regenerated dithizone solution

The concentration of the dithizone regenerated:

$$A = 0.300 - 0.070 = 0.230 \quad (\varepsilon = 41\ 400)$$

$$\text{Concentration} = 0.230/41\ 400$$

$$= 0.56 \times 10^{-5}\ M$$

Hence, the combining ratio of the metal-dithizone complex is 1:1.

On shaking the 'reverted' aqueous acidic phase with a solution of dithizone the metal could not be extracted until after the pH of the aqueous solution had been adjusted to pH = 12. The λ_{max} recorded for this metal-dithizone complex corresponds to the λ_{max} for the authentic Tl(HDz) complex. This confirms that the metal-dithizone complex formed by the reaction between Tl(III) and H_2Dz is a 1:1 thallium(I)-dithizone complex.

From the above calculations it can also be shown that only a third of the dithizone is consumed during the reaction between excess of Tl(III) and H_2Dz to form the Tl(HDz) complex. This suggests that Tl(III) may initially react with dithizone in the molar ratio 1:3 and that it is also effective in oxidizing two-thirds of the original dithizone to other products.

This still leaves open the question as to why and how the Tl(HDz) complex is formed in the organic phase by the reaction between Tl(III) and dithizone when it has been found that Tl(I) cannot be extracted by dithizone under acidic conditions (see p. 45). One could, however, postulate that Tl(III) reacts with dithizone to give an extractable thallium(III)-dithizonate complex and that this complex oxidatively disproportionates in the organic

phase as follows:

$$\overline{Tl(HDz)_3} \longrightarrow \overline{Tl(HDz)} + \overline{(HDz)_2}$$

i.e. to give the thallium(I)-dithizonate complex, Tl(HDz) and the neutral disulphide(III), $(HDz)_2$. The Tl(HDz) complex being unstable under acidic conditions consequently undergoes reversion to give Tl^+ in the aqueous phase and dithizone in the organic phase, according to the following equation:

$$H^+ + \overline{Tl(HDz)} \longrightarrow Tl^+ + \overline{H_2Dz}$$

The rate of the above reaction depending on the time and vigour of equilibration and increasing with the acidity of the aqueous phase (see p. 83).

To illustrate the decomposition of the Tl(HDz) complex, solutions containing (excess) Tl(III) and H_2Dz were shaken for 1 minute. The organic phase was withdrawn and the absorption spectrum of the resulting Tl(HDz) complex was recorded at regular intervals (Figure 11). The reversion is fairly slow as the complex is only in contact with a small percentage of the aqueous acidic solution (pH = 1) which is miscible with the organic solvent.

The possible fate of the disulphide(III) on equilibration with the excess of Tl^{3+} will be discussed in the following section.

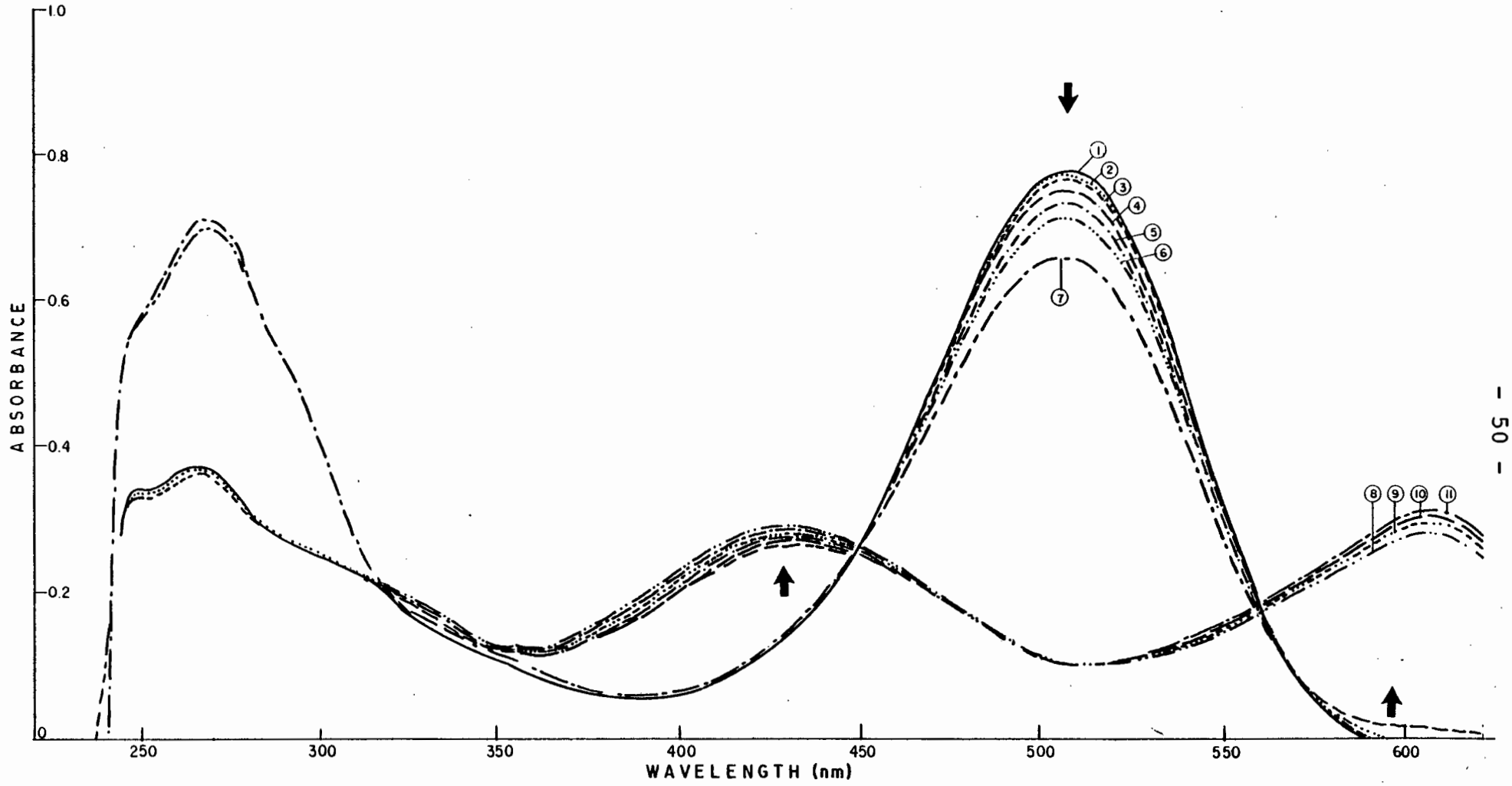


FIGURE 11: The reaction of thallium(III) with dithizone in chloroform (shaking time - 1 min). Absorption spectra illustrating the decomposition of the $Tl(HD_2)$ complex:
Spectra 1 - 7 recorded after 5, 10, 20, 30, 40, 50 and 80 min., respectively
Spectra 8 - 11 recorded after 240, 245, 250 and 255 min., respectively.

5.2 FORMATION OF THE DISULPHIDE(III)

To establish whether Tl(III) reacts with dithizone to give the disulphide as an intermediate oxidation product, it was necessary to prepare the disulphide (see Chapter 9 § (9.2.2) and study its behaviour in chloroform although its rate of decomposition in a variety of solvents had previously been reported [36].

The absorbance of a disulphide solution in chloroform was recorded at 2 min. intervals (Figure 12). The disulphide has a strong absorption band at 420 nm. This band spontaneously decreases in absorbance and there is a corresponding increase in absorbance at 605 nm and 266 nm, giving rise to isobestic points at 508 nm and 297 nm. The bands at 605 nm and 266 nm are attributable to the dithizone and meso, respectively and the total absorbance

$$= \ell\{[(HDz)_2]\varepsilon_{\text{disulphide}} + [H_2Dz]\varepsilon_{\text{dithizone}} + [\text{meso}]\varepsilon_{\text{meso}}\}.$$

The decomposition of the disulphide can thus be represented as follows:

$$\overline{(HDz)_2} \rightleftharpoons \overline{H_2Dz} + \overline{\text{meso}}$$

Clearly the rate of the disproportionation of the disulphide is rapid in chloroform, the heterolytic fission being kinetically favoured by the polar solvent [10].

Hence, referring to Figure 9, if the disulphide is formed in the initial stage of the reaction between Tl(III) and H_2Dz, one

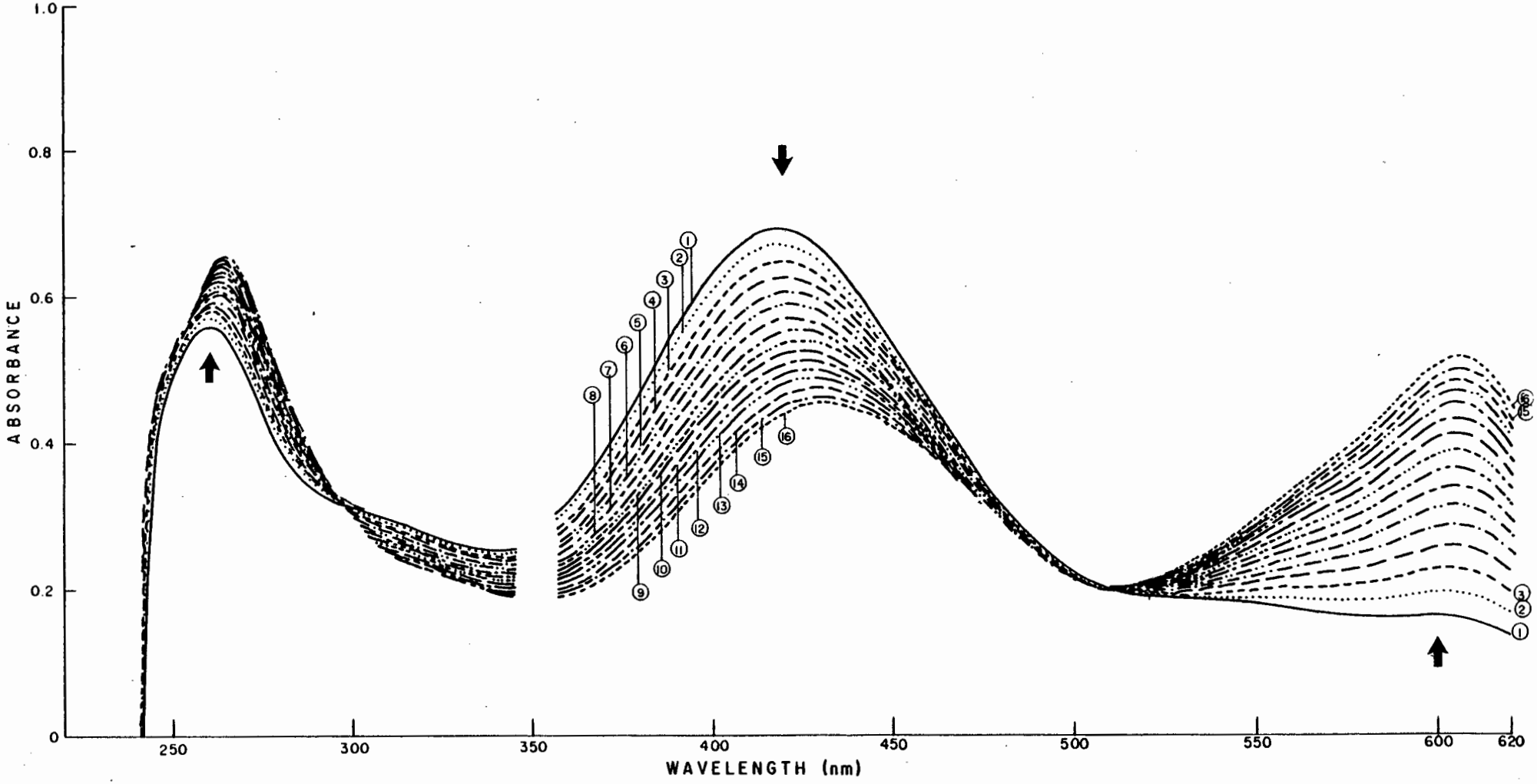


FIGURE 12: The absorption spectra of a disulphide(III) solution in chloroform, recorded at 2 min. intervals.

would expect to see a rapid decrease in the absorbance at ∿450 nm and a corresponding increase in absorbance at 605 nm and 266 nm, respectively. To establish whether this indeed occurs, a dithizone solution was added to a Tl(III) solution and the absorption spectrum of the resulting wine-red extract recorded at 2 min. intervals (Figure 13). The spectra show a rapid decrease in absorbance at 450 nm as well as at 525 nm and an increase in absorbance at 605 nm and 266 nm, respectively, thus confirming the presence of the disulphide. The foregoing observations can be represented by the following equations based on the assumption that a transient thallic dithizonate is formed initially:

$$Tl^{3+} + \overline{3H_2Dz} \longrightarrow \overline{Tl(HDz)_3} + 3H^+ \qquad (5\text{-}2)$$

$$\overline{Tl(HDz)_3} \longrightarrow \overline{Tl(HDz)} + \overline{(HDz)_2} \qquad (5\text{-}3)$$

$$\overline{(HDz)_2} \longrightarrow \overline{H_2Dz} + \overline{meso} \qquad (5\text{-}4)$$

$$H^+ + \overline{Tl(HDz)} \longrightarrow Tl^+ + \overline{H_2Dz} \qquad (5\text{-}5)$$

The overall reaction at pH = 1 would therefore be:

$$Tl^{3+} + \overline{3H_2Dz} \longrightarrow Tl^+ + \overline{2H_2Dz} + \overline{meso} + 2H^+ \qquad (5\text{-}6)$$

Clearly the intermediate reaction described by equation (5-3) is far too rapid, at least in chloroform, to allow for any detailed examination.

It has been reported that a number of cations react with the disulphide by cleaving the sulphur-sulphur bond to give the

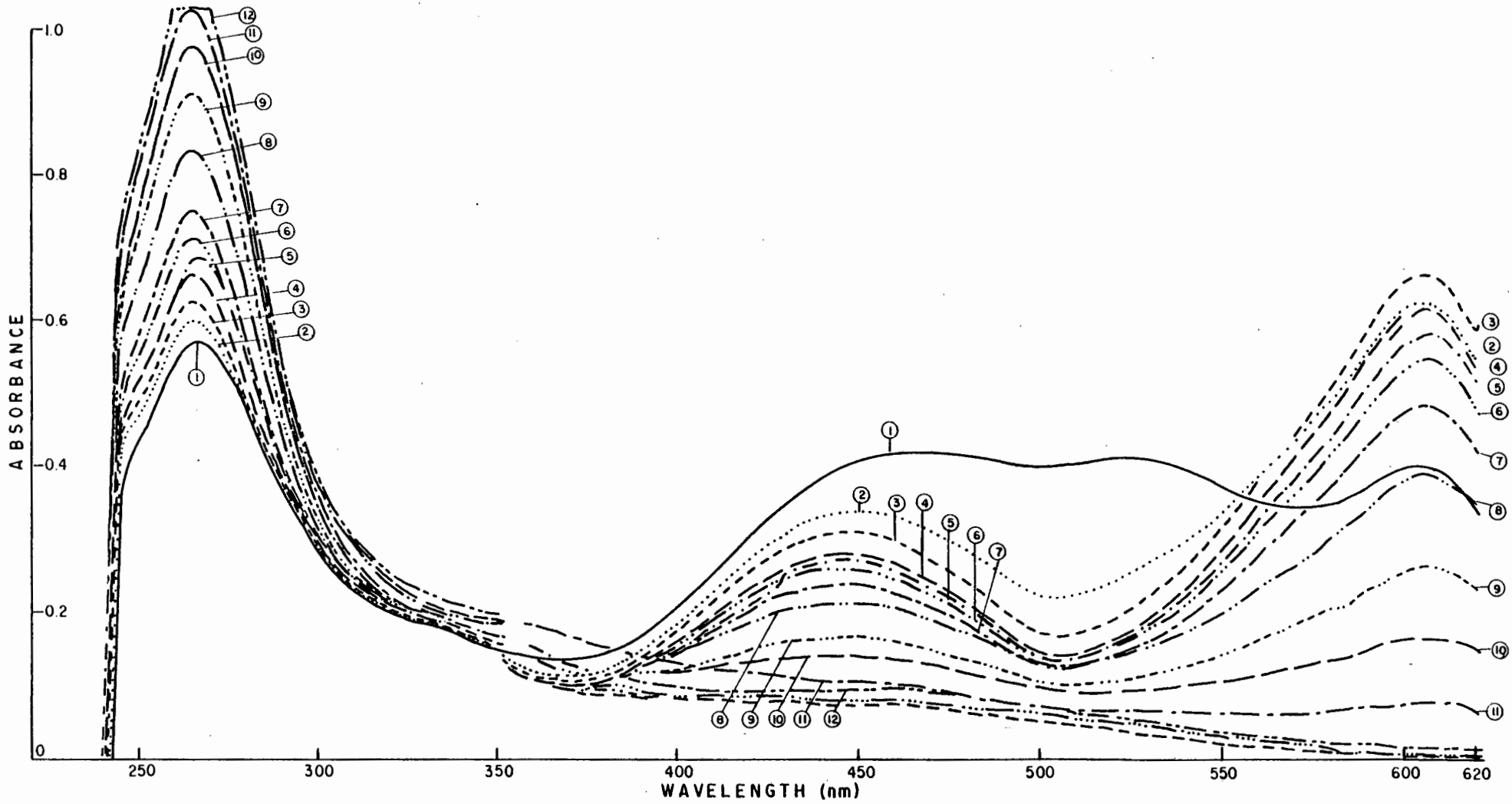


FIGURE 13: The interaction between thallium(III) and dithizone in chloroform. Absorption spectra of the wine-red organic extract, recorded at 2 min. intervals.

corresponding metal dithizonate and an equivalent amount of meso [10]. Therefore it was considered necessary to investigate the interactions between the disulphide and Tl^{3+} and Tl^{+}.

Interaction between Tl^{3+} and the disulphide

The spectra in Figure 14 show that when solutions containing Tl^{3+} and the disulphide are shaken together, there is a decrease in absorbance at 605 nm and a corresponding increase in absorbance in the region 500 - 520 nm. In addition, there is a large increase in absorbance at 266 nm. With time the absorbance at $\sim$500 nm and 420 nm decreases, and there is a reappearance and increase in absorbance at 605 nm. Furthermore, it was noted that the decrease in absorbance for the disulphide at 420 nm is faster after equilibration with a Tl(III) solution. To explain these observations the following hypothesis was suggested:

Tl^{3+} reacts with the disulphide by catalysing the cleavage of the S - S bond to give equimolar amounts of dithizone and meso, thereby increasing the overall rate of the disproportionation of the disulphide. The excess Tl^{3+} simultaneously oxidizes the regenerated dithizone according to the equations (5-2) - (5-6) given on p. 53.

On the basis of this hypothesis, the oxidation of the dithizone with the resulting formation of the Tl(HDz) complex should become more apparent if more dithizone is present in the disulphide solution. To test this hypothesis the experiment was repeated using the same disulphide solution 1½ and 2 hours after it had

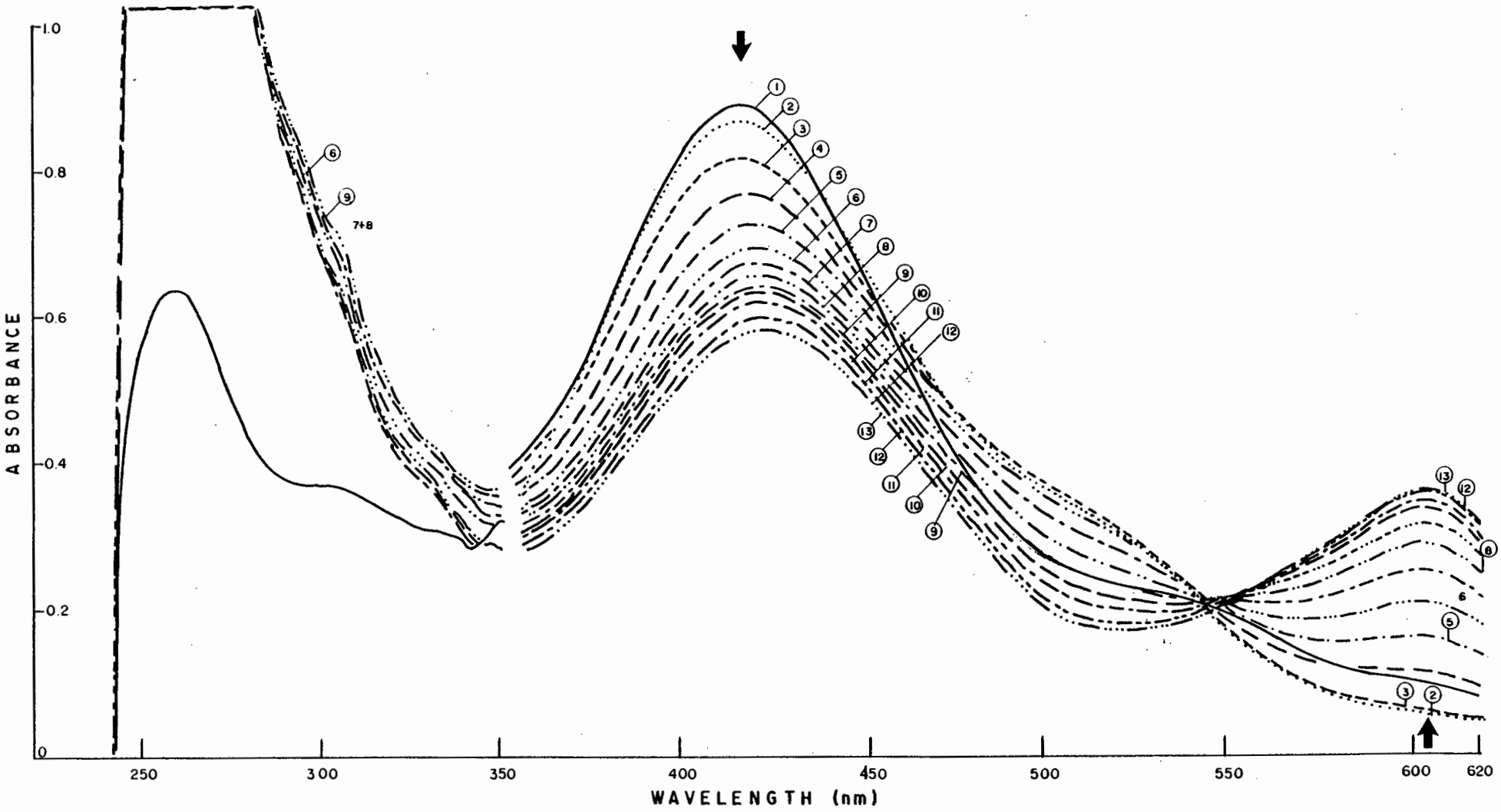


FIGURE 14: Interaction between Tl(III) and the disulphide(III). Absorption spectra of the:

1: disulphide solution in chloroform

2 - 13: disulphide solution after equilibration with a Tl(III) solution. Spectra recorded at 2 min. intervals.

been prepared (Figures 15 and 16). The spectra show that the absorption band at 420 nm has decreased and that the absorption band at 500 - 520 nm has now reached a well-defined peak at 508 nm. This confirms that a Tl(HDz) complex is formed and verifies the hypothesis suggested.

Interaction between Tl^+ and the disulphide

The interaction between Tl^+ and the disulphide was examined under acidic conditions (pH ≈ 1) (Figure 17). The spectra in Figure 17 show that, in comparison to Figure 12 (see p. 52), Tl^+ catalyses the heterolytic fission of the disulphide. Moreover, there is no evidence of a thallium(I)-dithizonate complex in the organic phase.

5.3 FORMATION OF THE MESOIONIC COMPOUND(IV)

In the preliminary investigation (Chapter 4) it was established that Tl(III) reacts with dithizone to give the mesoionic compound(IV) as the final reaction product. However, during the study of this reaction it was found that only ~80% of the dithizone taken could be accounted for by the presence of meso in the organic phase. This leaves open the question as to whether:

(a) the dithizone is oxidized to give meso plus non-absorbent material or water-soluble products,

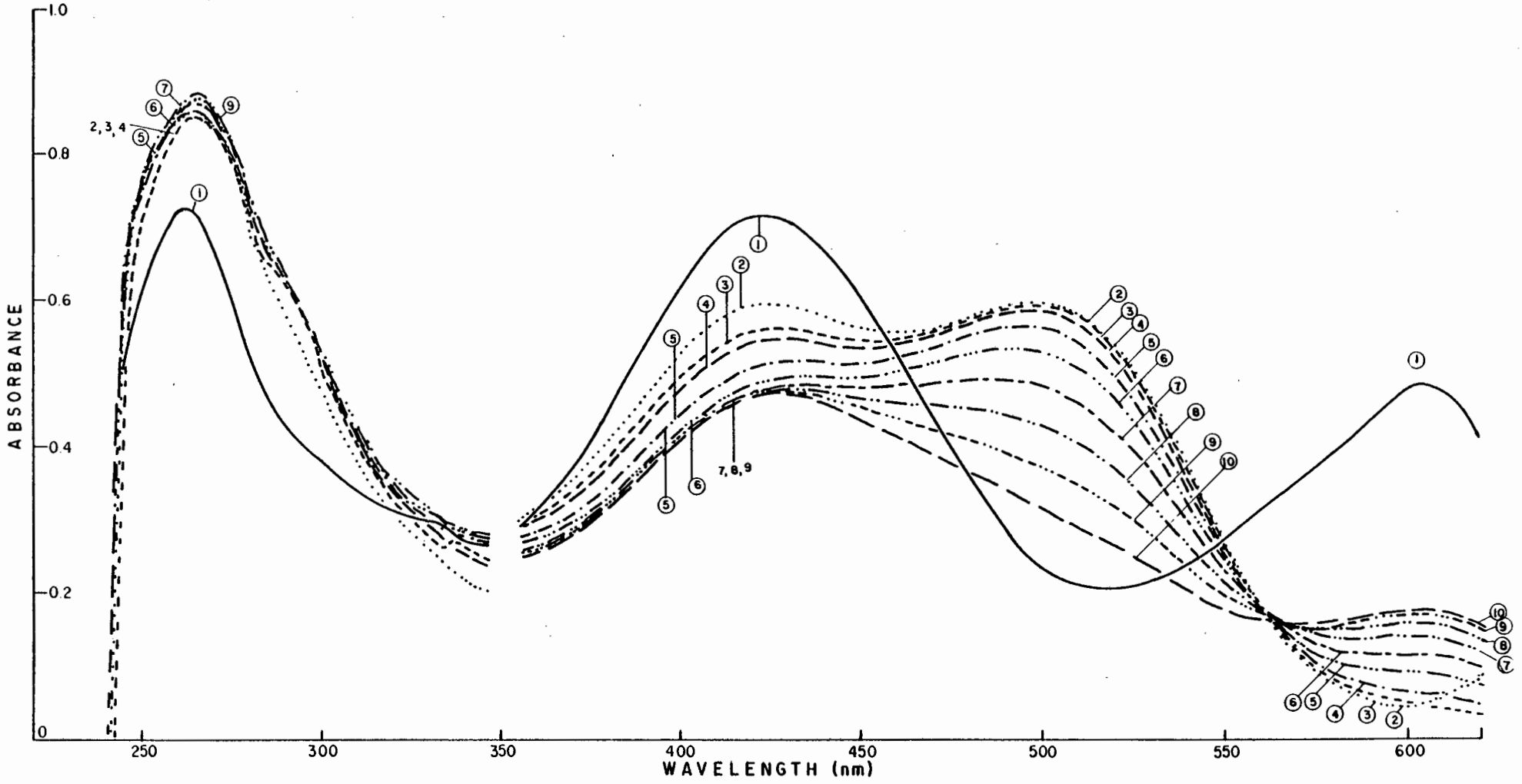


FIGURE 15: Interaction between Tl(III) and the disulphide(III). Absorption spectra of the:

1: disulphide solution in chloroform (1 hour after preparation)

2 - 10: disulphide solution after equilibration with a Tl(III) solution. Spectra recorded at 2 min. intervals.

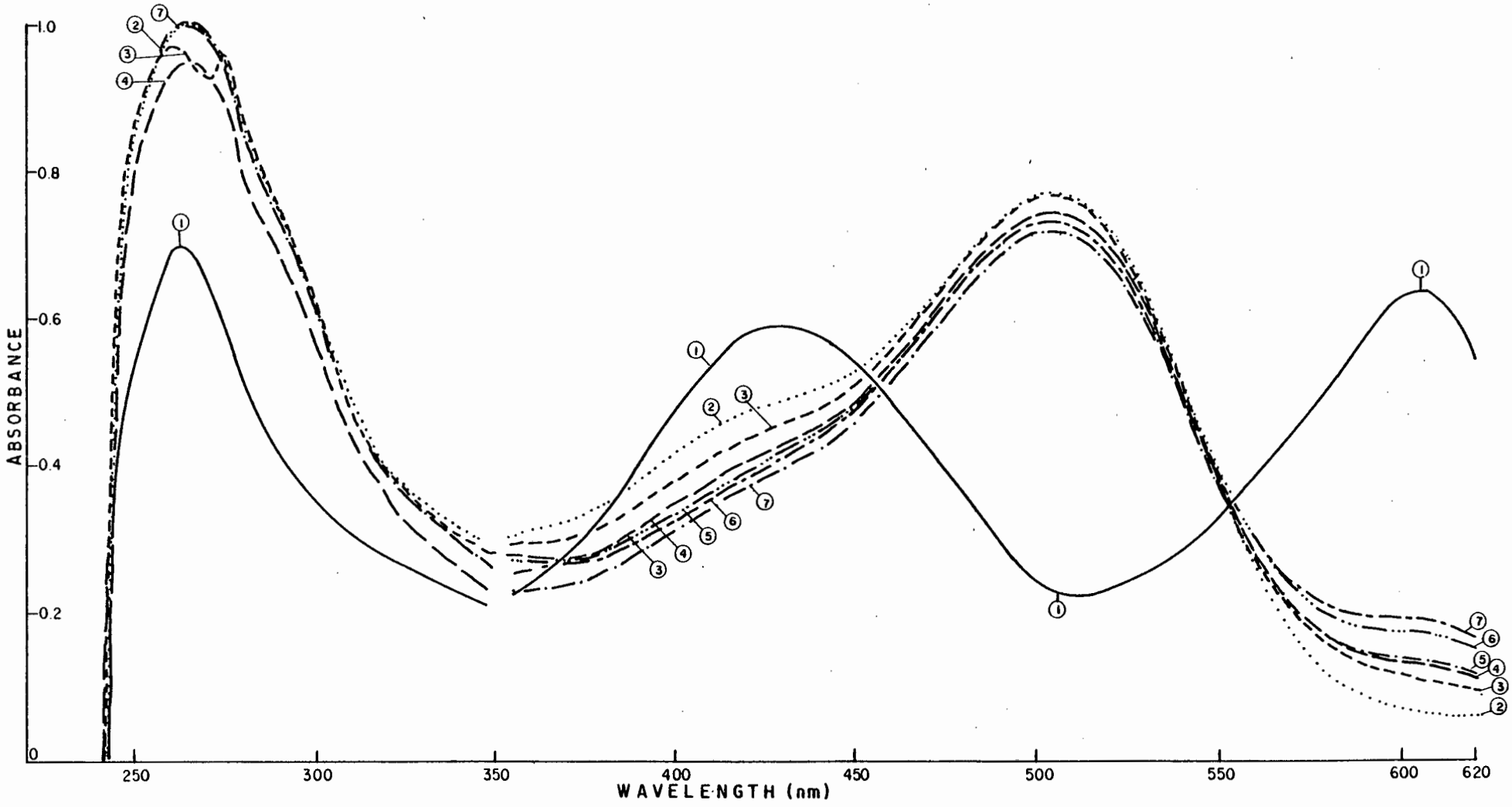


FIGURE 16: Interaction between Tl(III) and the disulphide(III). Absorption spectra of the:

1: disulphide solution in chloroform (2½ hours after preparation)

2 - 7: disulphide solution after equilibration with a Tl(III) solution. Spectra recorded at 2 min. intervals.

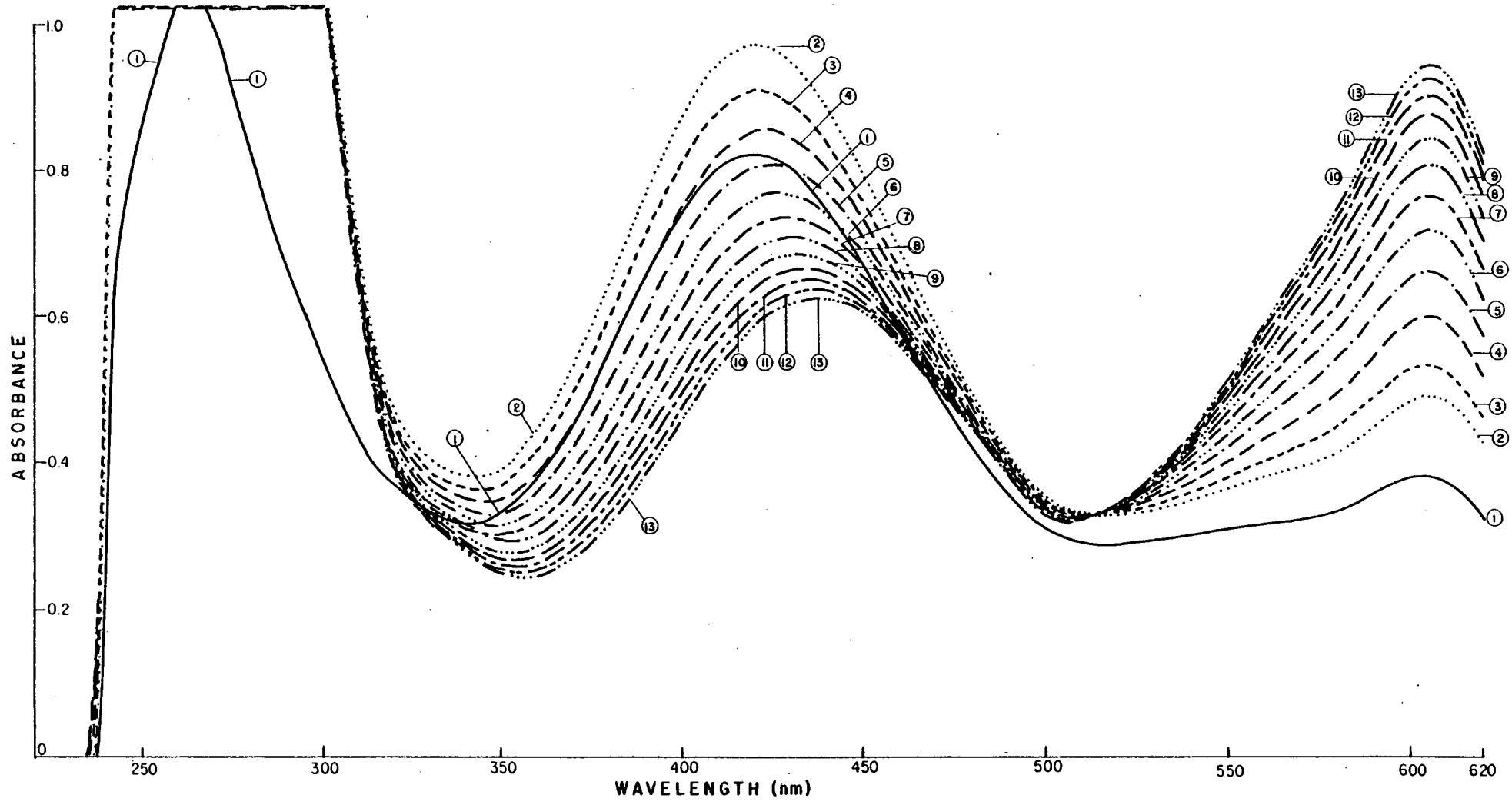


FIGURE 17: Interaction between Tl(I) and the disulphide(III). Absorption spectra of the:

1: disulphide solution in chloroform

2 - 13: disulphide solution after equilibration with a Tl(I) aqueous acidic solution. Spectra recorded at 2 min. intervals.

(b) complete conversion to meso is accompanied by the partitioning of this compound between the two phases,

(c) meso reacts with the Tl(III) and/or Tl(I) to give water-soluble complexes.

Consequently, the following had to be examined:

(i) The partitioning of the mesoionic compound between the two phases.

(ii) The interaction of Tl(III) and/or Tl(I) with the mesoionic compound.

(i) Partitioning of the mesoionic compound(IV) between aqueous perchloric acid and chloroform.

The acid dissociation constant (pKa) of meso determined in a perchlorate medium is -1.59 [33]. Hence, the amount of conjugate acid expected to partition into the acidic aqueous phase can be calculated from the Henderson-Hasselbach equation:

$$pH = pKa + \log \frac{[meso]}{[meso\ H^+]}$$

Therefore at pH = 1 only a small percentage of the mesoionic compound (0.26%) would be expected to partition into the aqueous phase. However, it was found that when a solution of meso in chloroform was equilibrated for 25 min. with an equal volume of 0.1 M $HClO_4$, 3% of the mesoionic compound partitioned into the aqueous phase:

Absorbance of meso (2.94×10^{-5} M), $A_o = 0.800$ ($\varepsilon = 27205$ cm^2 mol^{-1})

Absorbance of meso after equilibration with 0.1 M $HClO_4$,

$$A = 0.775$$

Therefore, the partition coefficient, $p = \frac{[meso]_o}{[meso]} = \frac{A}{A_o - A}$

$$= 31.00$$

This value obtained for the partition coefficient is slightly higher than that determined by Nabilsi [33] for the partition coefficient of meso between aqueous perchloric acid (pH 1 - 6) and chloroform, $p = 29.7 \pm 0.4$.

Furthermore, it was found that the concentration of meso in the organic phase on completion of the reaction between Tl(III) and dithizone, decreased as the acidity of the aqueous phase was increased. This was illustrated in the following experiment:

A dithizone solution was added to a thallium(III) solution (pH = 1) and equilibrated for 1 minute. After separation of the phases, the organic phase was transferred to another separating funnel containing the equivalent volume of 1 M $HClO_4$. The two phases were equilibrated for half a minute and then a portion of the organic layer was withdrawn and its absorption spectrum recorded at regular intervals (Figure 18). The spectra show a constant decrease in the absorbance at 266 nm. The solution in the cuvette was then returned to the separating funnel containing the remaining organic solution and 1 M $HClO_4$. The two phases were equilibrated for a further 20 minutes to ensure that the reaction

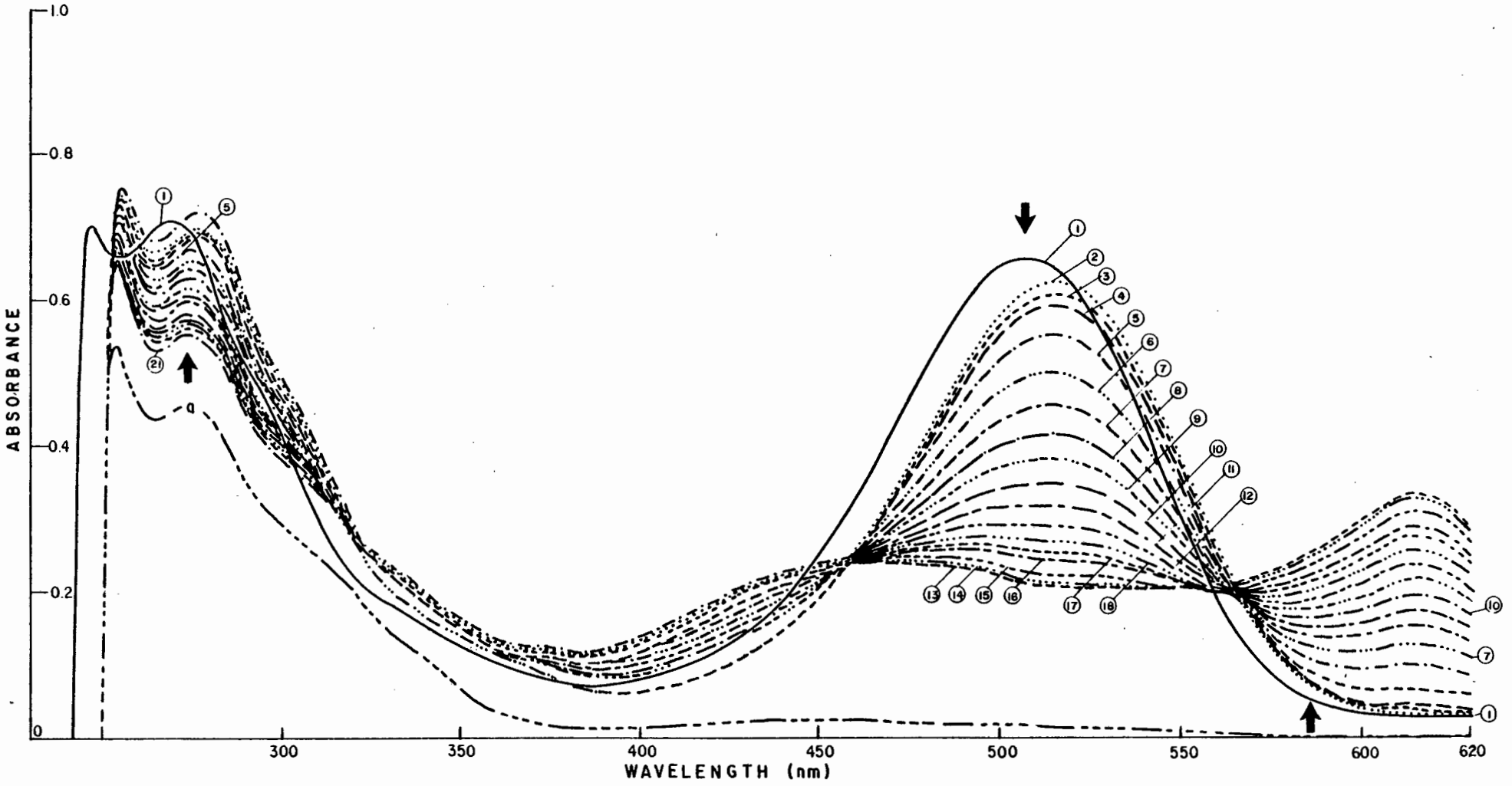


FIGURE 18: Interaction between thallium(III) and dithizone in chloroform: Absorption spectrum of:
1 - 18: the pink-red organic extract after shaking for ½ min. with 1 M $HClO_4$. Spectra recorded at 5 min. intervals
a: the yellow organic extract obtained following equilibration of the organic solution (18) with 1 M $HClO_4$ for 20 min.

*The displacement of spectrum 1 is due to instrumental error.

had completed. The absorption spectrum of this organic solution was recorded (Figure 18, spectrum a) and it was found that now only 70% of the dithizone could be accounted for by the presence of meso in the organic phase.

Clearly, the foregoing results show that meso does partition into the aqueous phase: the amount should depend on the acidity of the aqueous phase. Furthermore, since ~20% of the dithizone is unaccounted for by the presence of meso in the organic phase on completion of the reaction (at pH = 1) between Tl(III) and H_2Dz in $CHCl_3$ and that only 3% of meso was found to partition into the aqueous phase (pH = 1), suggests that other reactions involving meso are also taking place.

(ii) Investigation of the interaction between Tl(III) and the mesoionic compound(IV).

Experiments showed that Tl(I) does not react with the mesoionic compound under acidic nor alkaline conditions. On the other-hand, the following evidence strongly suggested that a reaction is taking place between Tl(III) and meso:

(a) There was a distinct colour change in the organic phase from orange to colourless.

(b) There was a reduction in the absorbance of the meso at 266 nm and a subsequent change in the spectrum (Figure 19, p. 67).

The absorbance at 266 nm could be taken as a measure of the concentration of unreacted meso and hence that of the reaction product - provided this product is formed stoicheiometrically and does not itself absorb at this wavelength.

The stoicheiometry of the meso-thallium(III) reaction product was determined by photometric titration, see Table 5.1. The absorption spectrum of each organic phase was recorded (Figure 19) and a graphical presentation of the results obtained is given in Figure 20.

Examination of Figures 19 and 20 shows that even when a great excess of Tl(III) reacts with meso there is a large residual absorbance at 266 nm. In addition, there is a shift in the λ_{max} from 266 nm to 268 nm. The possibility of the extraction of solvated Tl^{3+} from the perchlorate medium into chloroform and absorbing at 268 nm was considered. However, experiments showed that this does not occur. Consequently, the residual absorbance as well as the change in spectrum strongly suggests that a reaction is taking place to give colourless reaction products absorbing in the region of 266 nm. This gave rise to the following hypotheses:

(i) Tl^{3+} reacts with meso to give meso-thallium(III) complexes, $[Tl(meso)_n^{3+}](ClO_4^-)_3$, extractable into the organic phase.

(ii) Alternatively, Tl^{3+} oxidizes meso to give a new oxidation product.

TABLE 5.1 : Absorbance measurements for the photometric titration at 266 nm for the reaction of the mesoionic compound(IV) in chloroform with thallium(III) in 0.1 M $HClO_4$.

Volume of organic phase = volume of aqueous phase = 10 ml

Equilibration time = 25 minutes

$[Tl^{3+}]$ in 0.1 M $HClO_4$	[Meso±] in $CHCl_3$	Absorbance at 266 nm	Equivalent of meso
0.1 M $HClO_4$ - no Tl^{3+}	2.94×10^{-5}	0.775	100
0.628×10^{-5}	2.94×10^{-5}	0.510	65.81
1.256×10^{-5}	2.94×10^{-5}	0.315	40.65
1.57×10^{-5}	2.94×10^{-5}	0.280	36.13
3.14×10^{-5}	2.94×10^{-5}	0.250	32.26
6.28×10^{-5}	2.94×10^{-5}	0.250	32.26

From the graph (Figure 20) it is observed that 2.0×10^{-7} mole meso reacts with 1.4×10^{-7} mole Tl(III) i.e. a ratio of ~2 : 1.

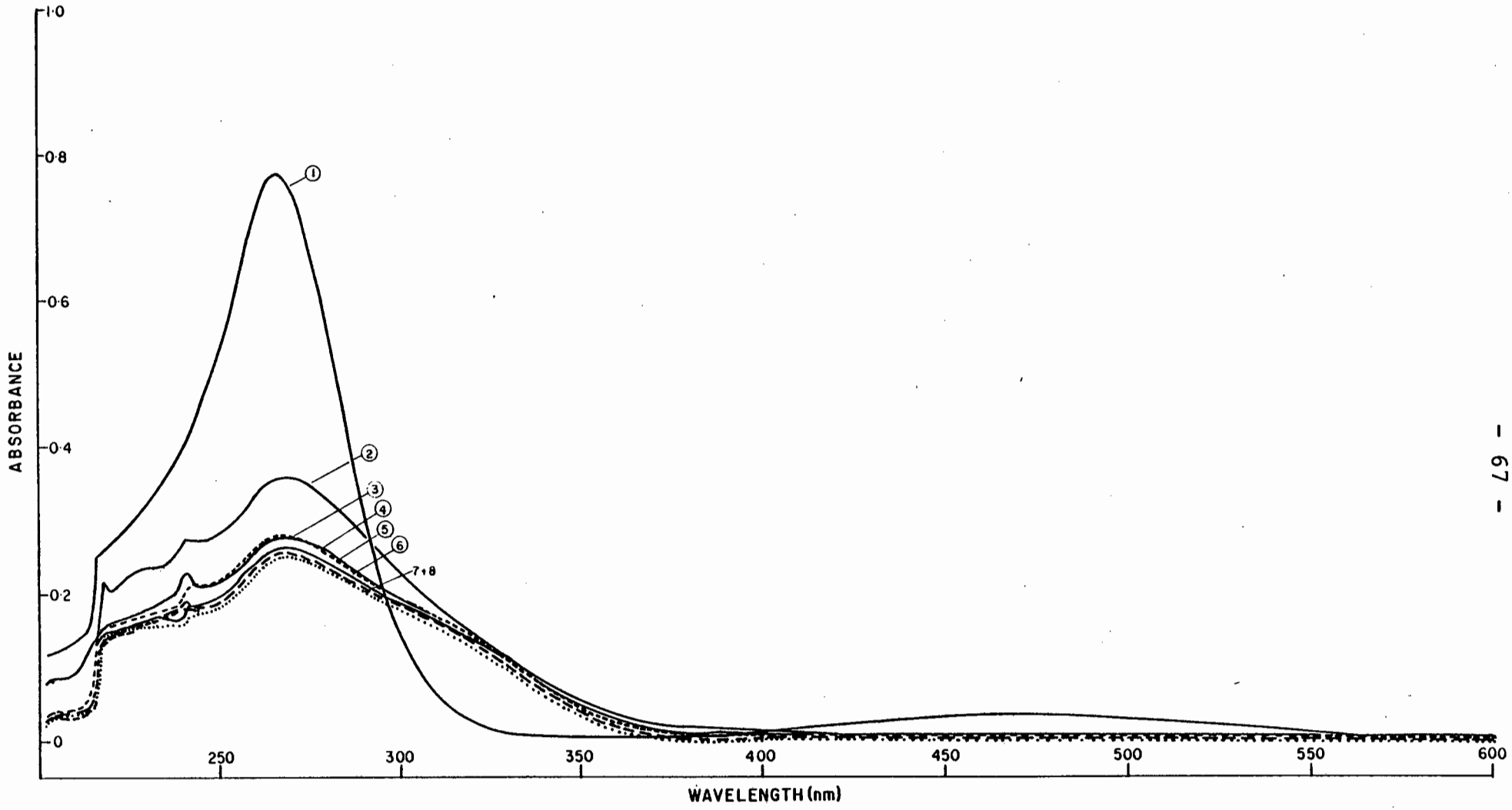


FIGURE 19: Interaction between Tl(III) and the mesoionic compound. Absorption spectra of:

1: solution of meso in chloroform (2.94×10^{-5} M)

2 - 8: the meso solution after equilibration (25 min.) with a Tl(III) solution of increasing concentration (Refer to Table 5.1).

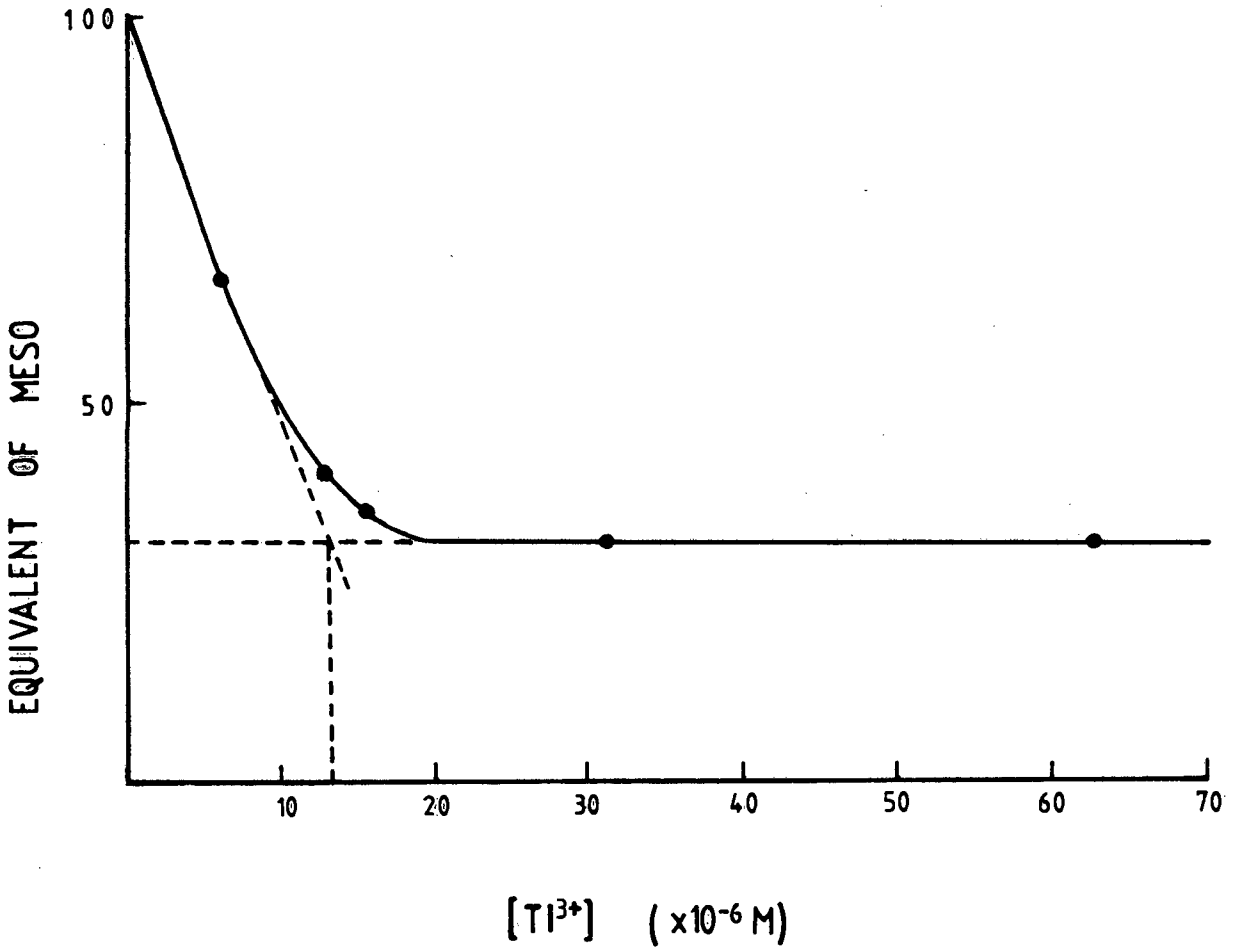


FIGURE 20: Graphical representation of the photometric titration at 266 nm for the reaction of the mesoionic compound (IV) in chloroform with thallium(III).

Investigation of the formation of thallium(III) - meso complexes

To establish whether complexation does take place, it was necessary to find a suitable method whereby the presence of thallium-(III) could be determined in both phases on completion of the reaction between Tl(III) and meso.

The complexometric EDTA titration using methylthymol blue as indicator, was found to be a suitable method for determining Tl(III) in the aqueous phase (see Chapter 9 § 9.2.3 for details). However, when the organic phase was mixed with the pH 10 buffer solution required for the titration, it underwent a colour change back to its original orange colour. This made it difficult to see a definite endpoint when trying to determine the Tl(III) in the organic phase. Atomic absorption spectroscopy (AAS) was therefore considered as an alternate method for determining thallium in the organic phase (see Chapter 9 § 9.2.4 for details). A possible explanation of the colour change in the organic phase, on addition of the pH 10 buffer solution, will be discussed later (p. 74).

To investigate the interaction between Tl(III) and meso, equal volumes of the solutions, of various concentrations, were equilibrated for 25 minutes. The phases were then separated and the presence of Tl(III) determined in the aqueous and organic phases by the EDTA titration method and AAS, respectively. The results obtained are given in Table 5.2.

TABLE 5.2 : Results obtained for the determination of thallium in both phases, on completion of the reaction between meso in chloroform and thallium(III) in 0.1 M $HClO_4$.

No.	No. of moles meso taken	No. of moles Tl^{3+} taken	No. of moles Tl^{3+} in aqueous phase	No. of moles Tl^{3+} in organic phase	No. of moles Tl^{+} in aqueous phase
i	5.7×10^{-5}	6.28×10^{-5}	2.38×10^{-5}	1×10^{-5}	2.895×10^{-5}
ii	10.26×10^{-5}	5.65×10^{-5}	2.1×10^{-6}	5.35×10^{-6}	4.905×10^{-5}
iii	5.7×10^{-5}	2.575×10^{-5}	-	2.34×10^{-6}	2.34×10^{-5}
iv	5.7×10^{-5}	5.15×10^{-5}	1.55×10^{-5}	1.11×10^{-5}	2.65×10^{-5}

From the foregoing results the following ratios could be calculated:

No.	$\frac{[Tl^{3+}]}{[meso]}$	$\frac{[Tl^{3+}]_{aq}}{[Tl^{+}]_{aq}}$	$\frac{[Meso]}{[Tl^{+}]_{aq}}$	$\frac{[Tl^{+}]_{aq}}{[Total\ Tl]}$	$\frac{[Tl^{3+}]_{org}}{[Total\ Tl]}$
i	1.10	0.8	1.96	0.64	0.16
ii	0.55	0.04	2.1	0.87	0.09
iii	0.45	0	2.4	0.91	0.09
iv	0.90	0.6	2.15	0.51	0.21

The results given in Table 5.2 show that, on completion of the reaction between Tl(III) and meso, Tl(III) is present in both phases. However, the total amount of Tl(III) determined in both phases did not account for the initial amount of Tl(III) taken. To explain this the following assumption was made:

Either (a) the thallium(III) had formed such stable complexes with meso that it could not be determined by EDTA titration, or, (b) that Tl(III) had oxidized the mesoionic compound and that the resulting Tl(I) would be present in the aqueous phase, since it has been found that Tl(I) does not react with meso.

The presence of Tl(I) in the aqueous phase was confirmed by EDTA titration after oxidation with a saturated solution of bromine water (see Chapter 9 § 9.2.3). The amount of Tl(I) determined coincided with the amount of Tl(III) unaccounted for.

Since Tl(III) was found to be present in both phases and Tl(I) in the aqueous phase, this suggests that the reaction between Tl(III) and meso involves both complexation and oxidation, thus supporting the hypotheses suggested (p. 65). However, at this stage no distinction can be made between the two reactions involved.

Oxidation of the mesoionic compound(IV) by Tl(III) and other oxidizing agents.

To test whether oxidation is one of the reactions involved between Tl(III) and meso other oxidizing agents with similar

reduction potentials to that of Tl(III), viz., Ce(IV) (+1.70 V) and $Cr_2O_7^{2-}$ (+1.33 V) [40], were used, to see if similar results could be obtained.

The absorption spectra recorded showed that Ce(IV) and $Cr_2O_7^{2-}$ react with meso in a similar way to that of Tl(III) (Figure 21).

However, it is evident from colour changes undergone in the aqueous phases, containing Ce(IV) and $Cr_2O_7^{2-}$: from yellow to colourless and green, respectively, that oxidation must have taken place.

In an attempt to obtain oxidation as the only reaction taking place, two other experiments were considered:

(i) To increase the reduction potential of the Ce(IV) solution, from +1.70 V to ~+1.87 V.

(ii) By using a strong oxidizing agent containing no metal ions that might complex with meso, $KMnO_4$ was considered.

Unfortunately both attempts failed. Although the reduction potential of the Ce(IV) solution was increased to ~+1.87 V in 4 M $HClO_4$ [40], there were no changes in the results obtained. When $KMnO_4$ was used an emulsion always resulted when shaking the two phases together. This resulted in the organic phase being turbid and hence unsuitable for spectrophotometric measurements.

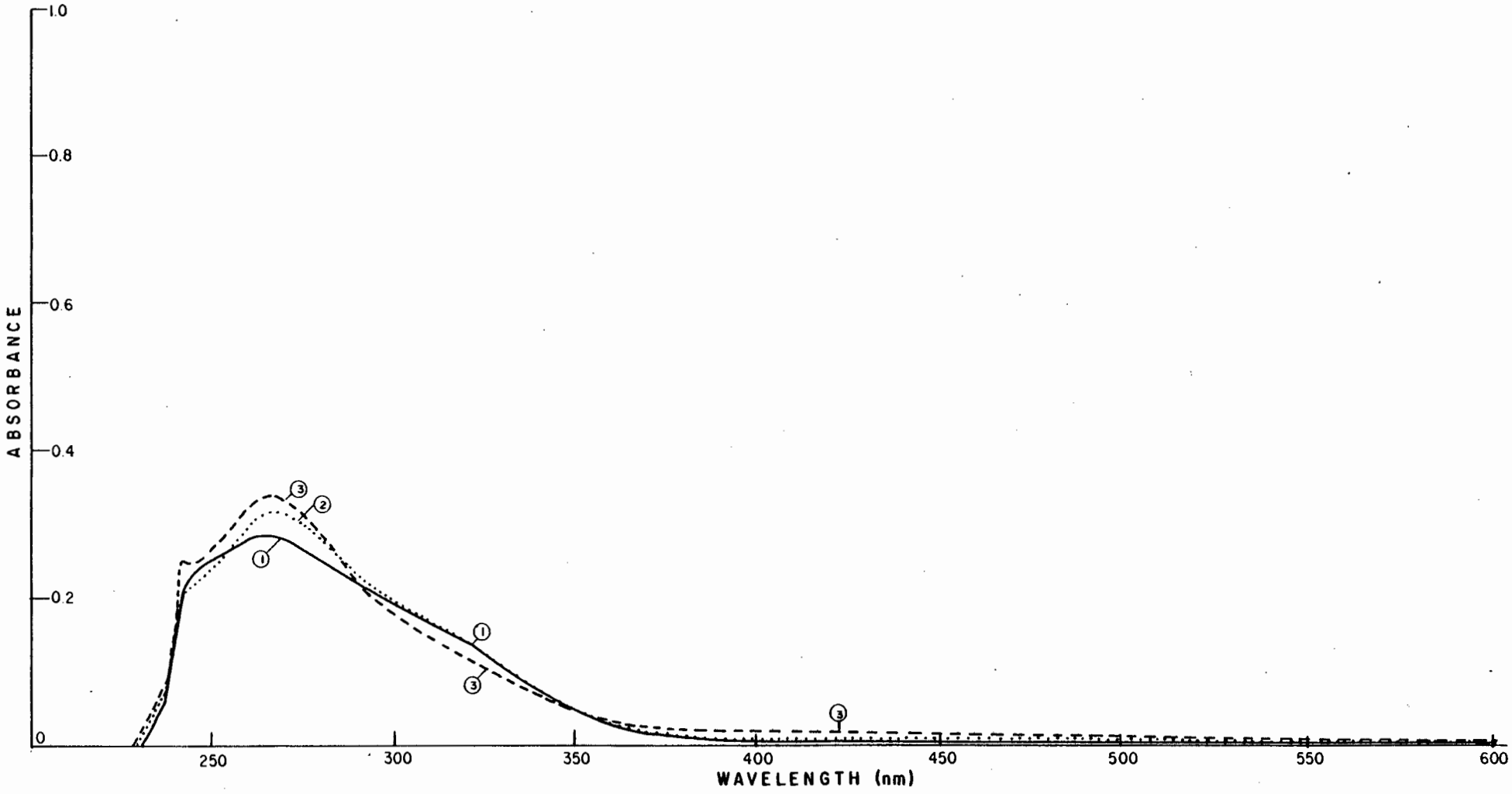


FIGURE 21: Absorption spectra of the mesoionic compound after equilibration with a - 1: Tl(III) solution 2: Ce(IV) solution 3: $Cr_2O_7^{2-}$ solution

Study of the effects of the pH 10 buffer solution and the reducing agent, ascorbic acid, on the reaction products formed by the reaction between Tl(III) and meso.

From the absorption spectra recorded (Figure 22), it is evident that when the organic phase containing the colourless reaction products is shaken together with a pH 10 buffer solution, the band at ~319 nm disappears. The absorption spectrum of this (orange) organic solution (Figure 22, spectrum 2) is similar to that of pure meso in chloroform. This suggests that meso is regenerated in the organic phase.

However, according to the absorption spectrum in Figure 22, spectrum 2, only 65% of the mesoionic compound was regenerated. This implies that another product, absorbing at 266 nm is still present in the orange organic solution. Therefore, one could postulate that since a pH 10 buffer solution is not a reducing agent that: (a) the product at ~319 nm is the Tl(III)-meso complex, which is reverted under alkaline conditions; and (b) the remaining product which absorbs at 266 nm, is the oxidation product.

Moreover, when the colourless organic solution is shaken together with a concentrated solution of ascorbic acid in water (pH = 2), the same results were obtained as with the pH 10 buffer solution. Presumably this reducing agent is not strong enough as no reduction appears to have taken place.

Up until now it was evident from the results obtained, that there are at least three reaction products present in the organic

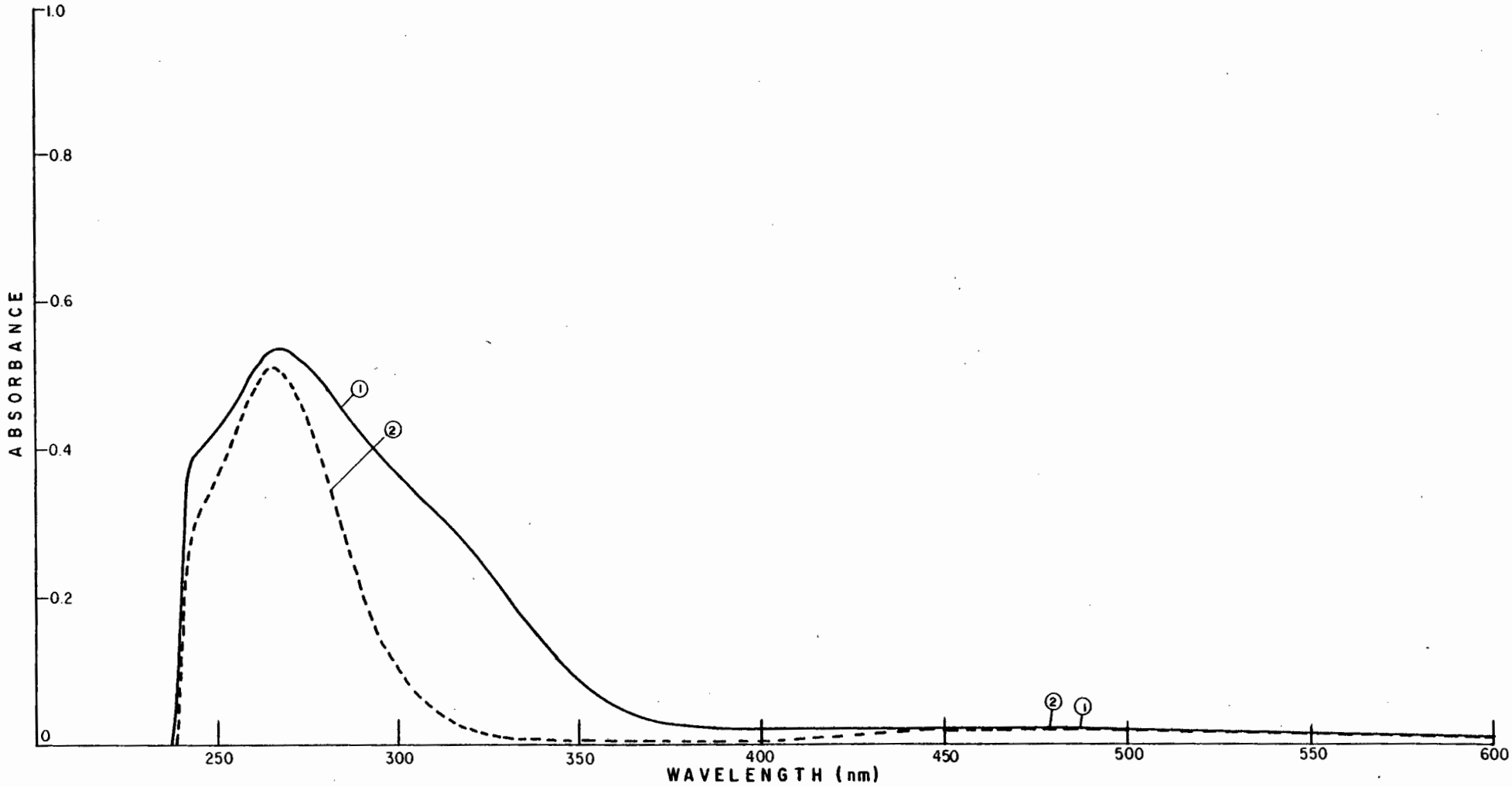


FIGURE 22: 1: Absorption spectrum of the organic phase on completion of the reaction of meso in $CHCl_3$ with Tl(III)

2: Same as (1); but shaken with pH 10 buffer solution (Absorbance scale = 2.0).

phase, on completion of the reaction between Tl(III) and meso. This was confirmed by thin-layer chromatography (TLC). The chromatogram showed two yellow spots, closely situated to each other, near the start of the chromatogram. The Rf value of the second spot corresponding to that of meso in chloroform. In addition, there was a colourless band (visible under ultra-violet light) which moved with the solvent front.

In an attempt to separate the components using column chromatography it was only possible to separate the colourless component which moved with the solvent front (Figure 23, spectrum 2). The absorption spectrum shows that this component absorbs strongly at 266 nm. When this colourless component is shaken together with the pH 10 buffer solution and the ascorbic acid solution, respectively, there was no change observed in the absorption spectra recorded. This supports the hypothesis that this component which absorbs at 266 nm is the oxidation product and the component absorbing at ~319 nm is the meso-thallium(III) complex.

According to the results given in Table 5.2 it is evident from the molar ratio, meso:Tl^{+}, that 2 moles of meso are oxidized by 1 mole of Tl^{3+}. In addition, from the graph in Figure 20, it can be shown that Tl(III) reacts with meso in the molar ratio 1:2, to give a product absorbing at 266 nm. On the basis of these results one could postulate that Tl(III) oxidizes meso to give the dication (XII):

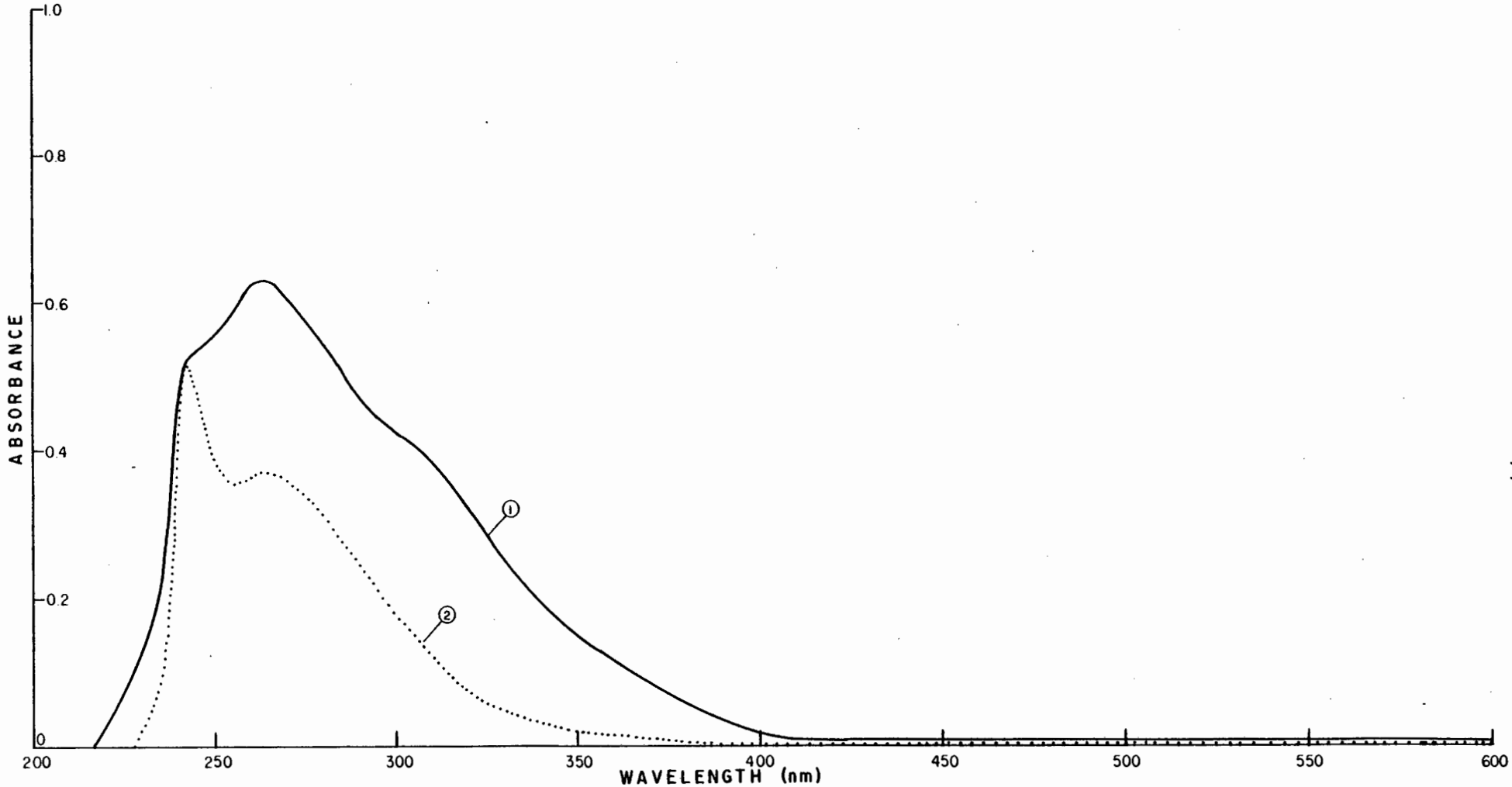


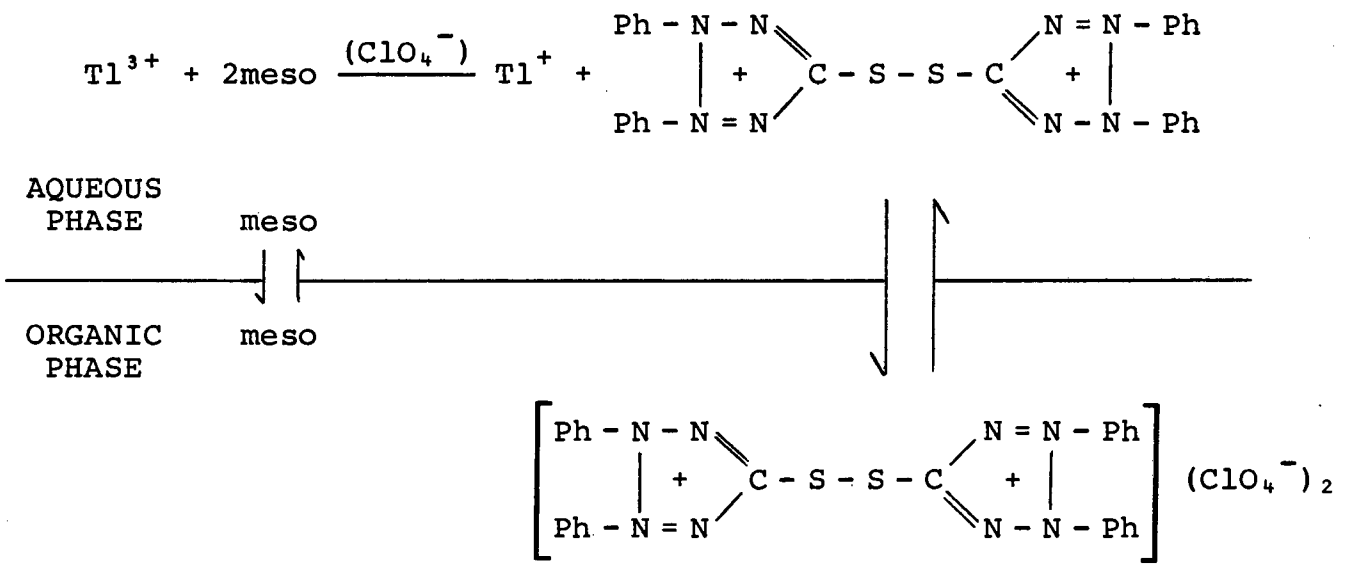
FIGURE 23: 1: Absorption spectrum of the organic phase on completion of the reaction of meso in $CHCl_3$ with Tl(III)

2: Absorption spectrum of the colourless component separated from the organic solution of 1.

(XII)

Since (XII) is a large cation it could well form an extractable ion-pair with perchlorate. Furthermore, according to its chromatographic properties the colourless reaction product is non-polar, which supports the postulated formulation of the oxidation product as (XII).

The postulated reaction scheme for the oxidation of meso by Tl(III) can be represented as follows:



Evidently then, the reaction between Tl(III) and meso appears to involve two reactions: complexation and oxidation, to give possibly a meso-thallium(III) complex and an oxidation product, possibly the dication (XII).

5.4 DISCUSSION

On the basis of the following results the interaction between (excess) Tl(III) and H_2Dz in $CHCl_3$ can be summarized as follows:

Tl(III) reacts with H_2Dz in the molar ratio 1:3 to give an initial wine-red extract: possible a transient thallic-dithizonate $[Tl^{III}(HDz)_3]$, which spontaneously undergoes oxidative disproportionation to give the disulphide(III) and the Tl(HDz) complex. The disulphide spontaneously decomposes, the rate of fission being increased in the presence of the Tl^{3+} and Tl^{+}, to give equimolar amounts of H_2Dz and meso. The Tl(HDz) undergoes reversion to give H_2Dz in the organic phase and Tl^{+} in the aqueous phase. In the presence of excess Tl(III) the dithizone is oxidized to give meso as the final reaction product. The mesoionic compound partitions between the two phases (p_{meso} = 31.00) and undergoes further reactions with the excess Tl(III): possibly metal-complexation and oxidation to give, presumably a meso-thallium(III) complex, $[Tl(meso)_n^{3+}](ClO_4^-)_3$ and an unspecified oxidation product, possibly the dication (XII).

The postulated reaction scheme for the interaction between excess Tl(III) and dithizone in chloroform can be represented by the following equations:

$$Tl^{3+} + \overline{3H_2Dz} \longrightarrow \overline{Tl^{III}(HDz)_3} + 3H^+$$

$$\overline{Tl^{III}(HDz)_3} \xrightarrow{\text{(oxidative disproportionation)}} \overline{Tl(HDz)} + \overline{(HDz)_2}$$

$$\overline{(HDz)_2} \longrightarrow \overline{H_2Dz} + \overline{meso}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$H^+ + \overline{Tl(HDz)} \longrightarrow Tl^+ + \overline{H_2Dz}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$\text{excess } Tl^{3+} + \overline{3H_2Dz} \longrightarrow Tl^+ + \overline{3meso} + 6H^+$$

$$\overline{meso} \rightleftharpoons meso$$

$$Tl^{3+} + n\,meso \longrightarrow \overline{[Tl^{3+}(meso)_n{}^{3+}](ClO_4^-)_3}$$

$$Tl^3 + 2meso \xrightarrow{(ClO_4^-)} Tl^+ + \overline{\left[\begin{array}{c} Ph-N-N \\ \quad | \\ Ph-N=N \end{array} + \begin{array}{c} \diagdown \\ C-S-S-C \\ \diagup \end{array} + \begin{array}{c} N=N-Ph \\ \quad | \\ N-N-Ph \end{array}\right](ClO_4^-)_2}$$

PART II

II-1 The effect of the pH of the aqueous phase on the reaction between Tl(III) and dithizone in $CHCl_3$.

On increasing the pH of an aqueous thallium(III) solution, there was an instantaneous formation of a brown precipitate due to the hydrolysis of the Tl(III) cation. Therefore, to avoid the precipitation of thallium(III) hydroxide, one would have to work in the pH range $\lesssim 1$.

From experiments carried out in part I of this chapter, it is evident that lowering the pH of the aqueous phase (pH < 1) will definitely have an effect on the course of some of the reactions involved:

(i) The partitioning of meso between the two phases depends on the $[H^+]$ of the aqueous phase. The amount of meso partitioning into the aqueous phase increases as the $[H^+]$ is increased. This was illustrated in Figure 18, p. 63.

(ii) Although the kinetics of the reactions involved in the interaction between Tl(III) and H_2Dz have not been studied in every case, the kinetics of the reaction between Zn^{2+} and H_2Dz (in a two-phase system) has been thoroughly studied [42]. According to Irving *et al.* [42] the rate equation for the Zn^{2+} - dithizone reaction is

$$\frac{d[Zn^{2+}]}{dt} = k[Zn^{2+}][H_2Dz]_o/[H^+].$$

These authors found that on lowering the pH of the aqueous phase, whilst maintaining other factors constant, there is a striking increase in the rate of the back-reaction,

i.e. the reversion of the zinc-dithizonate complex. Therefore, one can infer that the increase in $[H^+]$ will increase the rate of the reversion of the Tl(HDz) and $Tl(HDz)_3$ complexes during the course of the reaction between Tl(III) and H_2Dz. This was in fact observed for the extraction of the Tl(HDz) (cf. Figures 11 and 18); where, as the pH of the aqueous phase was lowered, the rate of the reversion of the Tl(HDz) complex increased.

II-2 The effect of the concentration of the reactants

In the presence of excess Tl(III), the reaction between Tl(III) and H_2Dz is very fast, to give a wine-red extract in the organic phase. On the otherhand, when H_2Dz was in excess a colour change in the organic phase, to give the wine-red extract, was only observed after the two phases had been gently shaken together (Figure 24). By comparing the absorption spectra Figure 24 and Figure 13 (p. 54), it was noted, that in the presence of excess H_2Dz the changes occuring in the organic solution are slightly slower.

Nevertheless, the overall rate of the reaction is such that in both cases constant absorbance measurements could be made after ~20 minutes of equilibration.

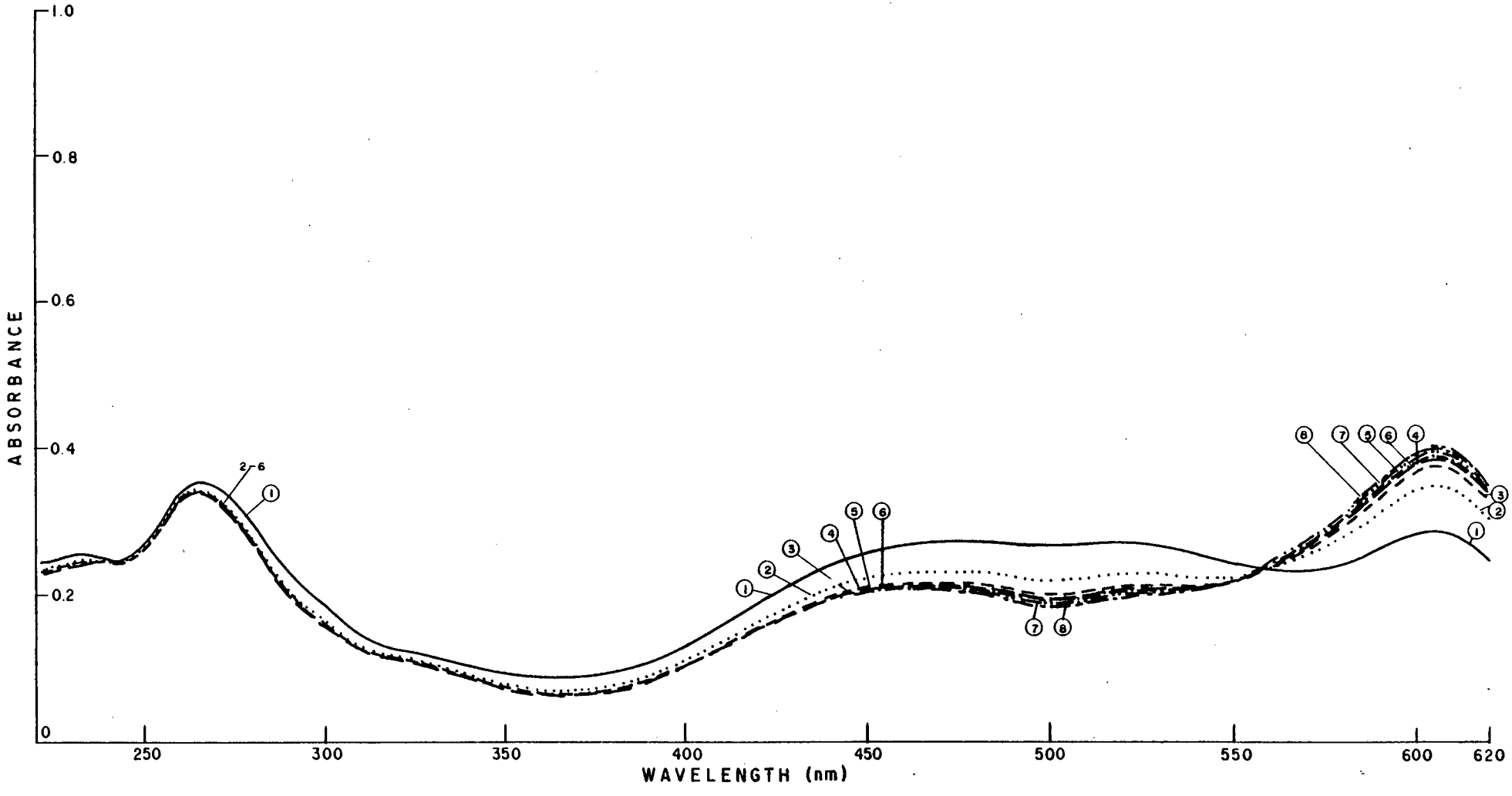


FIGURE 24: Interaction between thallium(III) and excess dithizone in chloroform. Absorption spectra (1 - 8) recorded at 2 min. intervals after the two solutions had been gently shaken together.

II-3 The effect of the order of mixing of the reactants

In all the experiments carried out so far, the dithizone solution has always been added to that of thallium(III). When the order of mixing was reversed there was no immediate colour change observed in the organic phase. On shaking the two phases together the overall rate of the reaction was rapid, the organic phase undergoing a colour change from pink to yellow within seconds.

Clearly, the rates of the various reactions involved depend on the order of mixing of the components, and presumably on the rate of the mixing of the two phases and interphase diffusion coefficients.

II-4 The effect of equilibration time

From the results obtained in Chapter 5 part I, it is clear that the thallium(III)-dithizone system involves a series of intermediate reactions - some heterogeneous - which do not all proceed at the same rate. Therefore, the period of equilibration would be significant, as after different periods of equilibration, the different reaction products will be present in the organic phase and in different proportions. However, it was found that after equilibration for 20 - 25 min., constant absorbance measurements could be made.

II-5 The effect of the nature of the organic solvent used in the reaction between Tl(III) and H_2Dz.

Up until now the postulated mechanism for the thallium(III)-dithizone reaction, to give meso as the final reaction product, strongly suggests that the disulphide is formed in the initial stage of the reaction. This implies that the course of the reaction, especially in the initial stage, would be affected by the polarity of the organic solvent used. The rate of the decomposition of the disulphide decreases as the polarity of the organic solvent decreases, owing to the nature of the mesoionic compound [10]. Therefore by changing the organic solvent from $CHCl_3$ to a non-polar organic solvent, e.g. CCl_4, the rates of the reactions involved in the initial stage would be expected to decrease. Consequently this could allow the reaction between Tl(III) and H_2Dz to be examined in greater detail.

Moreover, by changing the organic solvent from $CHCl_3$ to CCl_4 this will, in theory, alter the following parameters in the thallium(III)-dithizone extraction process:

(i) The partition equilibria - as dithizone and metal-dithizonates are less soluble in CCl_4 than $CHCl_3$ [41]. Furthermore, owing to the nature of the polar mesoionic compound, it would be expected to be less soluble in the non-polar organic phase. As a result, this will affect the partitioning of meso between the two phases.

(ii) The kinetics of equilibration - because of the solubility of the dithizone in CCl_4, more dithizone will be available in the

aqueous phase as dithizonate anions. Consequently, the rate of attaining extraction equilibrium will be faster in CCl_4 than in $CHCl_3$ [41, 42].

Clearly, the nature of the organic solvent may have a significant effect on the course of reaction between Tl(III) and H_2Dz, as well as an advantageous effect in view of examining the reaction in greater detail. Hence the matter was pursued, as described in the following chapter.

CHAPTER 6

INVESTIGATION OF THE INTERACTION BETWEEN THALLIUM AND DITHIZONE IN CARBON TETRACHLORIDE

6.1 PRELIMINARY STUDIES

When a solution of dithizone in CCl_4 (10^{-5} M - Figure 25) was added to an aqueous acidic solution containing excess Tl(III) (10^{-2} M), no colour change was observed in the organic phase. On gentle shaking of the separating funnel, containing the two solutions, the organic phase underwent a series of colour changes from green → brown → pink → orange → yellow and finally to colourless within 3 minutes. Therefore, to study the reactions in detail, only short periods of gentle shaking would be required.

The following experiments were carried out where equal volumes of Tl(III) and H_2Dz solutions were taken and the absorption spectra of the organic phases recorded after: the two phases had been allowed to stand in contact with each other for 1 minute and after the two phases had been gently shaken together for 1 sec., 5 sec., 15 - 30 sec., 1 min., 2 min. and 3 min., respectively (Figures 26 - 30).

The absorption spectra in Figures 26 - 29 show that during the reaction between Tl(III) and H_2Dz in CCl_4, the dithizone is consumed to give a pink extract in the organic phase which absorbs strongly at 507 nm and to a lesser extent at 275 nm. Subsequently, the absorbance of these two bands decrease and there is a corresponding increase in absorbance at 415 nm, giving rise to isobestic points at 450 nm and 310 nm, indicating the presence of two species changing one into another. Furthermore, from the spectra in Figure 30 it is evident that with longer periods of shaking, Tl(III) reacts with H_2Dz in CCl_4 to give no extractable products

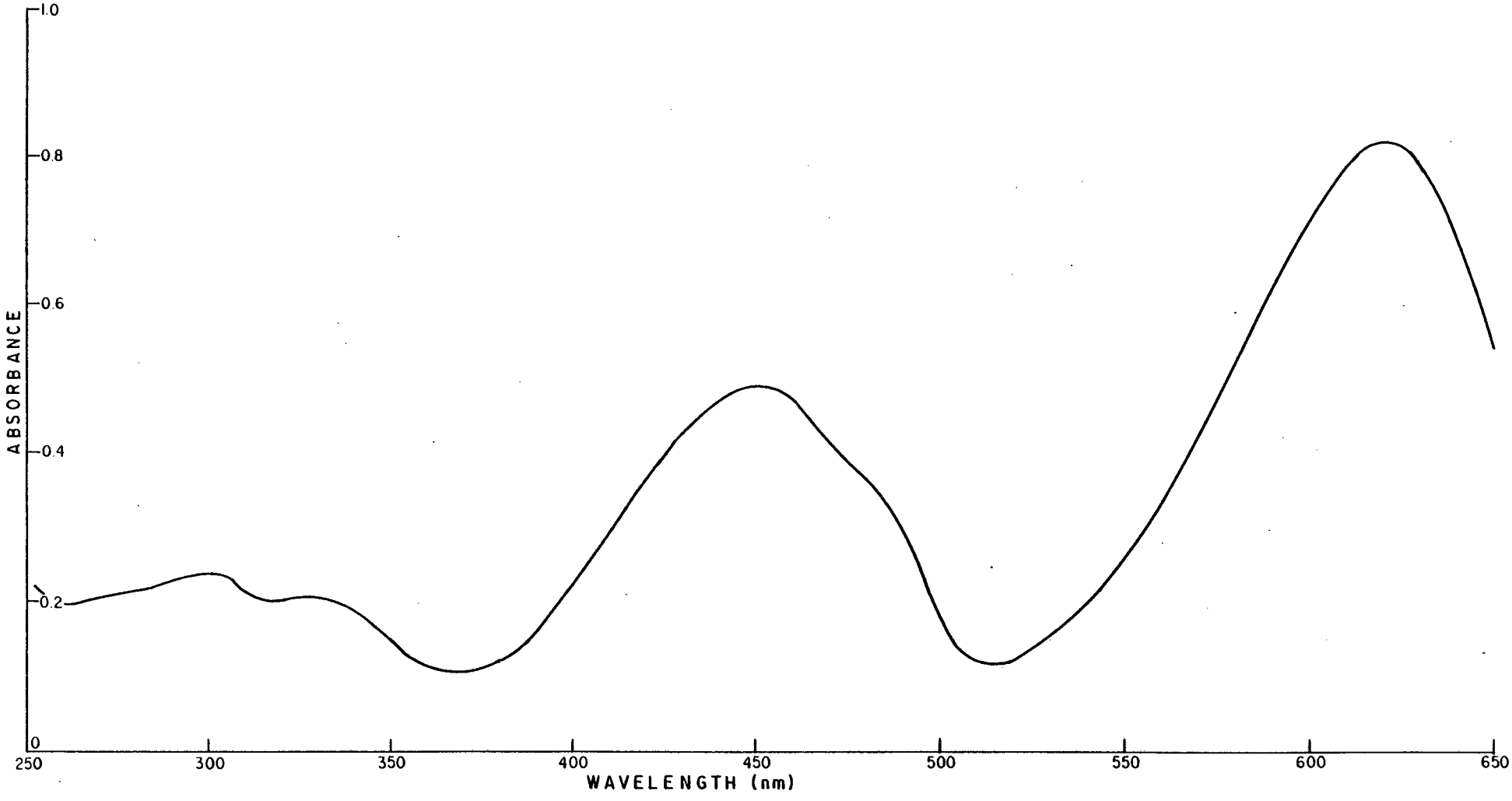


FIGURE 25: Absorption spectrum of a dithizone solution in carbon tetrachloride.

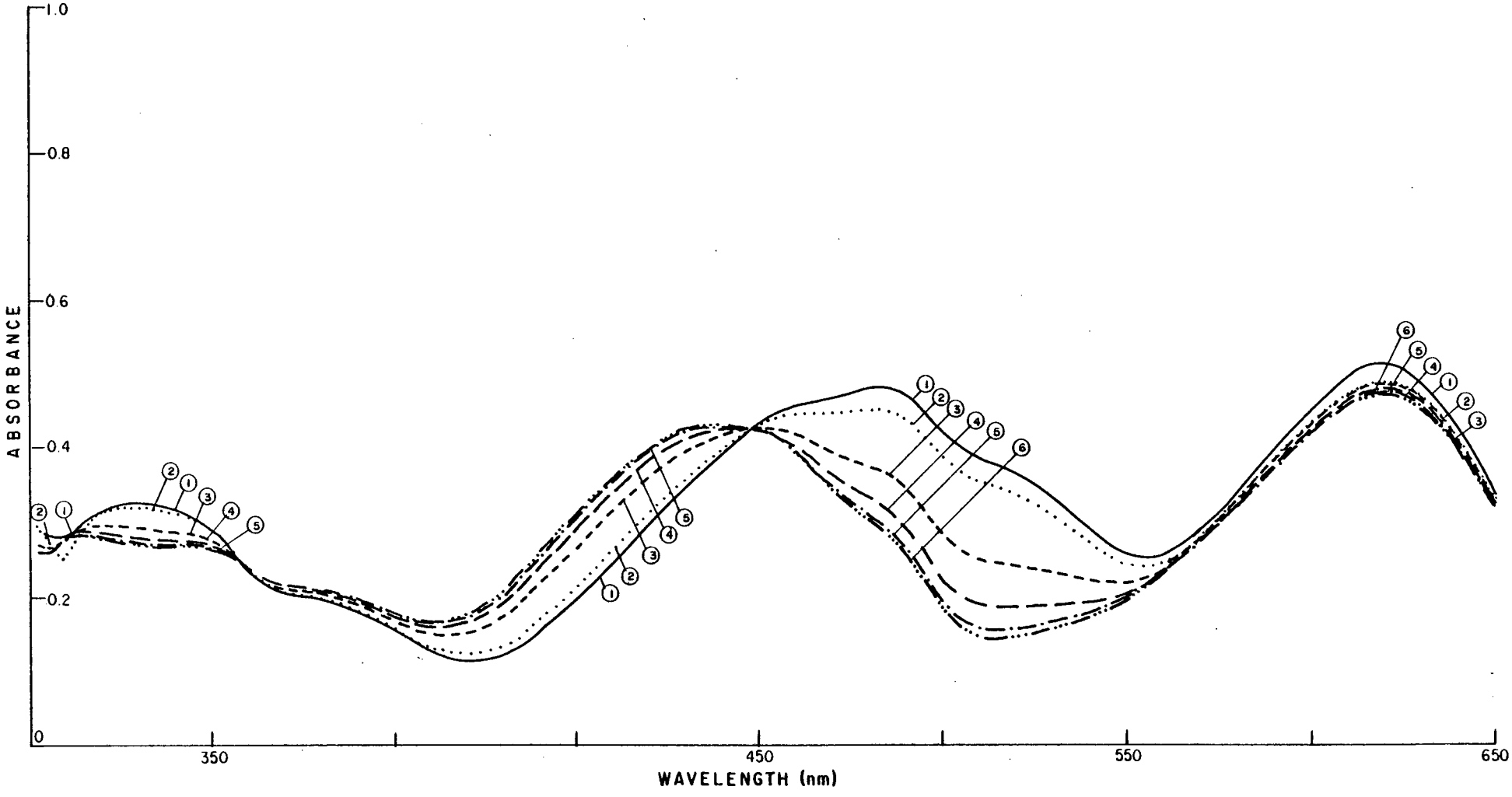


FIGURE 26: Interaction between Tl(III) and dithizone in CCl_4. Absorption spectra (1 - 6) recorded at 10 min. intervals after the two solutions were added together - no shaking of the two phases.

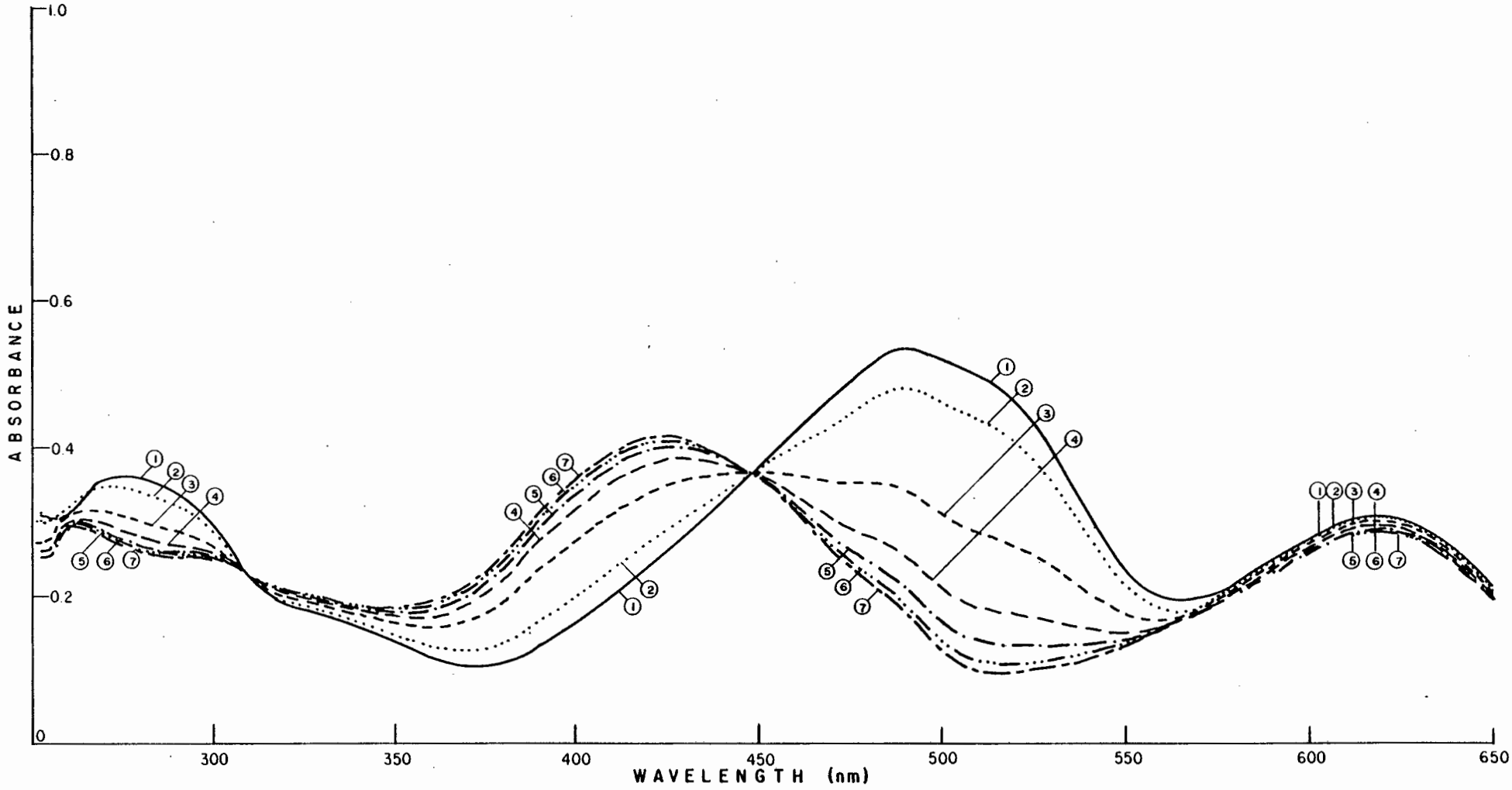


FIGURE 27: Absorption spectra of the reaction of dithizone in CCl_4 with Tl(III) after gentle shaking of the two phases for 1 sec. Spectra recorded at 10 min. intervals.

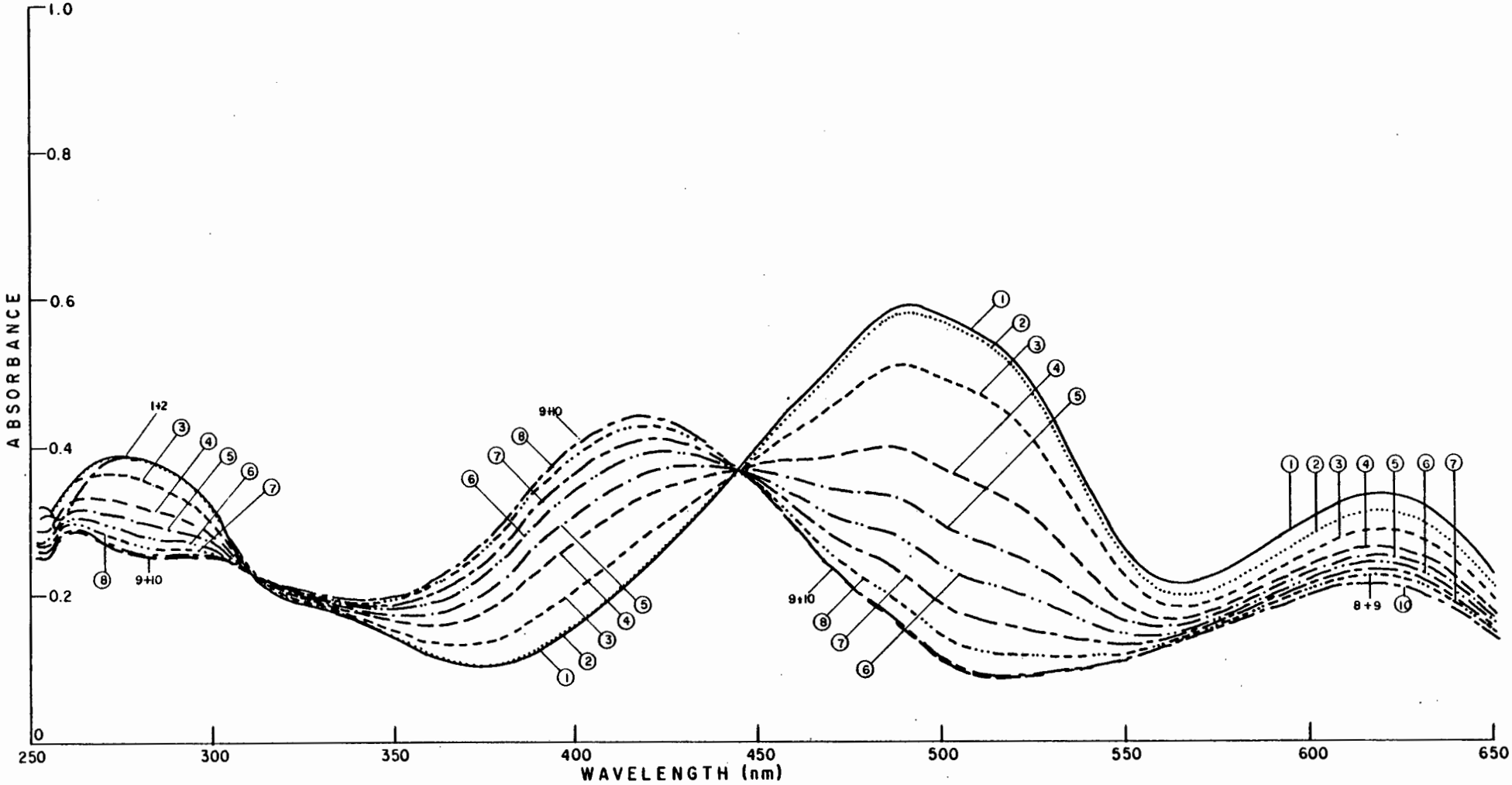


FIGURE 28: Absorption spectra of the reaction of dithizone in CCl_4 with Tl(III) after gentle shaking of the two phases for 5 sec. Spectrum 2 was recorded 2 min. after spectrum 1, while spectra 3 - 10 are recorded at 10 min. intervals.

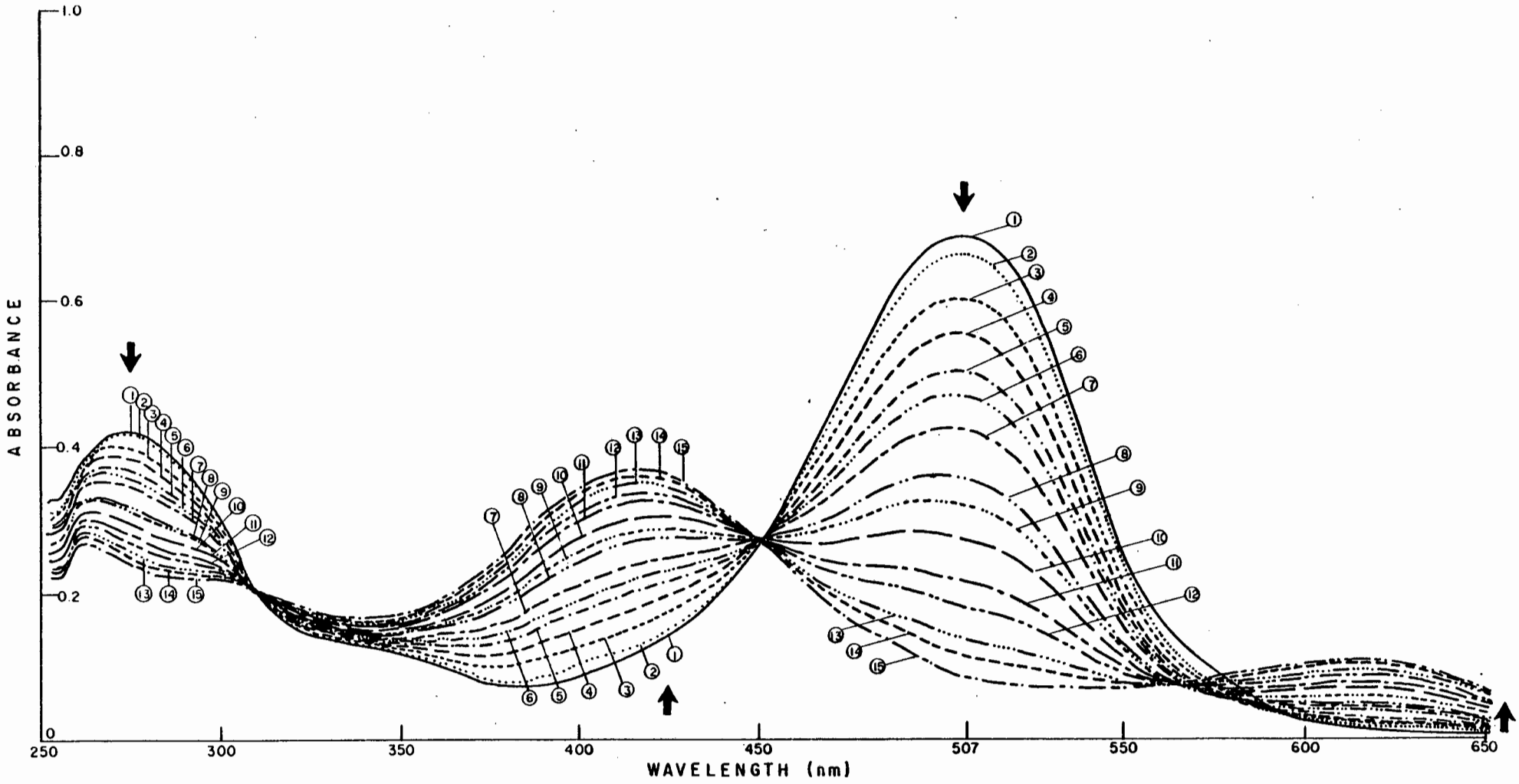


FIGURE 29: Absorption spectra of the reaction of dithizone in CCl_4 with Tl(III) after gentle shaking of the phases for 15 - 30 sec. Spectrum 2 was recorded 2 min. after spectrum 1, while spectra 3 - 15 were recorded at 10 min. intervals.

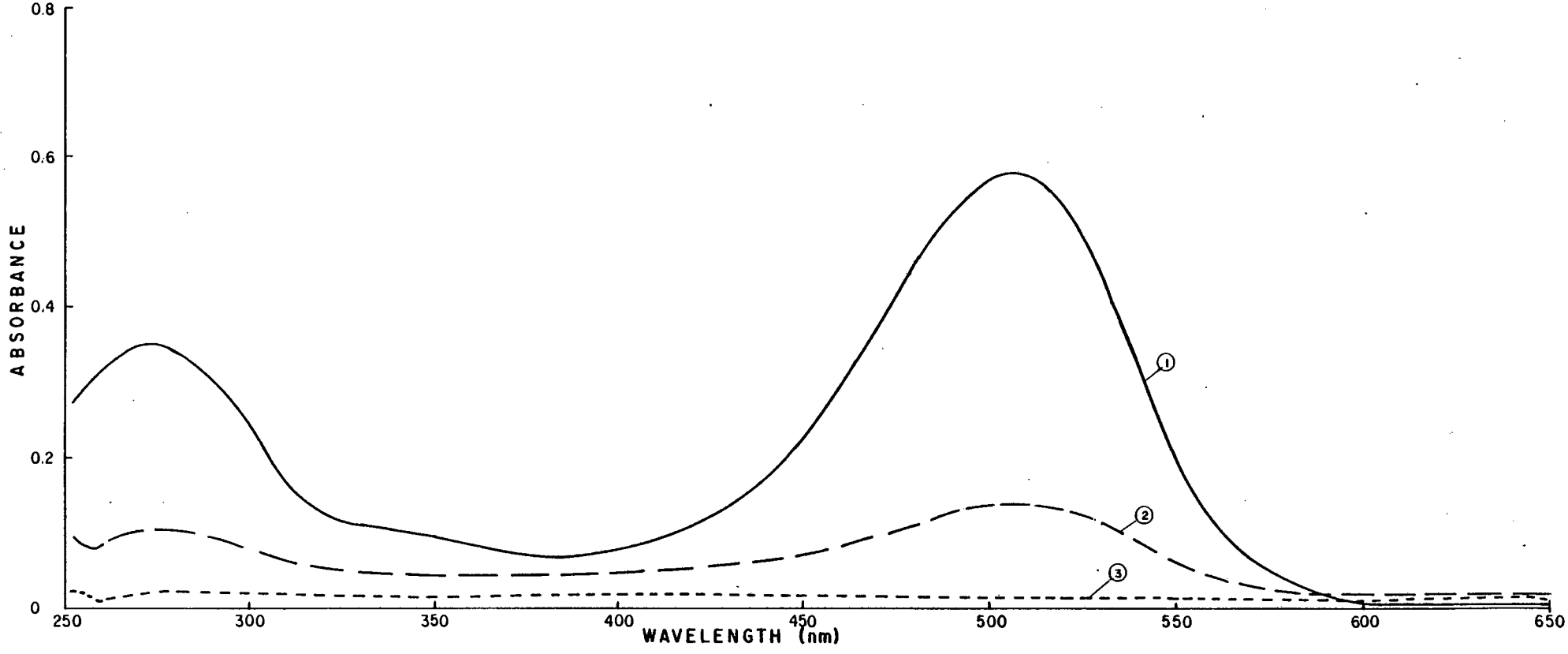


FIGURE 30: Absorption spectra of the reaction of dithizone in CCl_4 with Tl(III) after:

1: equilibration for 1 min. 2: equilibration for 2 min.

3: equilibration for 3 min.

in the organic phase.

Discussion

On the basis of the results obtained in the preceding chapter, it was initially assumed that the absorption bands at 507 nm and 275 nm (Figure 29) were a result of the formation of a Tl(HDz) complex and meso, respectively. However, the two clearly defined isobestic points would imply that the Tl(HDz) and meso are reacting together to give another product absorbing at 415 nm. Obviously this is not possible, as it has been established that dithizone and meso do not interact with each other (see p. 42). Furthermore, it has been found that the Tl(HDz) complex in CCl_4 has a major peak at λ_{max} 513 nm (ϵ = 25 700 cm^2 mol^{-1}) [43]. To confirm that the product absorbing at 507 nm is not due to formation of Tl(HDz), the extraction of Tl(I) by H_2Dz into CCl_4 was carried out.

It was found that the extraction of Tl(I) by H_2Dz into CCl_4 to give Tl(HDz) in the organic phase was only possible under alkaline conditions (pH 10 - 12). The absorption spectrum of the Tl(HDz) complex shows a major absorption band at 513 nm and a smaller band at 265 nm (Figure 31). Clearly, the Tl(HDz) complex absorbs at a different λ_{max} to the reaction product in Figure 29, thus confirming that the absorbance at 507 nm in Figure 29 is not due to the formation of a Tl(HDz) complex. However, the similarity of the two absorption spectra gave rise to the hypothesis that the reaction product formed may be a thallic-dithizonate complex, $Tl(HDz)_3$.

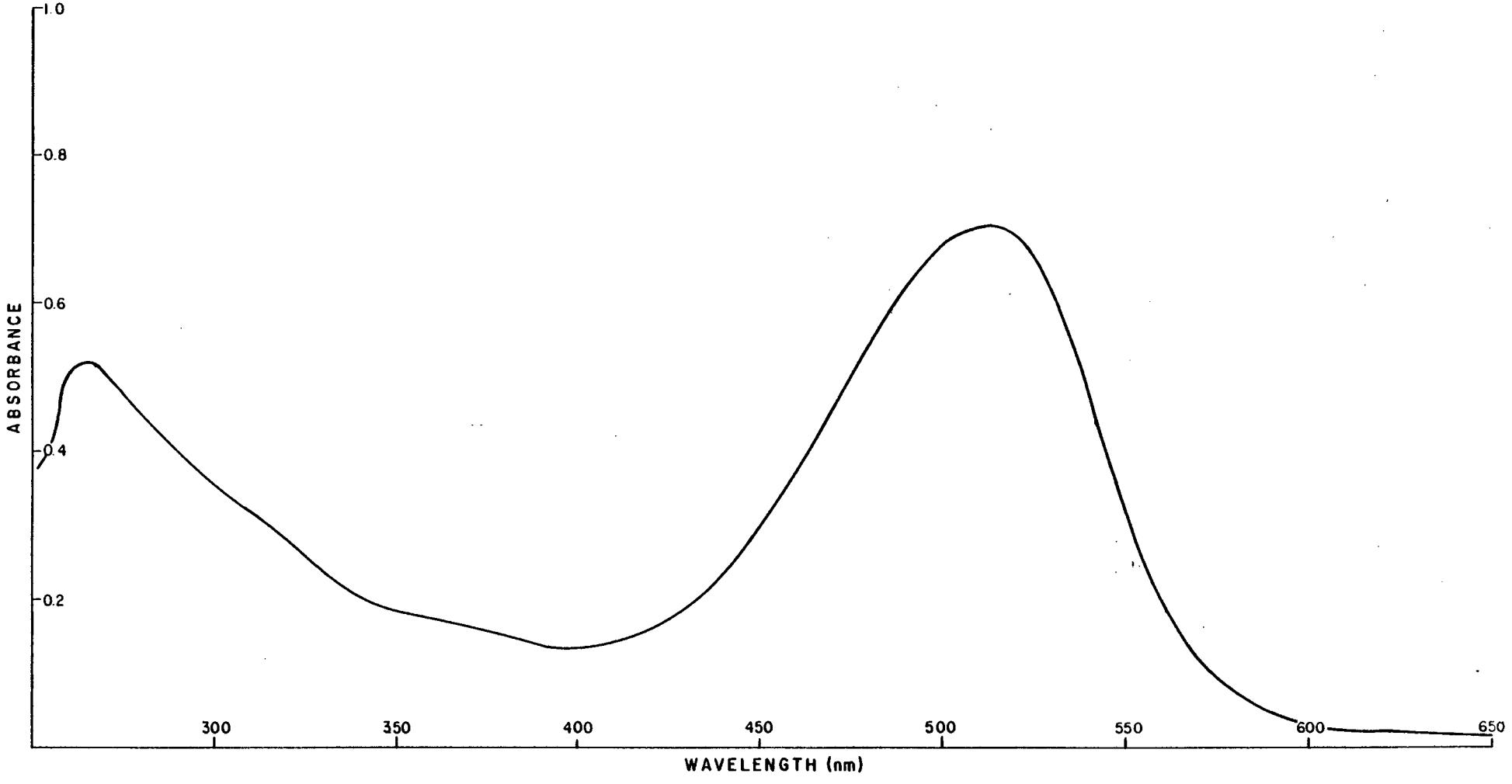


FIGURE 31: Absorption of thallium(I)-dithizonate complex [Tl(HDz)] in carbon tetrachloride (λ_{max} 513 nm; ε = 25700 cm^2 mol^{-1})

According to the literature, the disulphide has a major absorption band at 415 nm in CCl_4 [10]. Evidently, this suggested that the product absorbing at 415 nm in Figures 26 - 29 was due to the formation of the disulphide.

In the previous chapter it was established that Tl(III) reacts with H_2Dz to give meso as the final reaction product in the organic phase. However, the reaction in CCl_4 fails to account for the presence of meso in the organic phase when the reaction is complete. Studies of the properties of meso in CCl_4, as well as experimental values of $p_{CCl_4} = \frac{[meso]_o}{[meso]}$ have not been reported. However, one could speculate that, since meso is such a polar compound and CCl_4 a non-polar organic solvent, the mesoionic compound would preferentially partition into the aqueous phase. In fact it was found that a solution of meso in CCl_4 could not be prepared owing to the insolubility of meso in the non-polar organic solvent. However, when the CCl_4 containing the undissolved meso was equilibrated with 0.1 M $HClO_4$ it was found that while the mesoionic compound remained undissolved in the organic phase, a fair amount did partition into the aqueous phase, as indicated by the colour change in the aqueous phase from colourless to a pale yellow. Hence, this supports the hypothesis that the mesoionic compound would probably partition into aqueous phase and could presumably explain why the mesoionic compound is not present in the organic phase on completion of the reaction between Tl(III) and H_2Dz in CCl_4.

To test the hypotheses that the complex, $Tl(HDz)_3$, together with the disulphide, is formed by the reaction between Tl(III) and H_2Dz, detailed experiments were carried out as described in the following section.

6.2 FORMATION OF A THALLIUM(III)-DITHIZONATE

To establish whether the product absorbing at 507 nm and 275 nm (Figure 29) is a $Tl(HDz)_3$ complex, the stoicheiometry of the complex had to be determined. This was carried out by the following experiments.

The solutions containing the Tl(III) and H_2Dz were equilibrated for 15 - 30 sec. the organic phase was quickly withdrawn and first washed with double distilled water to remove any excess Tl(III). The washed organic layer (Figure 32, spectrum 1) was then shaken together with an equal volume of 1 M $HClO_4$ saturated with sulphur dioxide (SO_2). The SO_2 was present so that during the reversion procedure the Tl(III) could be reduced to Tl(I), thus avoiding possible oxidation of the regenerated dithizone. The organic phase containing the regenerated dithizone was removed and its absorption spectrum recorded (Figure 32, spectrum 2). The Tl(I) was re-extracted into the organic phase and the absorption spectrum of the Tl(HDz) complex was recorded using the regenerated dithizone solution as a solvent blank, so as to take into account the unreacted dithizone that may be present in the organic phase containing the Tl(HDz) complex (Figure 32, spectrum 3).

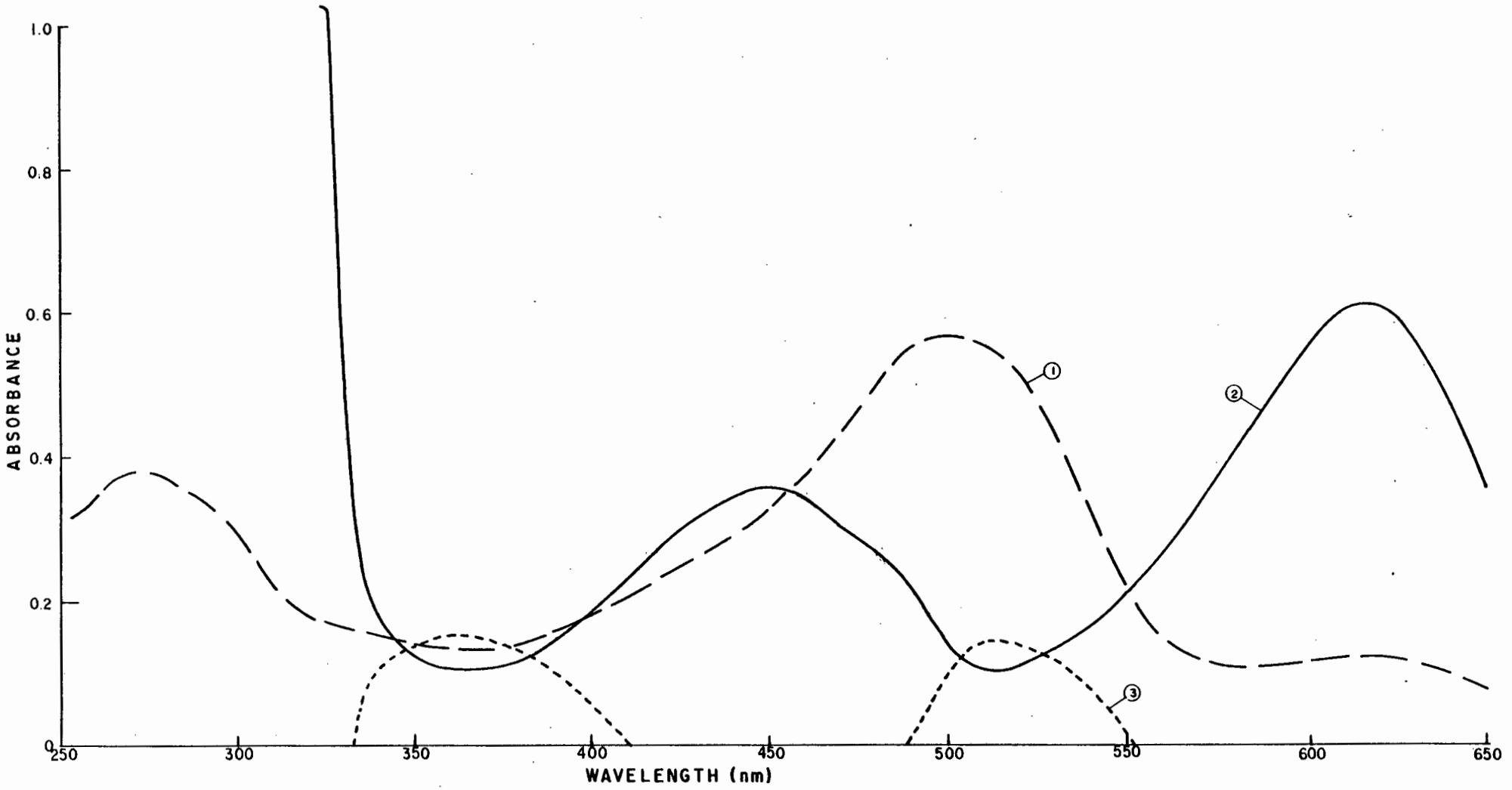


FIGURE 32: Absorption spectra recorded to determine the composition of the metal-dithizone complex formed by the reaction between Tl(III) and dithizone in CCl_4

1: Absorption spectrum of the washed organic phase, after equilibration (15-30 sec) of the two solutions containing Tl(III) and dithizone

2: Absorption spectrum of the regenerated dithizone solution obtained following the reversion of the complex represented by (1) above.

3: Absorption spectrum of the Tl(HDz) complex (λ_{max} 513 nm) - where the organic solution (2) was used as the solvent blank in the reference cell.

The composition of the thallium(III)-dithizone complex was calculated from the spectra:

Concentration of the dithizone regenerated:

$$c = 0.610/34\ 600$$
$$= 1.76 \times 10^{-5}\ M$$

Concentration of the Tl(HDz) complex:

$$c = 0.142/25\ 700$$
$$= 0.55 \times 10^{-5}\ M$$

Therefore $[Tl(I)] = 0.55 \times 10^{-5}\ M = [Tl(III)]$

The results show that the combining ratio for the thallium(III)-dithizone complex is 1 : 3.13, thus verifying the formation of the $Tl(HDz)_3$ complex.

It was noted that the SO_2 partitions into the organic phase and absorbs strongly in the ultra-violet region (spectrum 2). Furthermore, it was noted that under the reaction conditions employed for the re-extraction of Tl(I) by dithizone into the organic phase, there is also an absorbance at 360 nm (spectrum 3). The composition of this absorbing species is not known.

6.3 FORMATION OF THE DISULPHIDE(III)

To confirm the formation of the disulphide during the reaction between Tl(III) and H_2Dz, a solution of the disulphide in CCl_4 was prepared (see Chapter 9 § 9.3) and its behaviour in CCl_4 studied.

The disulphide solution is yellow in colour and gives rise to a major absorption band at 415 nm and two smaller bands in the ultra-violet region at 302 nm and 260 nm (Figure 33). The absorption spectra in Figure 34 illustrate the rate of the decomposition of the disulphide in CCl_4. As expected , the rate of decomposition is much slower in CCl_4 than $CHCl_3$.

To test whether the disulphide is formed during the reaction between Tl(III) and H_2Dz, a further experiment was carried out where the two solutions containing the Tl(III) and H_2Dz were gently shaken for 5 sec. and then allowed to stand in contact with each other until the colour of the organic phase had changed to yellow (~1½ hours). The absorption spectrum of this yellow solution shows a major band at 415 nm and two smaller bands at 302 nm and 264 nm (Figure 35). Clearly this absorption spectrum corresponds to that of the authentic disulphide solution in CCl_4, thus verifying the formation of the disulphide during the reaction between Tl(III) and dithizone.

A similar set of experiments to that outlined in Chapter 5 § 5.2 were carried out to investigate the interaction between the prepared disulphide solution in CCl_4 and solutions of Tl^{3+} and

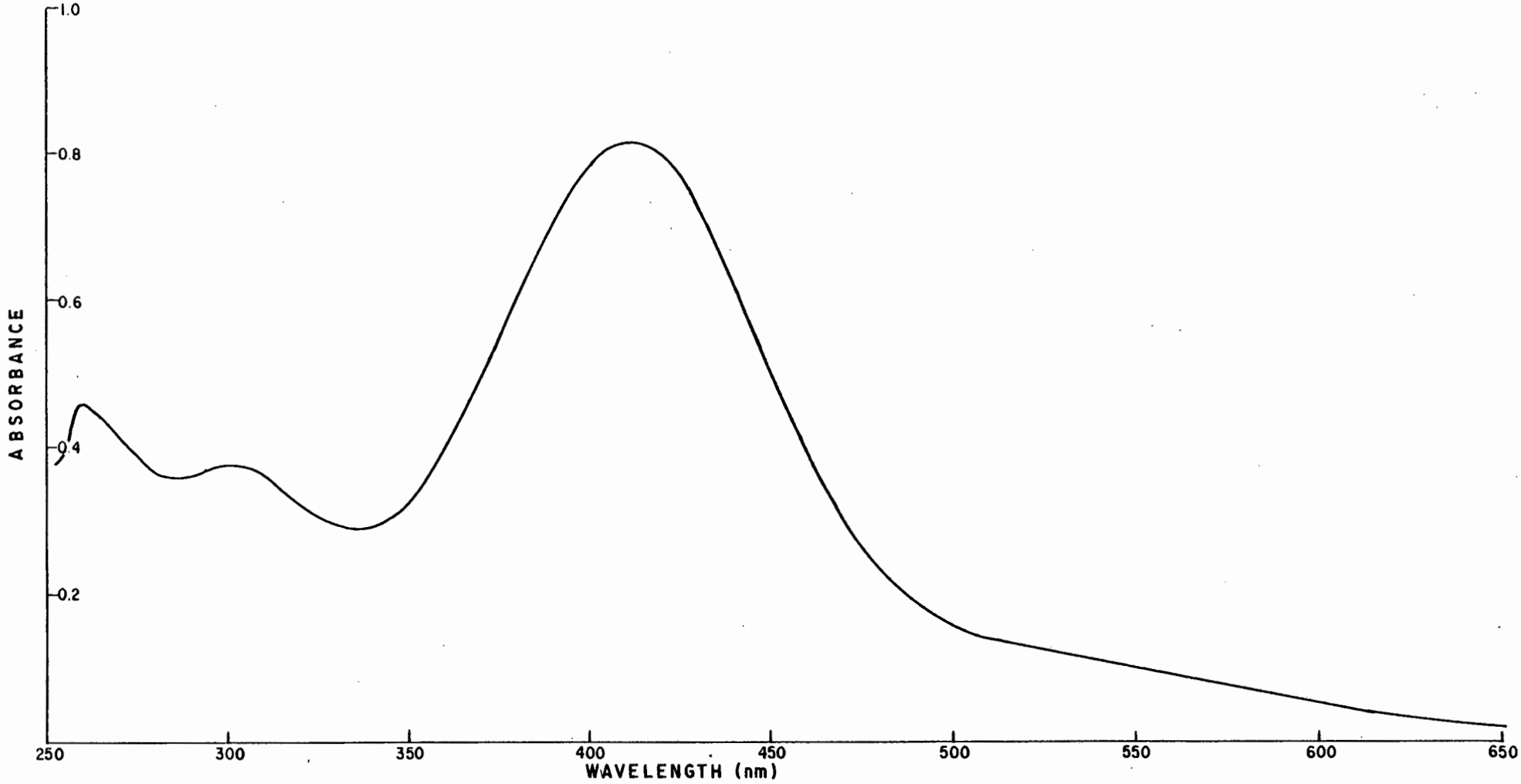


FIGURE 33: Absorption spectrum of the disulphide(III) in carbon tetrachloride.

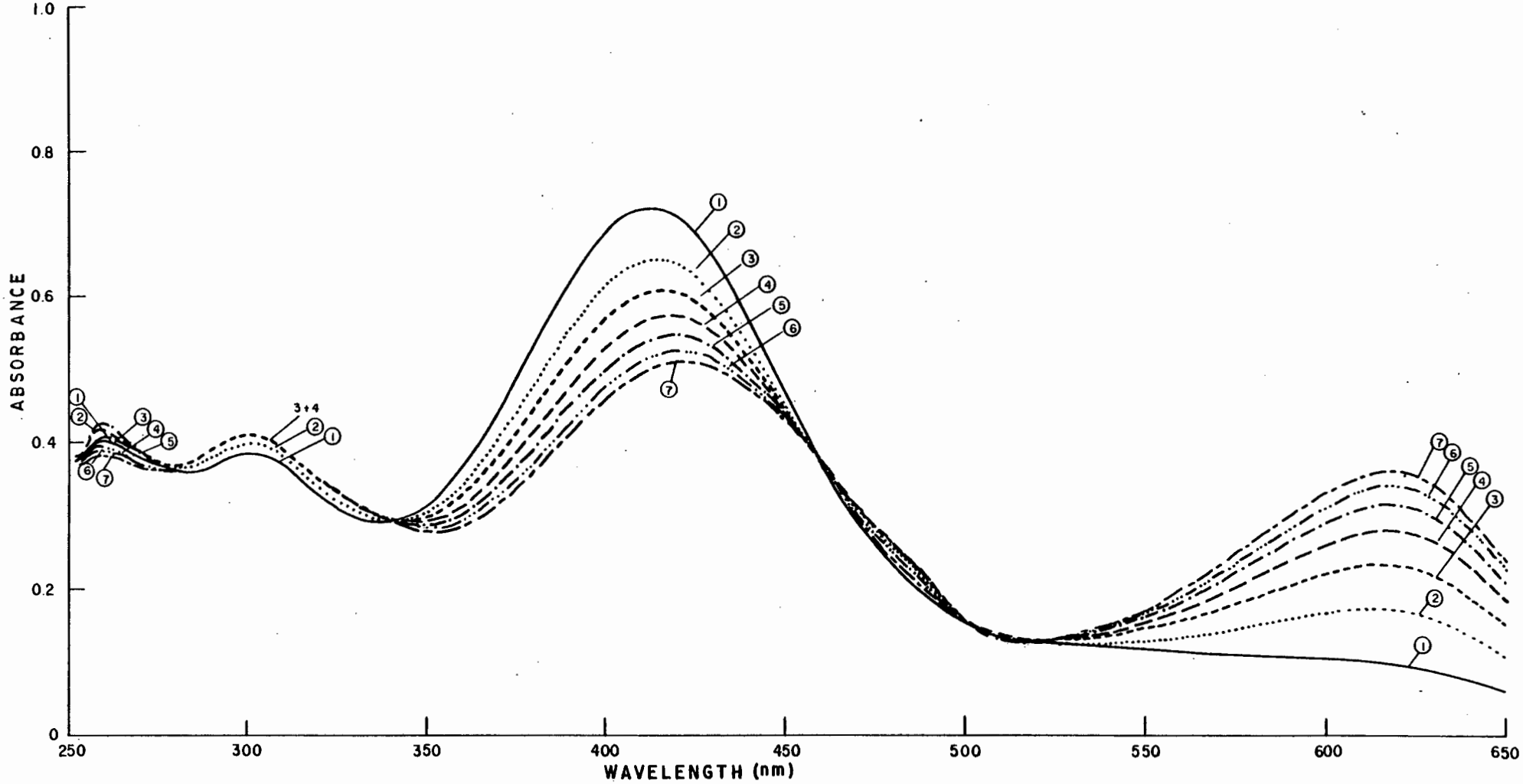


FIGURE 34: Absorption spectra of the disulphide(III) solution in carbon tetrachloride, recorded at hourly intervals.

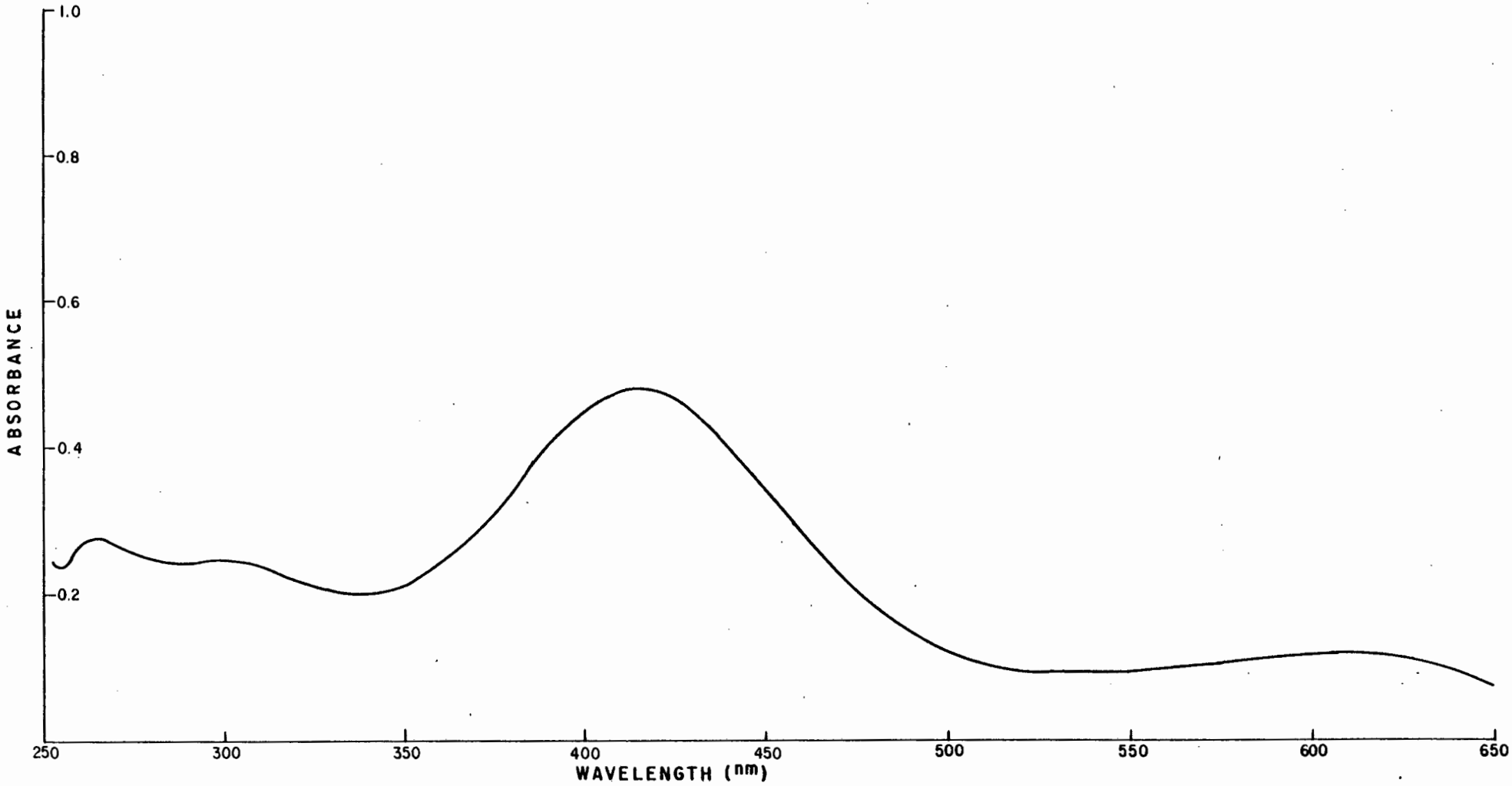


FIGURE 35: Interaction between thallium(III) and dithizone in CCl_4. Absorption spectrum of the yellow organic solution obtained after gentle shaking of the two phases for 5 sec. and then allowing them to stand in contact for ~1½ hours.

Tl^+, respectively (Figure 36). By comparing Figures 36 and 34 it is evident that, similar to the reactions of Tl^{3+} and Tl^+ with the disulphide in chloroform, the overall rate of the disproportionation of the disulphide in CCl_4 is increased in the presence of Tl^{3+} and Tl^+. However, from the spectra (Figure 36) it is also evident that, in the presence of Tl^{3+} and Tl^+, the disulphide does not decompose to give meso and dithizone in the organic phase. For reasons given on page 98, the mesoionic compound presumably partitions into the aqueous phase. To explain why the dithizone is not present in the organic phase one could postulate that, as in the Tl^{3+}-disulphide-chloroform reaction (see p. 55), the dithizone is oxidized by the excess Tl^{3+}. On the otherhand, for the reaction of Tl^+ with the disulphide, the dithizone would appear to be present in the aqueous phase. Unfortunately, due to the lack of time, further experiments could not be carried out to determine whether the dithizone is present in the aqueous phase, and if so, the form in which it would be present, i.e. whether or not it is associated with the Tl^+.

6.4 DISCUSSION

By studying the interaction between Tl(III) and dithizone in CCl_4, the following has been established:

(i) That a $Tl(HDz)_3$ complex and the disulphide are formed during the reaction between Tl(III) and H_2Dz. These

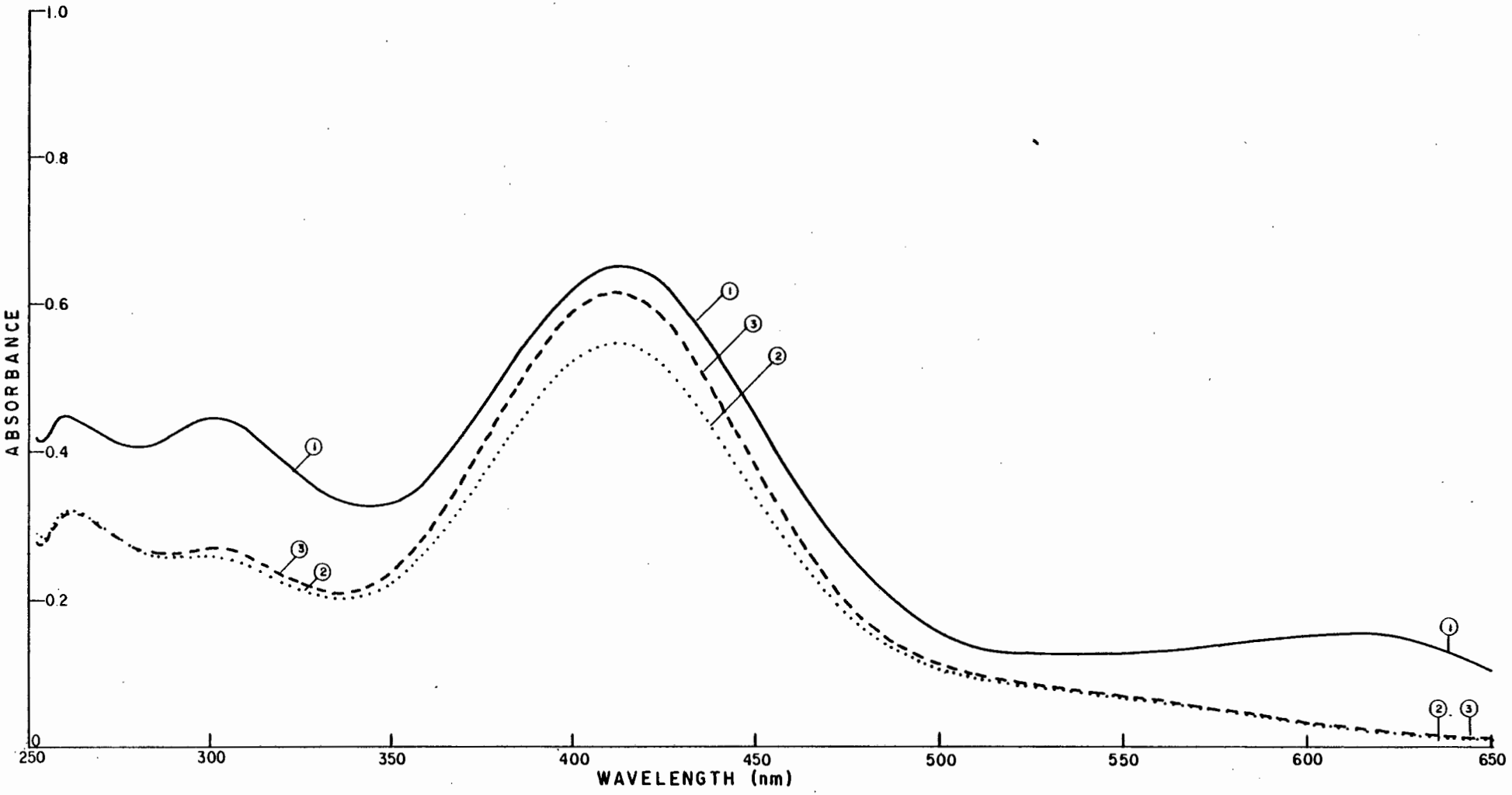


FIGURE 36: 1: Absorption spectrum of the disulphide(III) solution in CCl_4

2 - 3: Absorption spectra of the disulphide solution (1 above) after equilibration with a Tl(III) and Tl(I) solution, respectively.

products are in equilibrium with each other, which clearly indicates that the $Tl(HDz)_3$ complex is not stable and undergoes spontaneous oxidative disproportionation to give the disulphide and the resulting Tl(HDz) complex. Since there is no evidence of the Tl(HDz) complex in the organic phase during the course of the reaction between Tl(III) and H_2Dz in CCl_4 this suggests that the kinetics of the back-reaction of the Tl(HDz) complex to give Tl^+ in the aqueous phase and H_2Dz in the organic phase is much faster in CCl_4 than in $CHCl_3$.

(ii) The nature of the organic solvent does have a significant effect on the course of the reaction: the partition equilibria of the intermediate reactions, as well as the behaviour of the oxidation products formed differ in the two organic solvents. This results in different mixtures of products being present in the organic phase. In addition, the kinetics of the equilibrium is altered, the overall rate of the reaction being faster in CCl_4 than in $CHCl_3$.

The overall reaction scheme for Tl(III) and dithizone in CCl_4 can be summarized by the following equations:

$$Tl^{3+} + \overline{3H_2Dz} \longrightarrow \overline{Tl(HDz)_3} + 3H^+$$

$$\overline{Tl(HDz)_3} \rightleftharpoons \overline{(HDz)_2} + \overline{Tl(HDz)}$$

$$H^+ + \overline{Tl(HDz)} \xrightarrow{\text{rapid}} Tl^+ + \overline{H_2Dz}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$\overline{(HDz)_2} \longrightarrow \overline{H_2Dz} + \overline{meso}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$\overline{3meso} \longrightarrow 3meso$$

$$\text{excess } Tl^{3+} + \overline{3H_2Dz} \longrightarrow Tl^+ + 3meso + 6H^+$$

CHAPTER 7

DISCUSSION AND CONCLUSION

7.1 DISCUSSION AND CONCLUSION

On the basis of the results obtained in the preceding chapters, there is no doubt that the reaction between Tl(III) and dithizone is essentially oxidative in character. Moreover, the reaction is extremely complex in that it involves a series of intermediate reactions occurring successively, to give a number of reaction products in the organic phase. The complexity of the reaction is a result of the increase in the number of parameters (p and K_{ex}; cf. page 12) involved in the extraction procedure, as well as the nature of the oxidation products formed. The course of the intermediate reactions involved and the mixture of the reaction products present in the organic phase, are determined by the partition equilibria and the kinetics of equilibration for the individual reactions, as well as the rate of the decomposition of the disulphide. All these factors depend initially on the reaction conditions employed.

In the presence of excess Tl(III), the complexity of the system is increased. The excess Tl(III), as well as the resulting Tl(I), interacts with the disulphide and this results in an increase in the overall rate of the decomposition of the disulphide. Furthermore, the excess Tl(III) also reacts with meso. The reaction between Tl(III) and meso is extremely complex, in that it appears to involve both complexation and oxidation, to give possibly a meso-thallium(III) complex and an unspecified oxidation product, possibly the dication (XII). Clearly this complex Tl(III)-meso system require further investigation to elucidate the reactions involved and to characterize the reaction products formed.

In the present work, by studying the reaction between Tl(III) and dithizone in chloroform and carbon tetrachloride, conclusive evidence of the intermediate reactions taking place, and the reaction products formed, was obtained. Consequently, the objective of the present work has been met and a complete reaction scheme established, as summarized below.

Clearly, the extraction of Tl^{3+} by dithizone cannot be considered as a suitable method for the determination of thallium(III).

7.2 SUMMARY

The complete reaction scheme established for the reaction between thallium(III) and dithizone can be summarized as follows: Thallium(III) reacts with dithizone to give a $Tl(HDz)_3$ complex which undergoes spontaneous oxidative disproportionation to give the disulphide and the resulting Tl(HDz) complex. The disulphide decomposes by first order heterolytic fission to give equimolar amounts of dithizone and meso. The rate of the decomposition increasing in the presence of Tl^{3+} and Tl^{+}. The Tl(HDz) complex undergoes reversion to give Tl^{+} in the aqueous phase and dithizone in the organic phase. In the presence of excess Tl(III), the regenerated dithizone is oxidized to meso. The mesoionic compound partitions between the two phases and reacts with any excess Tl(III) available. The reaction between meso and Tl(III) appears to involve two reactions, complexation and oxidation, to give possibly a meso-thallium(III) complex, $[Tl(meso)_n^{3+}](ClO_4^-)_3$, and an unspecified oxidation product, possibly the dication (XII).

The complete reaction scheme can be represented by the following equations:

$$Tl^{3+} + \overline{3H_2Dz} \longrightarrow \overline{Tl(HDz)_3} + 3H^+$$

$$\overline{Tl(HDz)_3} \rightleftharpoons \overline{(HDz)_2} + \overline{Tl(HDz)}$$

$$\overline{(HDz)_2} \rightleftharpoons \overline{H_2Dz} + \overline{meso}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$H^+ + \overline{Tl(HDz)} \longrightarrow Tl^+ + \overline{H_2Dz}$$

$$\overline{H_2Dz} \xrightarrow{\text{excess } Tl^{3+}} \overline{meso} + 2H^+$$

$$\text{excess } Tl^{3+} + \overline{3H_2Dz} \longrightarrow Tl^+ + \overline{3meso} + 6H^+$$

$$\overline{meso} \rightleftharpoons meso$$

$$Tl^{3+} + nmeso \longrightarrow \overline{[Tl^{3+}(meso)_n{}^{3+}](ClO_4^-)_3}$$

$$Tl^{3+} + 2meso \xrightarrow{(ClO_4^-)} Tl^+ + \overline{\left[\begin{array}{ccccc} Ph\text{-}N{=}N & & & & N\text{-}N\text{-}Ph \\ | & & & & \| \\ & + & C\text{-}S\text{-}S\text{-}C & + & | \\ Ph\text{-}N\text{-}N & & & & N{=}N\text{-}Ph \end{array}\right] (ClO_4^-)_2}$$

(XII)

The course of these reactions and extent to which the reaction products are present in the organic phase depends on:
the pH of the aqueous phase, the concentration and order of

mixing of the reactants, the time of equilibration, and on the nature of the organic solvent used. The nature of the organic solvent has the most significant effect on the course of the reaction.

CHAPTER 8

THE MOLECULAR STRUCTURE OF DIPHENYLTHALLIUM(III)-DITHIZONATE

8.1 CRYSTAL PREPARATION

The diphenylthallium(III)-dithizonate complex was prepared by shaking a solution of dithizone in chloroform (0.01 M) together with an alkaline solution of diphenylthallium(III) chloride (0.02 M), until all the dithizone had reacted. The organic phase was removed and the organic solvent allowed to evaporate at room temperature. The residue was placed in a desiccator and dried under vacuum. The compound dissolved readily in various organic solvents; recrystallisation from hot ethanol gave small single crystals. A second recrystallisation was required in order to get suitable crystals for single-crystal X-ray analysis. The crystals were submitted for structural analysis and the X-ray structure was solved by Dr. A. Irving, Department of Physical Chemistry, University of Cape Town [44].

8.2 RESULTS AND DISCUSSION

A summary of the crystallographic data is given in Table 8.1. The relevant intramolecular bond lengths and angles are given in Tables 8.2 and 8.3, respectively. The molecular structure and the atomic nomenclature utilized in its description is shown in Figures 38 and 39. The crystals consist of discrete molecules (Figure 37), where each 5-co-ordinate diphenylthallium-(III) complex is associated with a dithizonate residue which acts as a bidentate chelating ligand, co-ordinating through the nitrogen and sulphur. The complex is also associated with the solvent of recrystallisation (ethanol) which co-ordinates through

TABLE 8.1 : SUMMARY OF CRYSTAL DATA*

Molecular formula	$C_{27}H_{27}N_4OSTl$
Molar mass (g mole^{-1})	659.97
Crystal system	monoclinic
Space group	$P2_1/c$
a(Å)	9.776(3)
b(Å)	16.761(4)
c(Å)	16.750(5)
β(°)	95.72(2)
V(Å^3)	2731
D_c(g cm^{-3}) (for Z = 4)	1.61
$R=\Sigma\|\|F_o\|-\|F_d\|/\Sigma\|F_o\|$	0.0457

*Full details of how crystallographic data were obtained and the structure solved are available from Dr. A. Irving, Department of Physical Chemistry, University of Cape Town.

TABLE 8.2 : BOND LENGTHS (Å) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

T1 - S6	2.649(3)
T1 - N1	2.62(1)
T1 - C71	2.12(1)
T1 - C71A	2.14(1)
T1 - OC	2.64(1)
N1 - N2	1.27(1)
N2 - C3	1.38(2)
C3 - N4	1.31(2)
N4 - N5	1.34(1)
N1 - C11	1.44(2)
N5 - C51	1.39(2)

TABLE 8.3 : BOND ANGLES (DEGREES) WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

CO - T1 - N1	157.5(3)
S6 - T1 - C71A	105.1(4)
C71 - T1 - C71A	152.7(5)
C71 - T1 - S6	102.1(3)
S6 - T1 - N1	70.2(2)
C71A - T1 - N1	97.9(4)
C71 - T1 - N1	92.2(4)
C0 - T1 - S6	87.6(2)
C0 - T1 - C71	90.4(4)
C0 - T1 - C71A	89.7(4)

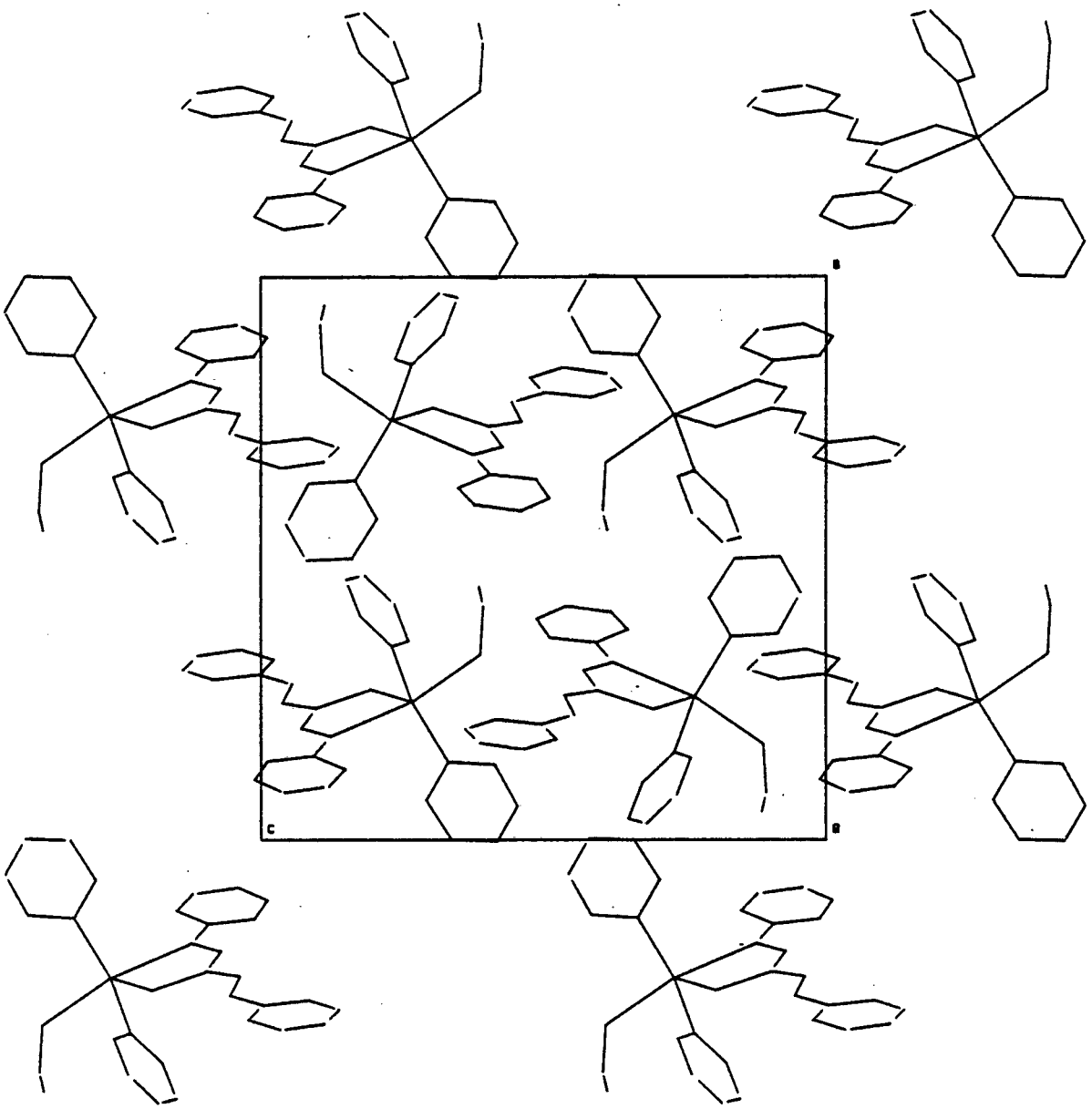


FIGURE 37: A projection of the molecular packing of the diphenylthallium(III)-dithizonate complex viewed down the x axis onto the (100) plane.

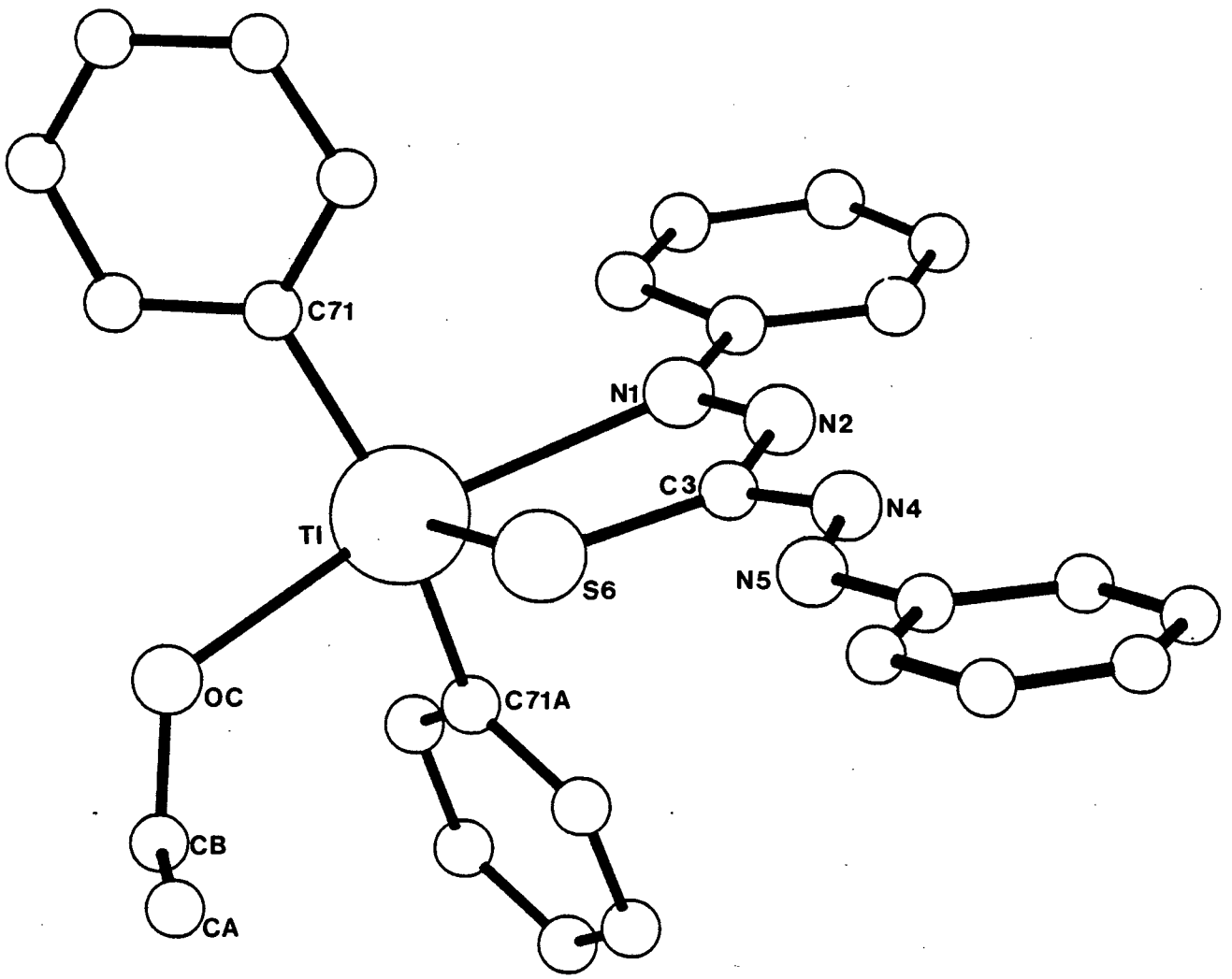


FIGURE 38: Perspective view of the molecular structure of diphenylthallium(III)-dithizone complex.

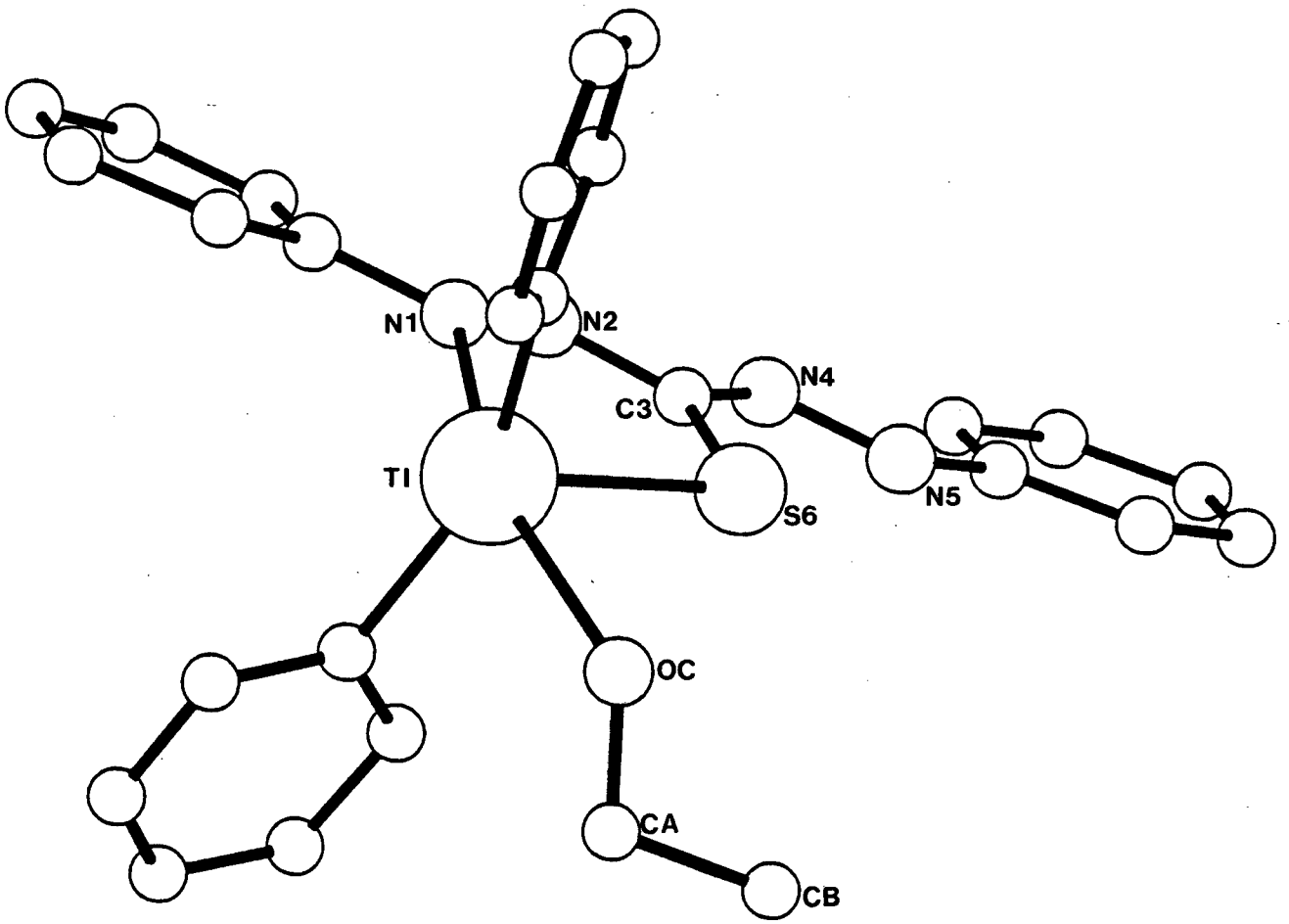


FIGURE 39: Perspective view of the molecular structure of diphenyl-thallium(III)-dithizone complex showing the planarity of the phenyl rings of the dithizone moiety.

the oxygen, the Tl - O bond length (2.64(1)Å) being well within the sum of the Van der Waals radii of the thallium (1.96Å) and the oxygen (1.40Å) atoms.

The thallium co-ordination

The co-ordination geometry around the Tl^{3+} atom may be described as a distorted trigonal bipyramid, where the S of the dithizonate ligand and the C's of the phenyl rings co-ordinate in the equatorial positions, while the N of the dithizonate ligand and the O of the ethanol co-ordinate in the axial positions. The distortion from the regular structure is evidenced by the deviation from linearity of the N1 - Tl - OC bond angle (157.5(3)°); the deviation from 120° of the C71 - Tl - C71A bond angle (152.7(5)°), as well as the deviation from the 90° S6 - Tl - N1 bond angle (70.2(2)°); the last distortion is thought to arise from the 'bite' limitation of the dithizonate ligand.

X-ray crystallographic studies have shown that the C - Tl - C bond angle in the diorganothallium(III) unit (R_2Tl) has a tendency to remain nearly linear, even in situations where a reduction in the C - Tl - C angle would produce a much more symmetrical overall arrangement of the ligands. The C - Tl - C bond angles in diakylthallium(III) derivatives are within the range (163° - 177°) [45 - 48]; while the C - Tl - C angle in the diphenylthallium(III)-complexes: diethyldithiocarbamato-diphenylthallium(III) and diphenyltropolonatothallium(III) is 148° and 162°, respectively [49]. This feature is also evident in the structure reported here.

According to Griffin *et al.*, steric factors do not appear to be of major importance in determining the C - Tl - C bond angle in diorganothallium(III) complexes. Furthermore, there is no correlation between the C - Tl - C angles and the co-ordination number of thallium. These authors propose that electronic factors are dominant in determining the tendency of the R_2Tl unit to remain near linear.

X-ray crystallographic studies have also shown that diorganothallium(III) complexes have a marked preference to form four-, five- and six-co-ordinate dimeric and polymeric structures. However, to date the diethyldithiocarbamatothallium(III) complex appears to be the one exception where the structure is a neutral diorganothallium(III) species where the TlR_2X unit is not oligomerized [49]. Griffin *et al.* suggest that the extent of oligomerization in diorganothallium(III) derivatives is largely controlled by the nature and size of the anionic ligand X^-. In the monomeric structure reported here, the lack of oligomerization may be attributable to steric factors: the dithizone residue being a bulky bidentate chelating ligand.

Other diorganothallium structures with anionic ligands having five membered chelate ring systems, with sulphur or nitrogen donor atoms, have as yet not been reported. Hence, no direct comparisons between (Tl - S) and (Tl - N) bond lengths can be made.

The dithizone residue

The measured bond lengths reveal a marked delocalisation of the π electrons within the N - N - C - N - N chain. While the formal double bonds C3 = N4 (1.31(2)Å) and the N1 = N2 (1.27(1)Å) are clearly extended in the comparison with isolated double bonds [where ·N = N· and :C = N are normally 1.25Å and 1.27Å, respectively]; the single bonds C3 - N2 (1.38(2)Å) and N4 - N5 (1.34(1)Å) are noticeably shortened [where :N - N: and :C - N: are normally 1.47Å]. Moreover, the measured N - CPh bond lengths: N1 - C11 (1.44(2)Å) and N5 - C51 (1.89(2)Å), imply that the delocalization of the electrons is extended from the nitrogen chain to the phenyl rings as they are shorter than or closer to 1.47Å. The bond lengths and angles pertaining to the phenyl rings are as expected.

There is a marked planarity of the dithizonate ligand (Figure 39), which allows for the extensive delocalization of electrons.

This structural characterization of the dithizone moiety corresponds to that found in previously reported studies of metal-dithizonates [20 - 25].

8.3 CONCLUSION

In view of the solvent of recrystallisation also co-ordinating to the Tl^{3+} ion, the molecular structure determination of the diphenylthallium(III)-dithizonate lends itself to further studies on the effects of different solvents of recrystallisation on the

molecular structure of the resulting compound. Furthermore, the structural characterization of the thallium(I)-dithizonate and the dimethylthallium(III)-dithizonate complexes, which still have to be determined, may also prove to be very interesting for further research.

CHAPTER 9

EXPERIMENTAL

9.1 GENERAL

The major difficulty in working with dithizone is its extreme sensitivity to trace metal impurities, its instability to light and air and the ready and rapid deterioration of its solution in impure solvents. Therefore it was imperative to employ specific procedures for its purification and general use, as well as the use of analytically pure reagents and solvents with especially clean glassware and by maintaining a very high standard of practical technique.

Glassware

All glassware used was thoroughly cleaned by allowing it to soak for at least 24 hours in a 10% contrad solution. The glassware was then rinsed with deionised water, a 5% (v/v) nitric acid solution, deionised water and finally with double distilled water and then allowed to dry in a dust-free environment.

Reagents and solvents

All reagents and solvents used were analytical reagent (AnalaR) grade and double distilled water was used throughout. Since the purity of the organic solvent used has a great influence on the stability of dithizone solutions and on the absorption spectra (particularly the ε values), all AnalaR organic solvents were always freshly fractionated before use.

To ensure that no metal impurities could have resulted from contamination during use, the purity of the materials used was

tested periodically by shaking them together with a dilute solution of dithizone in chloroform. Since dithizone is such a sensitive reagent it could therefore also be used to remove any impure metals present, by extraction, thus acting as a purifying reagent itself.

Preparation of metal-free aqueous ammonia:

Metal-free solutions of aqueous ammonia were prepared by either of the following two methods: (a) by passing ammonia gas into a beaker containing double distilled water, or (b) by isopiestic distillation [50]. The latter method involves adding ca. 500 ml ammonium hydroxide solution (AnalaR; sp. gr. 0.880) to a clean dry desiccator (capacity ~4 - 6 ℓ). A pyrex glass beaker (100 ml) containing double distilled water, to absorb the NH_3 gas, was also placed inside the desiccator and supported on a porcelain grid. The lid of the desiccator was replaced and the apparatus allowed to stand for several days (saturation requiring ~4 days). The isopiestic ammonia was then stored in a thoroughly cleaned polyethylene bottle.

Purification of dithizone solutions:

Analytical grade dithizone, supplied by Merck, Darmstadt, was used. An effective method of purifying dithizone solutions is by preparing a concentrated solution in a pure organic solvent (e.g. $CHCl_3$ or CCl_4) and shaking this together with metal-free aqueous ammonia or isopiestic ammonia. The dithizone is extracted into the aqueous phase as dithizonate anions (HDz^-)

and the main impurities, metal complexes and non-acidic oxidation products, remain in the organic phase. After rejecting the organic phase, the aqueous phase was repeatedly washed with portions of the organic solvent until they were either colourless or pure green. The aqueous phase was then acidified by either passing sulphur dioxide into the aqueous layer or by adding 3 M H_2SO_4, in the presence of freshly distilled organic solvent. The purity of the dithizone solution was checked by recording the absorption spectrum of the solution and measuring the peak ratio, $A_{\lambda max,1}/A_{\lambda max,2}$, which has been found to be the most sensitive index of reagent purity [6]. The peak ratio for dithizone in $CHCl_3$ is 2.59 and in CCl_4 1.73 [6]. Since dithizone solutions are known to deteriorate on standing, especially in direct sunlight, fresh volumes of the reagent solution were prepared periodically and stored in a dark cupboard or covered with aluminium foil and stored in a cool place for not more than a few days. As a result, dithizone solutions of different concentrations were used in this study. The purity of the dithizone solutions was always checked before its use. Dithizone solutions are known to obey the Beer-Lambert Law, therefore it was possible to calculate the concentration of the dithizone solutions directly from the absorption spectra as follows:

$$c = A/\varepsilon\ell \quad (\text{at } \lambda_{max,1} \text{ or } \lambda_{max,2})$$

Solvent	$\lambda_{max,1}$	ε_1	$\lambda_{max,2}$	ε_2
$CHCl_3$	605	41400	445	15900
CCl_4	620	34600	450	20000

Chromatography:

Thin-layer chromatography (TLC): Aluminium sheets coated with silica gel (Merck, Darmstadt) were used.

Column chromatography: Glass columns packed with silica gel (60 - 120 mesh) were used. All columns were prepared by first making a slurry of silica gel with the eluting solvent.

Instrument:

Electronic spectra were recorded on a Varian SuperScan 3 Ultraviolet-visible spectrophotometer. 1 cm matched quartz cells were used throughout.

PREPARATIONS

Preparation of thallium(III) solutions:

Thallium(III) solutions were prepared by dissolving specific known weights of $TlCl_3$ (Merck, Darmstadt) in 0.1 M $HClO_4$ (pH = 1) to give 10^{-2} - 10^{-4} M solutions. Since $TlCl_3$ is very hygroscopic it was necessary to determine the exact concentration of Tl(III) in each solution. This was performed by either of two methods: (a) by reducing the Tl(III) to Tl(I) with SO_2 and determining the concentration of Tl(I) by extraction with dithizone, using the reversion procedure (p.132) or (b) by standardization with EDTA using methylthymol blue as indicator (p.134).

Preparation of thallium(I) solutions

Thallium(I) solutions were prepared by dissolving specific known weights of $TlNO_3$ (Hopkins and Williams Ltd.) in 0.01 M $HClO_4$ to give 10^{-5} M solutions. The exact concentration of the solutions were determined by the reversion procedure.

Determination of Tl(I) using the reversion procedure [39]:

This was carried out by taking the aqueous solution containing the thallium(I) and metal-free ammonia (pH ~ 12) and shaking this together with an equal volume of a dithizone solution, for 1 - 2 minutes. After the two layers had separated, a portion of the organic phase was withdrawn into the sample cell. A further portion (usually 10 ml) was transferred into another separating funnel and reverted by shaking for 1 minute with an equal volume of 0.5 N sulphuric acid, or in some cases 1 M $HClO_4$. The reversion usually took place almost immediately on shaking, but in some cases it took longer and at least two minutes of shaking was required. After the two layers had separated, a portion of the regenerated dithizone solution was withdrawn into the reference cell. Thus the difference in absorbance was measured, giving only the absorbance of the Tl(HDz) complex (λ_{max} 508 nm, ε = 33000 cm^2 mol^{-1}). Hence, the exact concentration of the Tl(I) extracted could be calculated.

9.2 EXPERIMENTAL RELATING TO CHAPTER FIVE

9.2.1 Preparation of the mesoionic compound(IV) in $CHCl_3$ using potassium hexacyanoferrate(III) ($K_3Fe(CN)_6$) [10].

A solution of dithizone (1.01 g) in $CHCl_3$ (300 ml) was stirred mechanically (2 h) together with a solution of $K_3Fe(CN)_6$ (3.26 g) and potassium carbonate (4.10 g) in double distilled water (100 ml). The organic layer was transferred into an evaporating dish and placed on a steam-bath to allow the solvent to evaporate. The residue was taken up in boiling ethanol, treated with animal charcoal, filtered, and allowed to stand overnight to yield orange-red crystals of the mesoionic compound(IV). The crystals were filtered and allowed to dry (0.40 g, 40%; m.p. 170 - 172° decomp.). The purity of the compound was tested by TLC using $CHCl_3$ as the developing solvent. The thin-layer chromatogram indicated the presence of a yellow spot, the Rf value = 0.04 (literature value Rf_{ave} = 0.05). The absorption spectrum in $CHCl_3$ showed a strong band at 266 nm and a weaker band at 470 nm (Figure 8, p. 25). Repeat preparations were performed, and it was noted that by doubling the amount of $K_3Fe(CN)_6$ taken, better yields were obtained (~50%).

9.2.2 Preparation of the disulphide(III) by oxidation of dithizone with iodine [36]

A solution of dithizone (2 g) in chloroform (140 ml) was added to a solution of iodine in chloroform (40 ml, 0.1 M) and shaken together with double distilled water (100 ml) for 5 minutes.

The organic layer was removed and the solvent evaporated using a rotary evaporator. The residue was taken up in ether. Some of the residue remained undissolved and when this residue was added to chloroform, the solution turned green indicating that some of the disulphide had already decomposed to give dithizone and the mesoionic compound (IV). After having dissolved as much of the residue as possible in ether, this solution was then shaken together with an aqueous solution of potassium iodide and iodine. Small quantities of iodine were added until there was no further colour change in the aqueous phase, indicating that all the dithizone present had been oxidized. The organic layer was separated and dried over anhydrous sodium sulphate, filtered and chromatographed on a column of silica gel. The first fast-moving red fraction was the disulphide(III). It was finally purified by addition of cyclohexane to its ether solution whereupon the disulphide(III) separated as fine red particles (50 mg; m.p. 100° decomp.). The yield was low because of the decomposition of the disulphide, but the amount recovered was sufficient for the required experiments. The absorption spectrum of the disulphide(III) solution in chloroform showed a major absorption band at 420 nm and two weaker bands at 305 nm and 257 nm (Figure 12, p. 52).

9.2.3 Determination of thallium(III) by direct titration with ethylenediaminetetra-acetic acid (EDTA) using methylthymol blue as indicator

A suitable method for the determination of thallium(III) has been described by Strelow and Von S. Toerien [51], where

thallium(III) is determined by direct titration with EDTA using methylthymol blue as indicator. This method allows for the determination of Tl(III) in an alkaline medium since it was reported that halide ions, especially bromide, interfere when Tl(III) is titrated with EDTA in an acidic media. Hence this method could include the bromide oxidation procedure of thallium, which has been found by the authors to be the most elegant and reliable one. Since Tl(III) tends to hydrolyse even at fairly low pH values, the titration in alkaline media requires the presence of a suitable complexing agent which complexes Tl(III) strongly enough to prevent its precipitation by hydrolysis but not as strong as the chosen indicator. The experiments performed by the above-mentioned authors revealed that tartaric acid as the complexing agent and methylthymol blue as the indicator met the requirements for the complexometric titration of thallium-(III) in alkaline media (pH 7 - 10). They also found that with lower EDTA concentrations, of the order of 0.001 M EDTA, much sharper endpoints were obtained, also that the presence of 0.1 - 0.5 N HBr had no appreciable effect on the methylthymol blue endpoint.

The concentration of thallium(III) was calculated as follows:

$$\text{Concentration of Tl(III)} = \frac{\text{Volume of EDTA required} \times 0.001\ \text{M EDTA}}{\text{Volume of solution containing the Tl(III)}}$$

Reaction between thallium(III) and the mesoionic compound (IV):

Since the presence of bromide ions has been found not to influence the endpoint, it was also possible to determine the presence of Tl(I) during the study of the reaction between Tl(III) and the mesoionic compound (IV). On completion of the reaction between Tl(III) and meso in chloroform (Table 5.1, p. 66), the aqueous phase was removed and divided in half. The Tl(III) concentration was determined in the one half of the solution and in the other half the total thallium concentration was determined, after oxidation with a saturated solution of bromine water. Hence, the Tl(I) concentration could be calculated from the difference.

EDTA solution:

To prepare a 0.001 M EDTA solution, the disodium salt of EDTA (AnalaR) was dissolved in double distilled water. The EDTA solution was standardized against a zinc sulphate solution according to the known literature methods [40].

Methylthymol blue indicators;

The indicator was used as a solid mixture (1%) with finely ground potassium nitrate.

pH 10 buffer solution:

The pH 10 buffer solution was prepared by taking 70 g of ammonium chloride in 570 ml aqueous ammonia (sp. gr. 0.88) and diluting to 1 ℓ with double distilled water. This solution was transferred and stored in a polyethylene bottle.

9.2.4 Determination of thallium using atomic absorption spectroscopy (AAS)

On completion of the reaction between Tl(III) and meso in chloroform (Table 5.1, p. 66), an aliquot of each phase (250 µl) was diluted to 5 ml. The aqueous phase was diluted with 0.1 M $HClO_4$; and methylisobutyl-ketone (MIBK) was used as an alternate organic diluent since chloroform decomposes to phosgene on aspiration into the flame.

For thallium, a concentration of 50 ppm is well within the linear range [52]. As Beers Law is obeyed, it was considered sufficient to construct a calibration curve from a 50 ppm standard. A standard solution of thallium(I) (50 ppm) in 0.1 M $HClO_4$, as well as the samples, were aspirated into the air-acetylene flame, and the thallium samples quantified.

To test the suitability of AAS for the determination of thallium in the present study, the results obtained by AAS for the aqueous phase were compared to those obtained by the EDTA titration method. It was found that the values obtained by AAS were consistently higher. This is probably due to the presence of organic particles (the solvents of the two phases being miscible to a certain extent), which would enhance the sensitivity of the absorption readings. Nevertheless, the difference was always less than 10%.

The expected thallium content of the organic phase was calculated from the difference between the amount of thallium determined in the aqueous phase (by EDTA titration) from the initial known

amount of thallium taken. Since thallium cannot be extracted into the organic phase under the conditions employed (p. 65), a standard could not be prepared in the organic phase. Hence, for quantification of the organic samples, the calibration curve constructed from the aqueous standard was used. The results obtained by AAS compared well with the expected thallium content of the organic phase.

Since there is an error of approximately 10%, the results obtained can only be considered as semi-quantitative. However, there was an overall consistency in the results obtained.

Instrument: Varian Techtron 70 spectrometer.

9.2.5 Preparation of the Cerium(IV), potassium bichromate and potassium permanganate solutions

Cerium(IV) solutions:

Ammonium cerium(IV) sulphate solutions were prepared by dissolving 0.1590 g and 0.3360 g $(NH_4)_4Ce(IV)(SO_4)_4 \cdot 2H_2O$ in 50 ml 1M $HClO_4$ and 4 M $HClO_4$, respectively.

Potassium bichromate solution:

$K_2Cr_2O_7$ (0.0735 g) was dissolved in a mixture of 1 M $HClO_4$ and 3 M H_2SO_4 (50 ml).

Potassium permanganate solutions:

Specific known weights of $KMnO_4$ were dissolved in 3 M H_2SO_4 to give 10^{-3} - 1 M solutions.

9.3 EXPERIMENTAL RELATING TO CHAPTER SIX

9.3.1 Preparation of the disulphide in carbon tetrachloride (CCl_4)

A 5.57×10^{-3} M solution of dithizone in CCl_4 (70 ml) was added to a 1.08×10^{-2} M solution of iodine in CCl_4 (20 ml) and shaken together with distilled water (50 ml) for 5 minutes. The colour of the organic phase changed from green to a reddish-brown. After the layers had separated the organic phase was removed and dried over anhydrous sodium sulphate and filtered. The purity of the solution was checked by TLC. After suitable dilution the absorption spectrum was recorded. The disulphide in CCl_4 gave rise to a major absorption band at 415 nm and two weaker bands at 302 nm and 250 nm (Figure 33, p. 103).

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