Kinetics of catalytic oxidation of some aromatic compounds in two–phase systems

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KINETICS OF CATALYTIC OXIDATION

OF SOME AROMATIC COMPOUNDS

IN TWO-PHASE SYSTEMS

by

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KINETICS OF CATALYTIC OXIDATION OF SOME AROMATIC COMPOUNDS IN TWO-PHASE SYSTEMS

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R. M. Smith

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ACKNOWLEDGEMENTS

ABSTRACT.

A study has been undertaken of some oxidative coupling reactions which are catalyzed by copper chloride/pyridine catalyst solutions, gaseous oxygen being the oxidizing agent.

The oxidative coupling of thiophenol has been investigated in some detail. It has been discovered that, under certain conditions, one of the products of this reaction is diphenyl thiolsulphinate (PhSOSPh), a potential commercial antioxidant for synthetic rubbers, whereas previously diphenyl disulphide (PhSSPh) was reported to be the only product. The effect of several reaction variables upon both the rate of thiophenol oxidation and the relative yields of products from this reaction have been investigated. In particular, detailed study has been made of the effects of varying mass transfer rates upon the course of this gas-liquid reaction. It was found that both the selectivity and the rate of the reaction was dependent upon the rate of mass transfer of oxygen from the gas phase to the liquid phase. Specific regimes of mass transfer with chemical reaction have been characterized for given reaction conditions. A brief investigation into the compounds present during the course of this reaction gave results which support a theory of constant selectivity for the generation of thiolsulphinate throughout the course of the oxidation reaction. A kinetic scheme has been given for this reaction. From this kinetic scheme, an expression for the chemical reaction rate has been derived. Subsequently a differential equation representing the phenomenon of mass transfer with chemical reaction has also been derived. However, this equation was found to be very complex and was of little value.

A brief study has been made of the oxidative coupling of aniline, p-phenylenediamine and toluene-3,4-dithiol.

From knowledge of the oxidative coupling reactions of amines and thiols, the reaction course of the oxidative polymerization of p-aminothiophenol has been predicted. The experimental work on the oxidative polymerization of p-aminothiophenol gave good agreement in most points with the predicted reaction. In this polymerization reaction, oxygen was incorporated into the polymer chain, a phenomenon which has not been previously reported for oxidative coupling reactions using this catalyst system. Specific regimes of mass transfer with chemical reaction have also been characterized for given reaction conditions for this polymerization reaction.

NOMENCLATURE

a	area of gas-liquid interface
Ar	aryl group
b	liquid phase reactant
b_o	bulk liquid concentration of liquid phase
b'_o	concentration of liquid phase reactant at the interface
c	absorbing component
c_o	bulk liquid concentration of absorbing component
c'_o	concentration of the absorbing component at the interface
c_i	concentration of component 'i'
c'	equilibrium concentration of the absorbing component
D	diffusivity
E	activation energy
E'	enhancement factor
k	kinetic rate constant
k_o	kinetic rate constant for the reoxidation of the Cu(I) complex
k_{dis}	kinetic rate constant for the recombination of thiophenoxy radicals to form diphenyl disulphide
k_{th}	kinetic rate constant for the reaction of oxygen with thiophenoxy radicals
k_L	chemical absorption coefficient
k_L^o	physical absorption coefficient
k_g	gas phase mass transfer coefficient
P_g	partial pressure of gas
P_i	partial pressure of gas at the interface

py	pyridine
q	stoichiometric coefficient
R	a term used to denote any chemical group; the chemical group is specified in the text when R is used.
$\bar{R}$	gas constant
r	chemical reaction rate
s	rate of surface renewal
T	temperature
t	time
t*	lifetime of a surface element of liquid
t_D	diffusion time
t_r	reaction time
$\bar{V}_o$	average absorption rate in the absence of a chemical reaction
V	average absorption rate
v_d	rate of polymerization
x	distance from the interface
δ	thickness of the diffusion film
ϕ	selectivity of the thiophenol oxidation reaction for thiolsulphinate
$\not{\phi}$	volume of liquid per unit interface
[ ]	concentration of the term inside the brackets in grm. moles/litre.
$-\dfrac{d[\ ]}{dt}$	rate of removal of the term inside the bracket in grm. moles/litre/sec.
$(\quad)_{thiol/amine/total}$	the value of the expression in the brackets for the thiol/amine/total reaction.

I. INTRODUCTION

In recent years, copper-amine catalysts have been used in selective oxidative coupling processes for the synthesis of many important compounds. These catalysts are now used in the commercial production of poly(phenylene oxide) from 2,6-disubstituted phenols. The chemical kinetics of the oxidative coupling of these phenols has been studied in considerable detail. However, there are still many aspects of the reaction system which, as yet, are not fully understood. Other polymers which have been synthesized using this catalyst system are polydisulphides, polyacetylenes and azopolymers. Although these polymers have useful properties, there has been little or no investigation into the kinetics of these polymerization reactions. In addition to the substrate and the copper-amine catalyst, gaseous oxygen is required to propagate all these oxidative coupling processes; thus the mass transfer of the oxygen from the gas phase to the liquid phase needs to be considered. However, to the author's knowledge, no detailed study of the effects of mass transfer on these gas-liquid systems has been reported.

The purpose of this project was to develop the kinetics of these important oxidative coupling reactions which use copper-amine catalysts. This included the study of mass transfer effects, the kinetic study of known processes and the synthesis of new products including the kinetic study of their production. Such kinetic studies are necessary in order to design process plants for manufacturing the given chemical.

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2. REVIEW OF OXIDATIVE COUPLING REACTIONS

2.1 Introduction

Laidler (1) described oxidation reactions under three classes:-

(a) Direct interaction between molecular oxygen and a substrate, e.g. oxidation of iron.

$$4 \, Fe + 3 \, O_2 \longrightarrow 2 \, Fe_2O_3 \qquad (2.1.1)$$
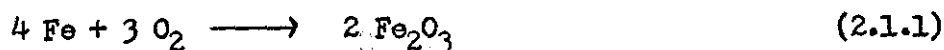
(b) Elimination of hydrogen from a substance, e.g. using a suitable catalyst, ethyl alcohol will split off hydrogen with the formation of acetaldehyde.

$$CH_3CH_2OH \xrightarrow{\text{catalyst}} CH_3CHO + H_2 \qquad (2,1.2)$$
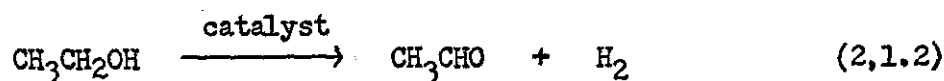
This particular type of oxidation is conveniently referred to as dehydrogenation.

(c) Removal of electrons from a molecule, e.g. oxidation of ferrous ions to ferric ions.

$$Fe^{2+} \longrightarrow Fe^{3+} + e \qquad (2.1.3)$$

This third type of reaction may actually be regarded as the essential process occurring in any kind of oxidation.

The term "oxidative coupling" is used in this thesis to describe the coupling of two molecules by the removal of hydrogen. The hydrogen is combined with oxygen to form water. Equation 2.1.4 describes the oxidative coupling of a compound of the general fomula, XH_y.

$$2 \, XH_y \xrightarrow{\quad y/2 \, O_2 \quad} X - X + y \, H_2O \qquad (2.1.4)$$
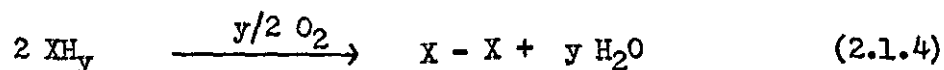
(where $y \geqslant 1$ and X is any chemical group.)

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Alternatively, the compound may couple at two or more sites in the molecule, in which case a polymer may be formed (equation 2.1.5). Usually a catalyst

$$n\ H_yXH_y\ \xrightarrow{\ ny/2\ O_2\ }\ (-X-)_n\ +\ 2ny\ H_2O \qquad (2.1.5)$$
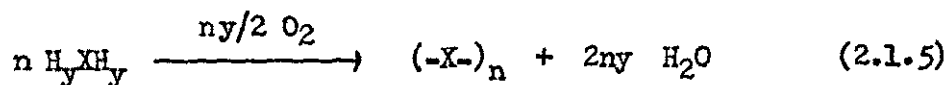
is required to effect the reaction.

In enzyme systems, practically all oxidation processes involve the removal of two hydrogen atoms from the substrate. Sometimes the transfer of hydrogen atoms is to molecular oxygen itself. Inthis case, the enzyme involved is usually referred to as the oxidase (1).

In recent years, oxidative coupling as a synthetic technique has had considerable use particularly in the field of natural products. The role of oxidative coupling in the biosynthesis of alkaloids and lignin, a naturally occurring polymer, has been recognised (2). Oxidative coupling reactions have been promoted by catalysts such as: manganese dioxide; lead dioxide; alkaline ferricyanide and chromium trioxide (3). In this present project, copper-amine catalysts have been used in the study of oxidative coupling reactions. This copper-amine system has kinetic and mechanistic similarities with the copper oxidases (particularly with tryosinase and ascorbic acid oxidase) used in enzyme oxidation reactions (3). An enzyme system has been used to oxidize 2,6-dimethylphenol to 3,3',5,5'-tetramethyldiphenoquinone (3). This is one of the products from the oxidative coupling of 2,6-dimethylphenol using the copper-amine catalyst, the catalyst used in this project. Thus the study of oxidative coupling reactions using the copper-amine catalyst may shed further light on the kinetics of complex enzyme reactions and vice-versa.

One advantage of oxidative coupling or enzyme reactions is that

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they are very selective reactions. Thus in the case of a large
molecule where a number of functional groups could possibly be
oxidized, an enzyme system, or one of the catalysts previously
mentioned, may selectively oxidize only one of the functional
groups and leave the remaining groups unaffected.

Recently, oxidative coupling, using a copper-amine catalyst,
has been widely used as a method of synthesizing new polymers. Such
polymers include: poly(phenylene oxide) of which poly(2,6-dim-
ethylphenylene oxide) is produced commercially (4); poly(acetylene)
(5); polydisulphides (6) and polyazoaromatics (2).

In this present project, the copper(I) chloride pyridine
catalyst was used in the study of the oxidative coupling of thiols,
amines, dithiols, diamines and aminothiols. Also studied was the
effect of mass transfer on the reaction rates and on selectivity
(where more than one product was formed).

2.2 Polymers produced, their properties and uses

2.2.1 Poly(phenylene oxide).

In 1959, Hay and co-workers (7) reported that certain
2,6-disubstituted phenols could be oxidatively polymerized to give
aromatic polyethers (equation 2.2.1).

$$n \underset{R}{\overset{R}{\bigcirc}}-OH \; + \; \frac{n}{2}O_2 \; \xrightarrow{Cu^+/amine} \; \left[-\underset{R}{\overset{R}{\bigcirc}}-O-\right]_n \; + \; nH_2O \qquad (2.2.1)$$
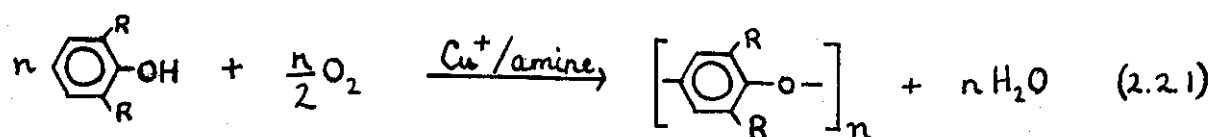
(where R = alkyl group.)

3,5,3',5'-tetramethyldiphenoquinone (Fig. 2.2.1) is formed
as a by-product.

4
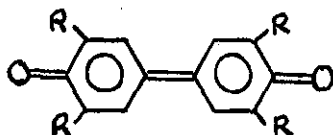
Fig. 2.2.1 : 3,5,3'5'-tetramethyldiphenoquinone

This was the first reported synthesis of a high molecular weight aromatic polyether, and also represented a new type of polymerization reaction.

In general, when the substituents, R, are small, such as methyl, the polymer is preferentially formed. If one of the substituents is as large as t-butyl, or if both are as large as iso-propyl, then the diphenoquinone is preferentially formed.

The polymer obtained by the oxidative coupling of 2,6-dimethyl-phenol is now a commercial material and has been given the name PPO (General Electric Co.,) poly(phenylene oxide). A modified poly(Phenylene oxide) has the trademark Noryl (General Electric Co.,). Favourable properties of PPO are excellent electrical insulation, good mechanical properties at elevated temperatures, dimensional stability under conditions of high humidity and mechanical load, good chemical resistance and hydrolytic stability. Thus numerous applications are found for these polymers.

2.2.2 Azopolymers.

In 1966, Bach(8) reported the preparation of linear polymers incorporating the azo linkage from the catalyzed oxidative coupling of primary aromatic diamines.

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$$n \; H_2N\text{-}Ar\text{-}NH_2 + n \; O_2 \xrightarrow{\;Cu^+/amine\;} (\text{-}Ar\text{-}N\text{=}N\text{-})_n + 2n \; H_2O \qquad (2.2.2)$$
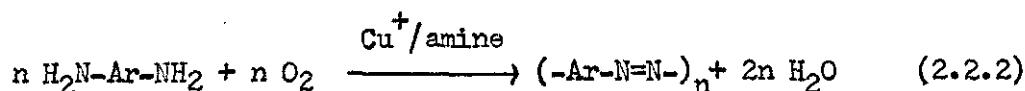
This was similar to the work of Kinoshita (9) where aniline was oxidized to azobenzene under similar reaction conditions.

All azopolymers are coloured owing to the presence of the strongly chromophoric azo group. The colour of the polymers ranges from yellow with isolated azo groups, to black, for polymers with a fully conjugated chain. They are reasonably stable to temperatures of more than $300^{\circ}C$ in air. The polymer fibres show a fair retention of tensile properties at temperatures up to about $400^{\circ}C$ and also show a comparatively strong resistance to degradation by light (10). Certain azopolymers are useful in the preparation of fibres, filaments, films and other shaped articles for use in thermally resistant applications and other textile end uses. They also may be used to prepare semi-conducting or photochromic materials and related products (11).

2.2.3 Polydisulphides

In 1966, Hay filed a patent (6) describing the oxidative coupling of dithiols to form poly(disulphides).

$$n \; HS\text{-}R\text{-}SH \xrightarrow[Cu^+/amine]{n/2 \; O_2} (\text{-}S\text{-}R\text{-}S\text{-})_n + n \; H_2O \qquad (2.2.3)$$
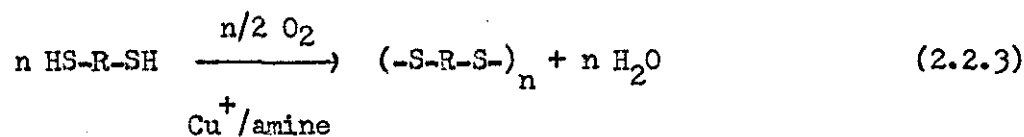
(R = alkyl or aryl group)

These polymers were fusible and produced tough , transparent films. When the monomer contains three or more thiol groups, the product is a three-dimensional cross-linked, insoluble, infusible polymer.

2.2.4 Poly(acetylenes).

In 1960, Hay reported (5) the oxidative coupling of a diacetylene to form poly(acetylene).

$$HC\equiv C-\bigcirc-C\equiv CH \ + \ \frac{n}{2}O_2 \ \xrightarrow{CuCl/py} \ \left[\bigcirc-C\equiv C-C\equiv C-\right]_n \ + \ nH_2O$$

$$(2.2.4)$$
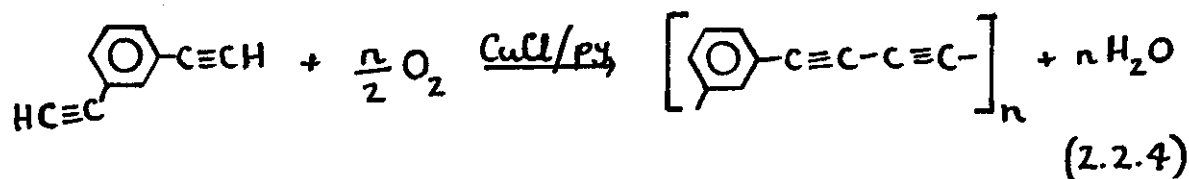
Light yellow films of the polymer, which were tough and flexible, could be cast from nitrobenzene at 160°C.

2.2.5 Poly(indigo) Polymers.

In 1966, Bach (12) reported the formation of poly(indigo) polymers, prepared by an oxidative coupling method. However, these polymers were prepared under different conditions, namely by using molecular oxygen and a suitable solvent such as dimethylacetamide, hexamethyl phosphortriamide or water. No catalyst was necessary. All poly(indigo) polymers are black infusible materials. They show semi-conducting properties and have a relatively high degree of thermal stability.

2.3 A study of the calaysts used.

The general method of preparation of the catalyst solution has been to dissolve the copper salt, usually copper (I) chloride in an inert solvent containing the desired ligand (3). If it is desirable, the same solvent can be used both as ligand and solvent for the reaction (10). Hay et al. (7), in the discovery of the oxidative polymerization of 2,6-dimethylphenol, dissolved copper (I) chloride in nitrobenzene containing pyridine as the ligand. The resulting solution was oxidized by molecular oxygen to give a green copper (II) complex, which was the catalyst used in the polymerization reactions.

Terent'ev and Mogilyanskii (13) reported that the two compounds $Cu_2Cl_2 \cdot 4py$ and $Cu_2Cl_2 \cdot 6py$ had been previously isolated by Lang. They reported the isolation of the second compound after dissolution of copper (I) chloride in pyridine in a sealed ampoule with cooling of the solution.

Finkbeiner et al. (3) found that $\frac{1}{4}$ mole of oxygen was consumed per mole of copper (I) salt in the initial oxidation of the copper (I) complex. This finding was confirmed by Price and Nakaoka (14) and Tsuchida et al. (15). Finkbeiner et al. (3) proposed that the equations shown below represented the oxidation of copper (I) chloride in pyridine. Equation 2.3.1 applies when water is absent and equation 2.3.2 applies when water is present.

$$4 \text{ CuCl} + O_2 \xrightarrow{C_6H_6/py} 2 \text{ } (CuCl_2) \cdot 2 \text{ CuO} \cdot n \text{ py} \qquad (2.3.1)$$

$$4 \text{ CuCl} + O_2 \xrightarrow[H_2O]{C_6H_6/py} 2 \text{ } (CuCl_2)_2 \cdot 2 \text{ Cu(OH)}_2 \cdot n \text{ py} \qquad (2.3.2)$$
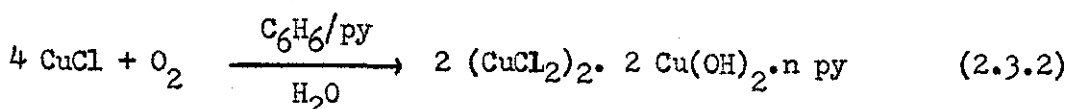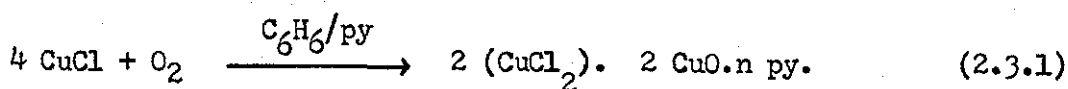
Tsuchida et al. (15) reported that the oxidation of the cuprous-amine complex by oxygen showed that the rate of oxidation was proportional to the copper (I) chloride concentration. From the results they calculated the value of the rate constant, K_0.

The copper (II) complex is the active catalyst, oxidizing the monomer whilst being itself reduced to the copper (I) complex. The function of the oxygen is to reoxidize the copper (I) complex to the copper (II) complex. A simplified reaction scheme for the catalytic reaction is shown below.

$$\text{Cu (I) complex} + O_2 \xrightarrow{K_0} \text{Cu (II) complex} \qquad (2.3.3)$$

$$Cu(II) \text{ complex} + \underset{(monomer)}{\text{substrate}} \longrightarrow Cu(I) \text{ complex} + \underset{\text{substrate}}{\text{"oxidized}}$$
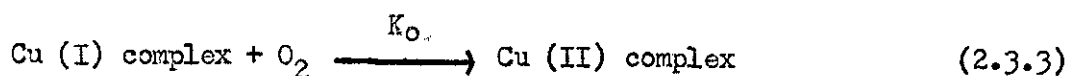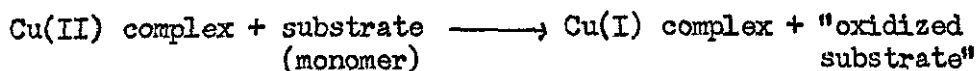
$$(2.3.4)$$

Thus 2,6-dimethylphenol can be completely oxidized when an equivalent amount of the copper (II) chloride pyridine catalyst is used in the absence of oxygen (3). Also it was shown that the use of an equivalent amount of the copper (II) compound was indistinguishable from the catalytic oxidation in terms of the products obtained. Kinoshita (9), in studying the oxidative coupling of aniline, reported that the product of cuprous chloride oxidation in pyridine would oxidize aniline to azobenzene in the absence of oxygen.

2.3.1 Effect of Ligand Ratio

In the polymerization of 2,6-dimethylphenol, the relative yield of the two products polyphenylene oxide and diphenoquinone was dependent upon the ligand (pyridine) to copper ratio, the diphenoquinone formation being favoured by a low ligand: Cu ratio.

Endres (16) suggested two possible mechanistic interpretations:-

(a) A single copper pyridine complex was used for both types of coupling, its concentration increasing with either copper or pyridine concentration; the molecularity of the rate determining step with respect to the complex was greater for C - O coupling (polymer formation) than for C - C coupling (diphenoquinone formation).

(b) Several distinct copper pyridine complexes in equilibrium, their relative concentrations depending on the stoichiometric concentrations of copper and pyridine. One of these complexes may

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be specific for C-O coupling while another is specific for C-C coupling.

In a later paper (17) by the same workers, only the latter mechanism was proposed. Investigation of the near infrared spectra of the compounds formed when copper (I) chloride was oxidized in o-dichlorobenzene at various pyridine: Cu ratios seemed to confirm the existence of two different complexes (3).

2.3.2 Copper (I) Chloride Pyridine/Methanol Catalysts

When copper (I) chloride was oxidized in a methanol/pyridine mixture, a deep green crystalline material was precipitated (3); this compound was found to have the empirical formula pyCuOCH$_3$Cl (equation 2.3.5). Copper (I) chloride oxidized in methanol in the absence of pyridine gave a pale-yellow product with the empirical formula CuOCH$_3$Cl (equation 2.3.6).

$$Cu(I)Cl + MEOH + py \xrightarrow{O_2} pyCuOCH_3Cl \qquad (2.3.5)$$

$$Cu(I)Cl + MeOH \xrightarrow{O_2} CuOCH_3Cl \qquad (2.3.6)$$
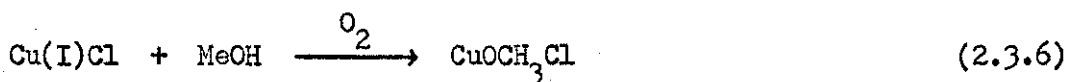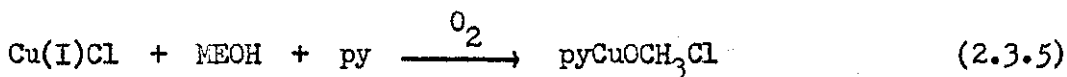
Both of these materials, pyCuOCH$_3$Cl and CuOCH$_3$Cl, were reported (3) to be at least as active as copper (I) chloride in the oxidation of 2,6-dimethylphenol when used in equivalent amounts based on the copper content. Like the product obtained when copper (I) chloride was oxidized in pyridine, the compound pyCuOCH$_3$Cl showed the same trend in relative yields of products when the ligand: Cu ratio was varied. However, no mention was made concerning the selectivity of the reaction when CuOCH$_3$Cl was used as the catalyst, nor has any reaction mechanism been reported for oxidative coupling reactions using this catalyst. These two compounds have been prepared

by a number of metathesis reactions in addition to the preparation by
the oxidation of copper (I) chloride. A schematic representation
of these metathesis reactions was given by Finkbeiner et al (3). All
attempts to determine the molecular weight of $pyCuOCH_3Cl$ were
unsucessful since the compound was either insoluble or reacted with
the solvent used.

2.3.3 Structure of the Copper Catalysts

On the basis of the means of preparation, Finkbeiner et al.
believed that the structure of the copper chloride pyridine/methanol
catalyst was the one shown in Fig. 2.3.1
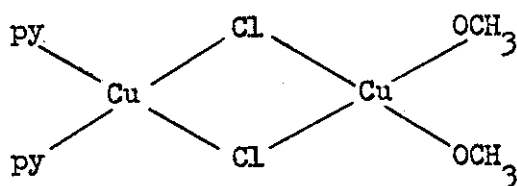
Fig. 2.3.1. Structure of $pyCuOCH_3Cl$

They postulated that at low ligand: Cu ratios (about 1:1)
copper (I) chloride is oxidized to $pyCuOCH_3Cl$, which at higher
ligand: Cu ratios reacts with excess pyridine to form a compound
$py_2CuClOCH_3$.

$$4\ CuCl + O_2 + 2CH_3OH + 4\ py \longrightarrow 2(pyCuOCH_3Cl)_2 + 2\ H_2O \qquad (2.3.7)$$

$$pyCuOCH_3Cl + ROH \longrightarrow pyCuClOR \longrightarrow diphenoquinone \quad (2.3.8)$$

(where R = 2,6-dimethylphenyl)

High ligand: Cu ratio:-

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(2.3.10)
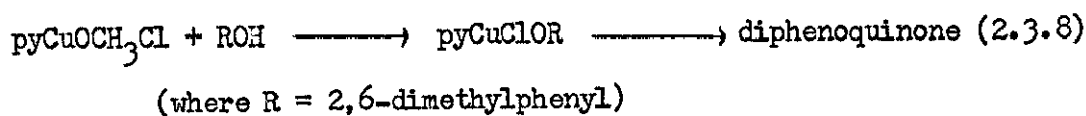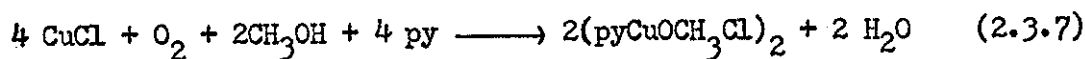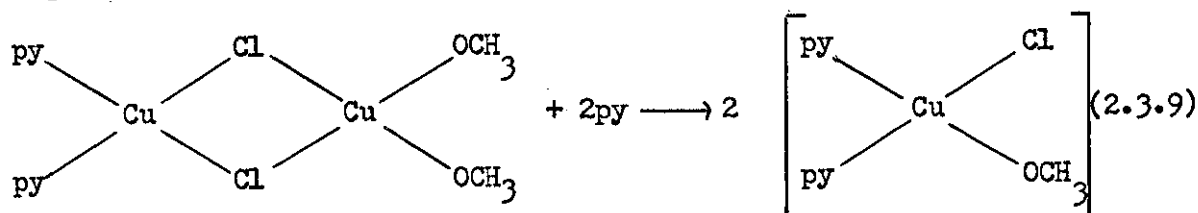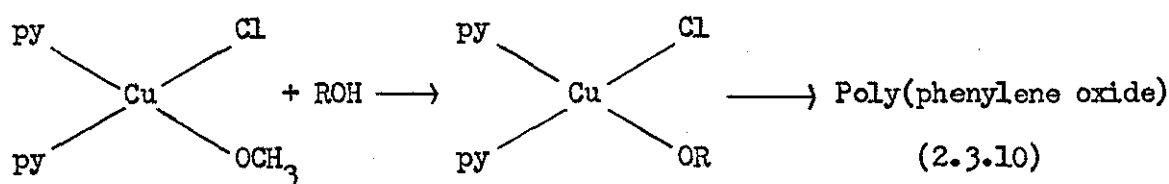
Attempts at replacing the methoxy group in pyCuOCH$_3$Cl with alkoxy groups from ethanol or 2-propanol gave a brown crystalline material with the empirical formula py$_4$Cu$_4$Cl$_6$O; this compound had a much reduced catalytic activity in comparison with pyCuOCH$_3$Cl. Attempts at replacing the methoxy group in PyCuOCH$_3$Cl with aryloxy ions led either to no reaction or oxidation of the aryloxy group. Blanchard et al. (18) were unsuccessful in their attempted preparation of compounds of the type shown in Fig 2.3.2.

Fig. 2.3.2 Structure of the compound Blanchard et al. attempted to prepare.

Their conclusion was that these compounds were extremely labile, unstable intermediates.

Finkbeiner et al. (3) suggested that when copper (I) chloride is oxidized in the absence of methanol, the methoxy group would be replaced by hydroxide or oxide. These structures can be visualized for the case of a hydroxide group (A and B in Fig. 2.3.3), but the substitution of an oxide group must bring about a change in configuration.
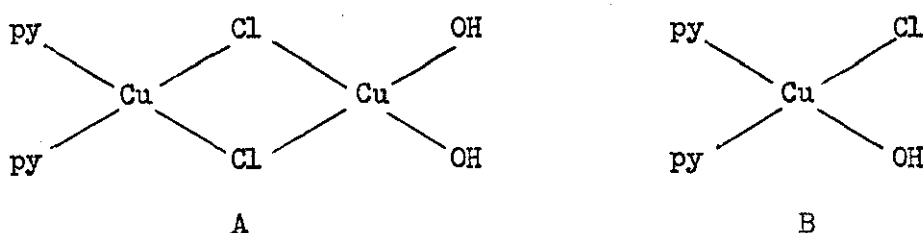
Fig. 2.3.3 Possible structures of the copper (I) chloride pyridine complex.

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At low ligand: Cu ratios, the structure A could conceivably be transformed into a structure such as C (Fig. 2.3.4),

$$py \diagdown \quad \diagup Cl \diagdown$$
$$Cu \qquad Cu \quad ≡ \quad 0$$
$$py \diagup \quad \diagdown Cl \diagup$$
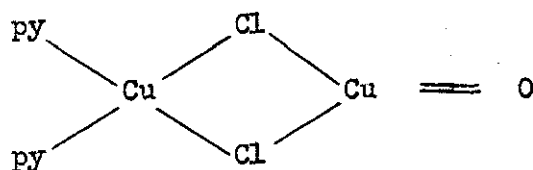
Fig. 2.3.4. Possible structure of the copper (I)
chloride pyridine complex.

but at higher ligand: Cu ratios, the structure B must be drastically altered to incorporate an oxide group whilst still retaining the same py : Cu : Cl ratio.

Water is a product of all oxidative coupling reactions, and so after the first few percent of reaction, there would be hydroxyl groups available for the formation of the structures A and B. However, even before the start of the reaction, there would probably be an appreciable concentration of hydroxyl groups present, unless great care had been taken in drying the reactants to produce anhydrous conditions.

Price and Nakaoka (14) suggested that the structure shown in Fig. 2.3.5 was the active catalyst produced from Copper (I) chloride and pyridine.

$$HO \diagdown \quad \diagup Cl \diagdown \quad \diagup py_2$$
$$Cu(II) \qquad Cu(II)$$
$$py_2 \diagup \quad \diagdown Cl \diagup \quad \diagdown OH$$
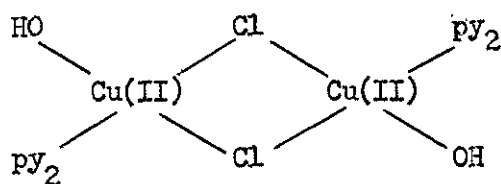
Fig. 2.3.5 Structure of the copper (I) chloride
pyridine catalyst, suggested by Price and Nakaoka.

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This structure would be formed as follows:-

$$
\begin{array}{c}
\text{H}_2\text{O} \diagdown \quad \diagup \text{Cl} \diagdown \quad \diagup \text{py}_2 \\
\qquad \text{Cu(I)} \quad \text{Cu(I)} \qquad + \text{O}_2 \longrightarrow \\
\text{py}_2 \diagup \quad \diagdown \text{Cl} \diagdown \quad \diagdown \text{H}_2\text{O}
\end{array}
\qquad
\begin{array}{c}
\text{H}_2\text{O} \diagdown \quad \diagup \text{Cl} \diagdown \qquad \diagup \text{py}_2 \\
\qquad \text{Cu(II)} \diagdown_{\text{O}}^{\text{O}} \text{Cu(II)} \\
\text{py}_2 \diagup \qquad \diagdown \text{Cl} \diagdown \text{H}_2\text{O}
\end{array}
\qquad (2.3.11)
$$

A B

$$
\text{A} + \text{B} \longrightarrow
\begin{array}{c}
\text{HO} \diagdown \quad \diagup \text{Cl} \diagdown \quad \diagup \text{py}_2 \\
\qquad \text{Cu(II)} \quad \text{Cu(II)} \\
\text{py}_2 \diagup \quad \diagdown \text{Cl} \diagup \quad \diagdown \text{OH}
\end{array}
+ 2\text{H}_2\text{O}
$$

$$(2.3.12)$$
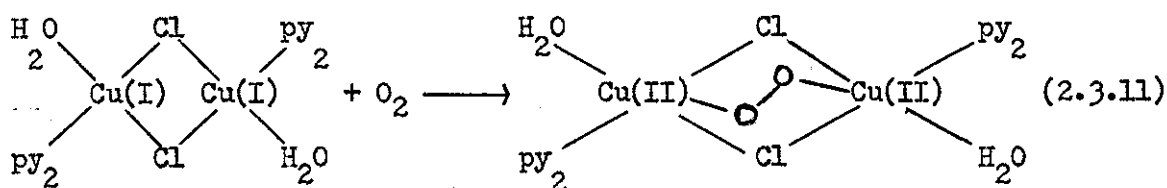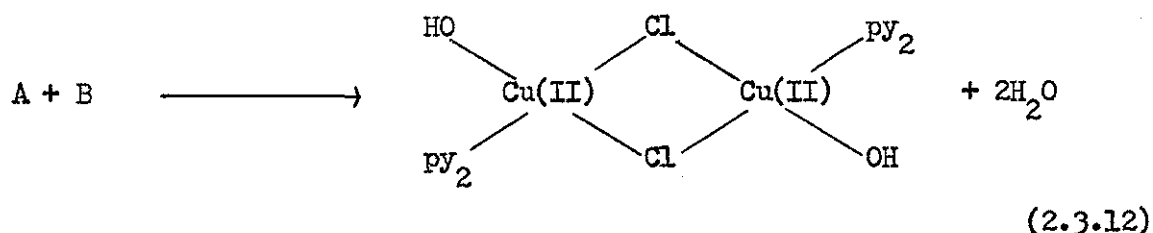
The suggestion that the oxidation of Cu(I) to Cu(II) involves direct interaction of two copper (I) atoms with a molecule of oxygen is supported by the kinetics of this process in melts (19) where the reaction rate is equal to $\text{K.A} \left[\text{Cu}^+\right]^2 \cdot \left[\text{O}_2\right]$ (K = kinetic rate constant and A = surface area). The data were interpreted as indicating a rate controlling process involving two copper (I) ions and oxygen in the surface of the melt, producing an intermediate "peroxide" structure. Price and Nakaoka (14) state that earlier suggestions of a "monomeric" copper catalyst (evidently py_2 Cu OH Cl or Py_2 Cu OCH_3 Cl) seemed difficult to reconcile with a rate determining step involving simultaneous oxidation by oxygen of two Cu(I) complexes to Cu(II) complexes; this would require a second order dependence on copper concentration as observed for copper (II) melts. One alternative would be a rate determining step involving oxygen converting Cu(I) to Cu(II) and O_2^{2-} (or Cu(II) and O_2^-), but they stated their preference for the idea of a dimeric catalyst species. Their postulated mechanisms concerning the influence of ligand ratio of relative yields of products will be dealt with in section 2.4.

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2.3.4 Effect of Various Ligands

This section describes the use of ligands, other than pyridine in the catalyst.

White and Klopfler (20), in their study of the polymerization of 2,6-diphenylphenol, found that monoamines, whether primary, secondary or tertiary, when used as catalyst ligands polymerized the monomer to polymers with moderately high molecular weights. Bio-tertiary amines did not produce high polymers unless the two nitrogen atoms were separated by either two or three carbon atoms. In cases where the number of carbon atoms linking the nitrogen atoms was only one or was four or more, very low polymers resulted. They put forward the possible explanation that amines which cannot form stable five or six-membered cyclic chelates with the copper tend to form polymeric compounds which are much less stable than the cyclic species and that the complexes precipitate from solution. Ethylene diamine and its N,N'-diethyl derivative were completely unreactive for polymerization, although the latter produced a relatively large amount of the diphenoquinone. A bis-secondary amine, N,N'-dimethyl-1,3-propane diamine formed a very reactive catalyst.

Hay reported (21) that in the oxidative coupling of acetylenes, the ligand N,N,N', N'-tetramethylethylenediamine formed a catalyst of greater reactivity than did pyridine.

Bach and Black (10), in the polymerization of diamines, found that N,N-disubstituted amides such as dimethylacetamide (DMAc) or hexamethyl phosphortriamide yielded catalytically active complexes with copper (I) chloride. The catalytic activity of these compounds

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was less than that of the pyridine complex. They assigned the structure $(DMAc)_2 Cu(OH)Cl$ to the DMAc complex from similarity to the copper (I) chloride pyridine structure $py_2 Cu(OH)Cl$, postulated by Finkbeiner et al.(3).

2.3.5 Poisoning of the Copper(I) Chloride Pyridine Catalyst.

Endres et al (17) found that at low ligand: Cu ratios, water, which is one of the products of the reaction, has an auto-retardation effect; this could be eliminated by using a suitable drying agent such as magnesium sulphate. They observed that the separation of another liquid phase or solid copper salt accompanied auto-retardation. These effects were not seen at high ligand: Cu ratios. This auto-retardation effect by water was also reported by White and Klopfer (20).

Terent'ev and Mogilyanskii (13), in the oxidative coupling of amines, reported that the reaction did not occur in the presence of ammonia or when pyridine was acidified. Kinoshita (9) found that when equimolar potassium hydroxide in methanol was added to a copper (I) chloride pyridine complex, its catalytic activity was lost. Price and Nakaoka (14) found that the addition of acetic acid, hydrogen bromide or hydrochloric acid either almost or completely stopped the oxidative coupling reaction. In the oxidative coupling of benzil using a copper (I) chloride pyridine complex, Kinoshita (9) reported that the reaction terminated after a certain amount of benzil had been oxidized. He deduced that the product, benzoic acid deactivated the catalyst.

Blanchard et al. (18) reported that when the compound $XC_6H_4(CH_3)_2OH$ was polymerized (equation 2.3.13) using a copper (I) chloride pyridine complex, the reduced complex (or spent catalyst)

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had the formula py_2CuClX and was inactive as a catalyst; thus the reaction stopped after all the catalyst had been used once.

$$X-\text{(ring)}\underset{Me}{\overset{Me}{-}}OH \xrightarrow[O_2]{CuCl/py} \left[\text{(ring)}\underset{Me}{\overset{Me}{-}}O-\right]_n + py_2CuClX \quad (2.3.13)$$
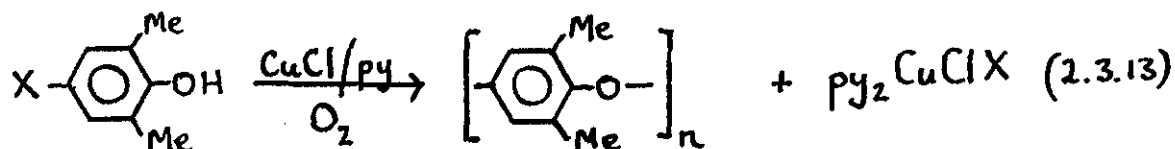
A similar effect was reported by Price and Nakaoka (14), who, when they added bromophenol to their reaction mixture, found that the reaction rate soon decreased. They suggested that this was due to the release of hydrogen bromide, which they showed to be a strong inhibitor. The two explanations may be equivalent since the hydrogen bromide may have formed the inactive complex $py_2CuClBr$.

2.3.6 Use of Other Salts in the Preparation of Catalysts

Terent'ev and Mogilyanskii (13) reported that the salts: $Fe\ Cl_2$; $Fe\ Cl_3$; $Co\ Cl_2$; $Cu\ Cl_2$; $Cu_2\ Br_2$ and $Cu_2\ I_2$ with pyridine gave no reaction in the oxidative coupling of amines. Kinoshita (22) found that a cuprous acetate pyridine complex had no catalytic activity in the oxidative coupling of aniline. Finkbeiner et al (3) found that the compounds: $Cu\ Cl_2$; $py_2\ Cu\ Cl_2$; $Cu(OH)_2$ and py $Cu(OR)_2$ (where R = 2,4,6-trichlorophenyl or 2,6-dichlorophenyl) with pyridine gave either no reaction or a very slow reaction in the oxidative coupling of phenols. White and Klopfler (20) reported that cuprous bromide as well as cuprous chloride produced high polymers from 2,6-diphenyl-phenol. Hay (23) reported that other copper (I) salts (Bromide and acetate) could be used in the polymerization of 2,6-dimethylphenol and that cuprous acetate was an active catalyst in the polymerization

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of acetylenes (21). In their work on the oxidative coupling of
2,6-dimethylphenol, Price and Nakaoka (14) reported that copper (I)
chloride was much superior as a catalyst to cupric acetate (15% of
the $Cu_2 Cl_2$ rate) or cuprous bromide (3% of the $Cu_2 Cl_2$ rate).
Cuprous cyanide, copper powder and cupric chloride, bromide, oxide
and carbonate were ineffective as catalysts.

<p style="text-align:center"><u>2.4 Kinetics and Mechanisms of the Oxidative
Coupling of Phenols</u></p>

In the oxidative coupling of 2,6-disubstituted phenols,
n/2 moles of oxygen are consumed by n moles of the phenol (equation
2.4.1).
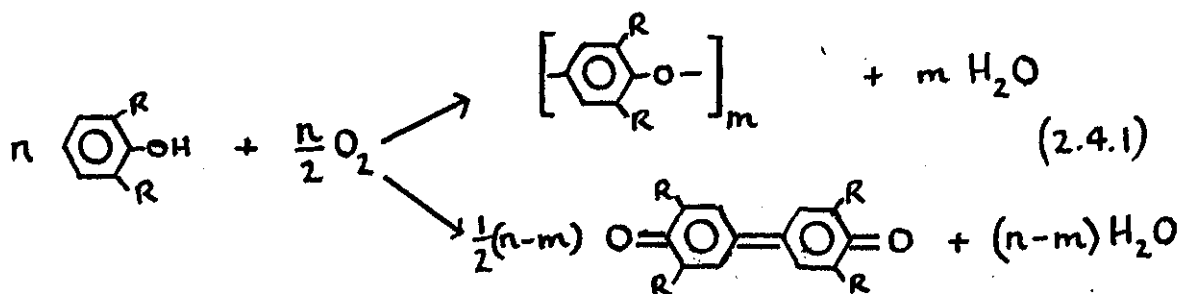
Thus, the rate and extent of the reaction at any time, t, can
conveniently be calculated from a series of readings, taken during
the course of the reaction, of the total volume of oxygen consumed.

Finkbeiner et al (24) produced the first paper describing the
mechanisms and kinetics of the oxidative coupling of 2,6-disubstituted
phenols using a copper (I) chloride pyridine complex as catalyst.
For a mixed solvent of 80% benzene to 20% pyridine, their graph of
oxygen consumption against time showed an induction period followed
by rapid oxygen uptake to approximately the equivalence point, where-
upon the oxygen consumption essentially ceased. At constant catalyst

concentration this induction period became progressively shorter as the monomer (2,6-dimethylphenol) concentration was increased, until it finally disappeared.

A simplified reaction mechanism postulated by some authors (3,15,25) for the oxidation of 2,6-dimethylphenol is shown in scheme 2.1.

Coordination of the monomer $\qquad$ Cu(II)complex + monomer species $\xrightarrow{K_1}$ Cu(II)—monomer species $\qquad$ 1.

Electron transfer and dissociation $\qquad$ Cu(II)—monomer species $\xrightarrow{K_2}$ Cu(I)complex + monomer radical $\qquad$ 2.

Reoxidation of the catalyst $\qquad$ Cu(I)complex $\xrightarrow{K_0}$ Cu(II)complex $\qquad$ 3.

polymer growth $\longrightarrow$ monomer radicals $\longrightarrow$ polymer $\qquad$ 4.
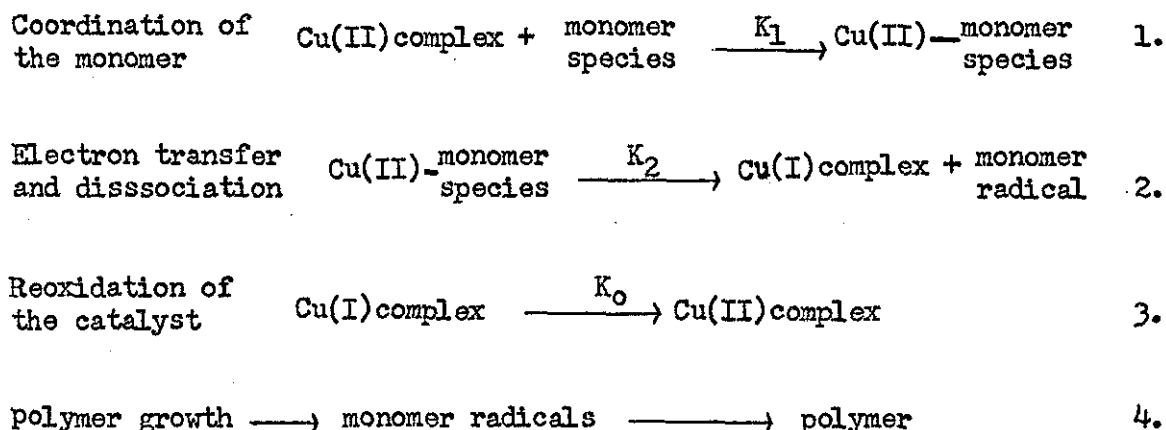
Scheme 2.1   General reaction mechanism for the
oxidative coupling of phenols.

To explain some of their results, Tsuchida et al (15) separated step 2 into two steps; these were the electron transfer step, K_e (reduction of Cu(II) to Cu(I) and oxidation of the coordinated monomer species), and the dissociation step, K_d (dissociation into the Cu(I) complex and monomer radical). Also they proposed that step 1, was a reversible reaction. They showed that the rate of oxygen consumption was equal to the rate of dissociation.

2.4.1 Effect of Ligand Ratio.

In their work on the kinetics of the oxidative coupling of 2,6-dimethylphenol using a copper(I) chloride pyridine complex,

Endres et al (17) studied the effect of varying the ligand (pyridine):
Cu ratio over the range 0.67:1 to 2420:1. They did this by varying
the pyridine concentration at constant copper salt and monomer
concentrations. The lower limit represented the minimum ligand:
Cu ratio required for complete oxidation of copper (I) chloride in
an inert solvent (O-dichlorbenzene), whilst the upper limit corresponded
to the copper salt in pure pyridine.

Effect of Ligand : Cu Ratio on Relative Yields of Products.

The effect of the ligand: Cu ratio on the relative yields of
products (17) was as shown in Fig. 2.4.1. At the lowest ligand: Cu
ratio (0.67:1), a rather slow reaction led predominantly to C - C
coupling (diphenoquinone). Increasing the ligand:Cu ratio favoured
C - O coupling (polyphenylene oxide) formation at the expense of C - C
coupling. Tsuchida et al.(15) repeated this work under similar
conditions and found the same type of behaviour. Endres et al. (17)
found that as the ligand: Cu ratio was increased, the intrinsic
viscosity (and thus the molecular weight) of the polymer increased.

Effect of Ligand: Cu Ratio on the Reaction Rates.

The effect of the ligand: Cu ratio on the overall rate as measured
by oxygen consumption, was as shown in Fig. 2.4.2. The overall rate
rose to a maximum in the region of ligand: Cu ratio of 100:1, and
then decreased as pyridine became the major part of the reaction mixture.
Tsuchida et al.(15) again found the same type of behaviour in their
work with a maximum rate at a ligand:Cu ratio of 100:1. In a similar
study of the effect of the ligand:Cu ratio using copper(I) chloride,
2,6-dimethylphenol and nitrobenzene as the inert solvent, Price and
Nakaoka (14) reported a maximum rate of oxygen absorption over the ligand:
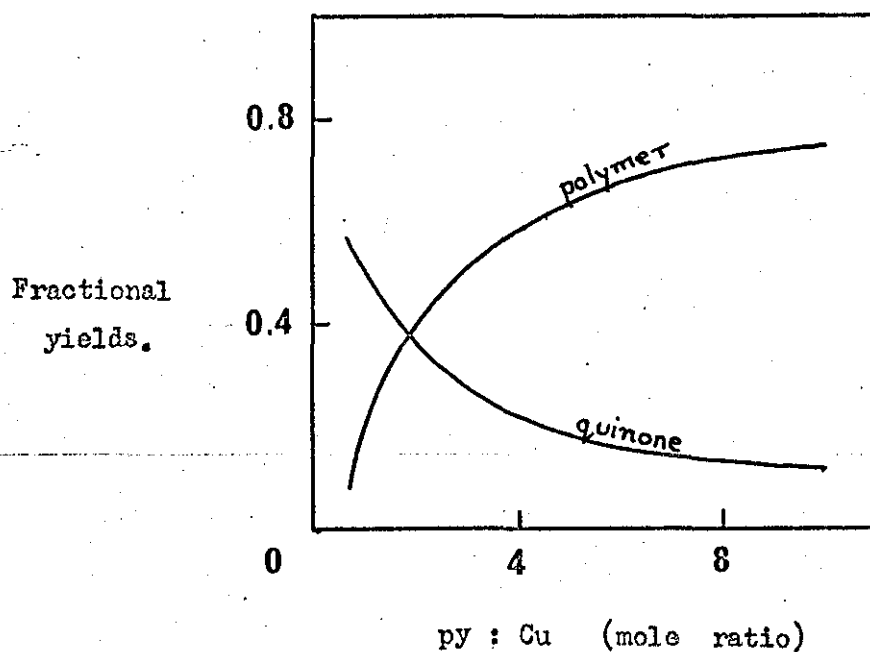
Fig. 2 .4.1. Effect of ligand : Cu ratio
on the yields of products.
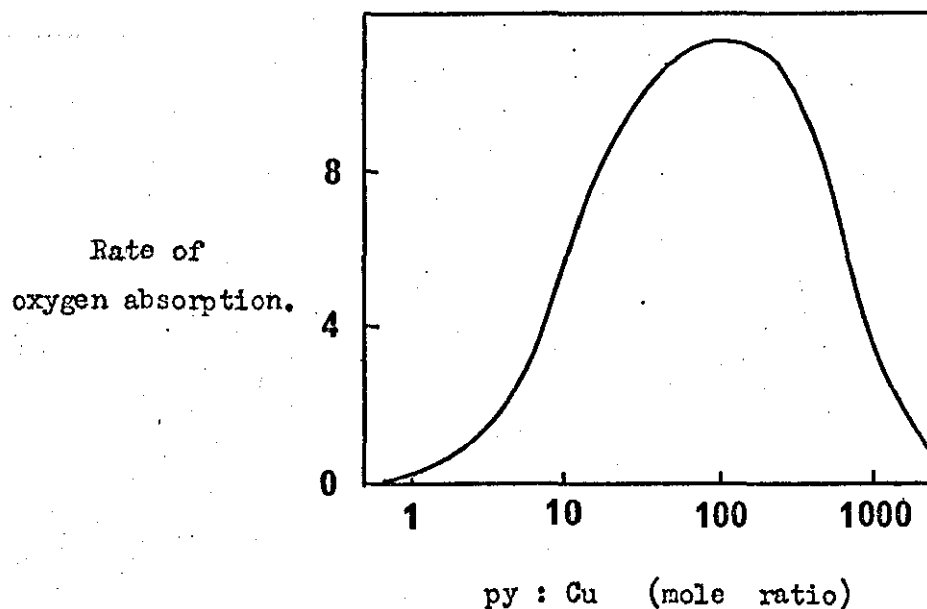
Fig. 2.4.2. Effect of the ligand : Cu
ratio on the overall rate.

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Cu ratio range 15:1 to 30:1. They made no mention of the relative yields of the two products.

At a constant ligand: Cu ratio of 1:1 or 2:1 and a constant monomer concentration, Endres et al (17) reported that higher catalyst concentrations increased the overall rates and favoured C - O coupling. Varying the initial monomer concentration, at a constant catalyst concentration and a constant ligand: Cu ratio of 3:1 had little effect on either the rate of oxygen consumption or the relative yields of products.

Tsuchida et al (15) reported that for the oxidation of the copper(I) chloride complex alone, the value of K_o (the kinetic rate constant) reached a maximum at a ligand:Cu ratio of 3:1. They suggested that this was the result of two opposing effects:-

(a) pyridine ligands promoting the rate of the oxidation reaction by raising the oxidation potential of the copper ion, and

(b) excess pyridine interfering with the attack of the oxygen molecule on the copper(I) ion by filling up the coordination sites on the copper(I) ion and thus lowering the oxidation rate.

Effect of Temperature.

Endres et al. (17) found that increasing the reaction temperature favoured C - C coupling at the expense of C - O coupling. This is in contrast to the work by Hay (26) who used the ligand N,N,N',N'-tetramethylethylenediamine together with copper(I) chloride as a catalyst at a ligand: Cu ratio of 2:1 in the oxidative coupling of 2,6-diphenyl-phenol. He reported that increasing the reaction temperature favoured polymer formation (C-O coupling). No explanation was given in either paper for these effects.

Endres et al (17) gave no explanation for the observed effects of ligand: Cu ratios upon the kinetics. The explanations given by Tsuchida et al (15) and Price and Nakaoka (14) are given in section 2.4.7.

Unless otherwise stated, the kinetic studies considered in the rest of this section 2.4 apply to regions of high ligand: Cu ratio, where the amount of diphenoquinone formed is negligible.

2.4.2 Effect of the Monomer on the Kinetics.

Effect of Monomer Concentration.

Brooks (25) studied the heterogeneous polymerization of 2,6-dimethylphenol using a copper(I) chloride pyridine complex, where the polymer was precipitated out of solution during the course of the reaction. He reported that both in pure pyridine and in a mixed solvent (20% pyridine to 80% methanol), the reaction was apparently zero order with respect to the monomer. Price and Nakaoka (14) established conditions within which oxygen diffusion was not the rate controlling step for their study of the kinetics of the oxidative coupling of 2,6-dimethylphenol. They found that the kinetics were independent of monomer concentration. However, both Brooks and Price and Nakaoka appear to have reached this conclusion because for any one particular monomer concentration the graph of oxygen consumption vs time was virtually a straight line for over 90% of the reaction. Tsuchida et al. (15) also obtained this straight line relationship for any one particular reaction, but for a series of reactions at varying initial monomer concentrations, their plot of reaction rate against initial monomer concentration was as shown in Fig. 2.4.3.
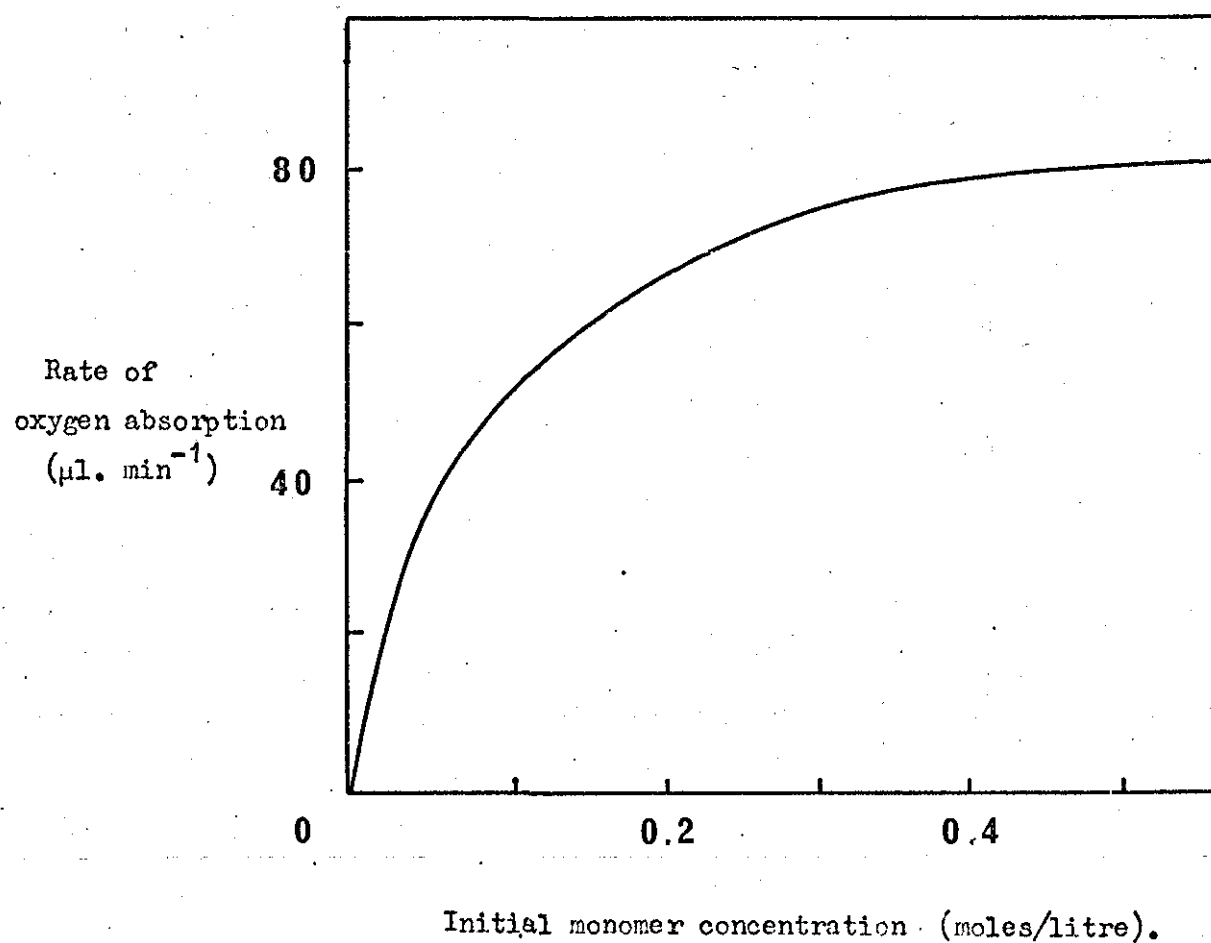
Fig. 2.4.3. Reaction rate vs initial monomer
concentration (results of Tsuchida et. al).

Fig. 2.4.3. is a typical graph for enzyme reactions. This result is discussed further in section 2.4.7.

Effect of Monomer Structure.

Hay (23) reported that no appreciable reaction occurred in the attempted oxidation of 2,6-dichlorophenol or 2,6-dinitrophenol, using a copper (I) chloride pyridine catalyst. This, he reported, was not surprising since the redox potential of these phenols was considerably higher because of electronegative substituents. White and Klopfler (20) found that 2,6-diphenylphenol had a lower reactivity than 2,5-dimethyl-phenol in oxidative coupling reactions. They suggested that this was due to two reasons, (a) the increased steric hindrance of the phenyl groups adjacent to the hydroxyl groups and (b) the higher oxidation potential existing when there are no electron-donating o-methyl groups. Price and Nakaoka (14) reported on the oxidative coupling of a number of analogues of 2,6-dimethylphenol. These results again indicated the importance of electron-donor groups increasing the rates of oxygen consumption and of electron-withdrawing groups in retarding the rate. A substituent in the 2 position was found to have more effect on the rate than one in the 4 position.

Oxidation of Phenol.

Hay (23) reported that the oxidation of phenol itself by a copper chloride pyridine catalyst produced only a complex tarry residue. He stated that the phenoxy radical was a resonance hybrid of the following structures:-

$$\oplus \bigcirc\!-\!O^{\ominus} \longleftrightarrow \cdot\bigcirc\!=\!O \longleftrightarrow \bigcirc\!=\!O \longleftrightarrow \bigcirc\!-\!O\cdot \qquad (2.4.2)$$
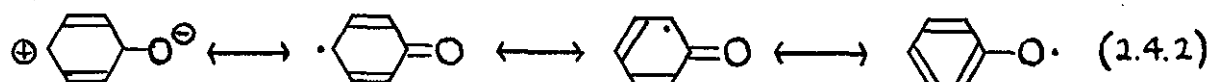
C - C coupling of the radicals could occur at the 0- and p- positions as well as C - O coupling. Therefore it is not surprising that the oxidation of phenol yielded only a complex mixture.

2.4.3 Effect of the Catalyst on the Kinetics.

Finkbeiner et al (24) reported an order of dependence of 2.67 upon the catalyst concentration. This was a somewhat unusual value and is contrary to the value of 1.0 reported by both Brooks (25) and Price and Nakaoka (14). Brooks found the reaction to be first order with respect to the copper (I) chloride concentration up to a certain catalyst concentration. Above this concentration, the rate of polymerization was virtually independent of catalyst concentration in the pyridine solvent system and in the mixed solvent system the rate of polymerization tailed off above a certain concentration. In these regions, he suggested that the reaction rates were probably controlled or modified by mass transfer of oxygen from the gas phase to the liquid phase.

Effect of Catalyst Ligands.

Endres et al (17) found that a copper (I) chloride complex with ligands of increased steric hindrance decreased the rate of oxygen absorption both at high and low ligand: Cu ratios; at low ligand: Cu ratios, the fractional yield of the C - C coupled product was increased.

From their reaction mechanism, Tsuchida et al (15) derived the following expression:-

$$v_d \quad \propto \quad K_1' \times K_e \qquad\qquad (2.4.3)$$

(rate of polymerization)

where $K_1' = K_1/K_{-1}$, the complex formation constant between Cu(II) amine and monomer.

K_e = kinetic rate constant for the electron transfer step.

Thus ligands such as pyridine, which have low steric hindrance (i.e. high K_1') and promote electron transfer i.e. high K_e, (because of the conjugated system giving good electron-accepting properties) are more effective as ligands than those, such as Bu_2NH, which have a high degree of steric hindrance (low K_1') and do not promote electron transfer (low K_e). For further information concerning other ligands which have been used, refer back to section 2.3.4.

2.4.4. Effect of Solvent on the Kinetics.

Endres et al.(17) conducted a series of experiments at a constant ligand: Cu ratio of 3:1 using the solvents benzene, chlorobenzene and o-dichlorobenzene, which has a range of dielectric constants 2.3 to 7.5. The results indicated that the dielectric constant of the solvent had very little or no effect on either the rate of reaction or the relative yields of products. However, the variation in the properties of the solvents was not very great. Price and Nakaoka (14) studied the effect of a number of solvents on the rates of oxidative coupling. The relative reactivities of the solvents were as shown below:-

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methanol = 2-propanol) dimethylformamide = bromobenzene)

1,4-dioxane = nitrobenzene) chloroform = benzyl alcohol)

dimethyl sulphoxide) pyridine.

Although the solvents methanol and 2-propanol gave the highest oxidative coupling rates, the resultant polymer was not very soluble in these media and precipitated out of solution before a very high molecular weight polymer was completed. Brooks (25) found that the rate of polymerization increased as the methanol fraction of the mixed solvent (pyridine/methanol) increased. Finkbeiner et al (24) also reported that the use of a pyridine/benzene solvent gave faster reaction rates than pure pyridine.

Tsuchida et al (15) proposed a theory to explain the solvent effect. During the electron transfer step, the extent of charge separation decreases, and thus a solvent such as pyridine which is more polar than an inert solvent such as o-dichlorobenzene would tend to stabilize the complex A (Fig. 2.4.4) and thus would decrease the value of K_e.

Fig. 2.4.4. Electron transfer step in oxidative
coupling reactions.

2.4.5 Effect of Oxygen Pressure on the Kinetics.

Finkbeiner et al (24) reported that a plot of log (reaction rate)

vs log (oxygen pressure) gave a straight line of slope 1.33 over a variation of oxygen partial pressure 300-760 mm. Hg. Price and Nakaoka (14) found that the reaction was first order with respect to the oxygen pressure over the range 0.5 to 1.5 atmospheres.

Tsuchida et al (15) found that a copper (I) chloride aliphatic amine catalyst gave no polymerization reaction in the absence of oxygen, whereas a copper (I) chloride pyridine catalyst did give a reaction. They also found that their experimentally determined K_2 values were larger than what would be expected from their K_o values (see scheme 2.1). Their explanation of these effects are given in section 2.4.7.

2.4.6   Other Kinetic Effects.

From a study of the effect of reaction temperature, Finkbeiner et al.(24) suggested that the reaction had a very low activation energy approximately 3-5 kcals/mole. They also reported that experimental work with 2,6-dimethyl-4-deuterophenol indicated that the loss of hydrogen in the 4 position was an easy reaction and not rate determining.

A phenomenon of the oxidative coupling of 2,6-dimethylphenol, which was reported only by Brooks (25), was the evolution of small amounts of gas at the initial mixing of the monomer and catalyst solutions. However, the method used by Brooks for measuring oxygen consumption ("frictionless piston" ; also upon mixing the reactants, there was no change in the closed volume of the apparatus) would be more sensitive for detecting this initial evolution of gas than the more conventional U-tube manometer used by other workers (14, 17). There seemed to be no direct relationship between the amounts of gas

evolved and the concentration of the reactants.

In experiments using a mixed solvent system, Brooks (25) reported that the precipitation of polymer from solution after about 10% reaction had no effect on the rate of oxygen absorption.

2.4.7 Postulated Mechanisms.

Endres' Mechanism (17).

The mechanism proposed by Endres et al. has previously been described in section 2.3.1., and is shown schematically in Scheme 2.2.

$$\text{Cu(II) L}_n \quad + \quad \text{L}_m \rightleftharpoons \text{Cu(II) L}_{n+m}$$

C - C coupling $\qquad\qquad$ C - O coupling
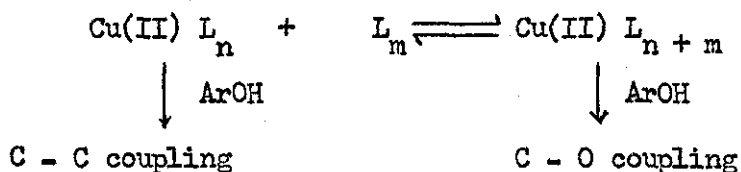
L = amine ligand, Ar = 2,6-disubstituted aryl group

m and n are integers $\geqslant$ 1

Scheme 2.2. Reaction mechanism proposed by Endres.

The other ligands involved in the complexes are omitted for the sake of clarity. This scheme accounts quantitatively for the observed effects of ligand ratio, catalyst concentration and steric hindrance in the ligand.

Finkbeiner's Mechanism.

Finkbeiner et al (3) postulated that in a copper(I) chloride pyridine/methanol system, the structure A (Fig. 2.4.5) led predominantly to C - C coupling and the structure B led predominantly to C - O coupling. (see section 2.3.2).

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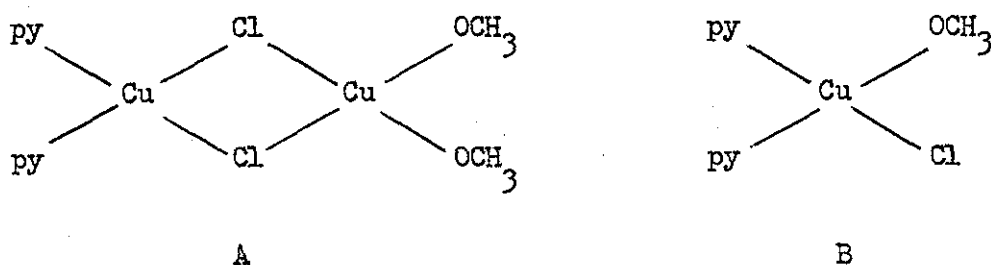
Fig. 2.4.5. Structure of the copper(I) chloride
pyridine complexes.

However, he did not explain why each structure should favour
the specific type of coupling.

Brook's Mechanism (25).

The reaction mechanism proposed by Brooks was for high pyridine:
Cu ratios (the region in which his experiments were conducted) where
the polymerization rates were simultaneously first order with respect
to copper(I) chloride concentration and zero order with respect to
monomer concentration. The following scheme was postulated:-

$$Cu(I) \text{ species} + \text{oxygen} \xrightarrow{K_1} Cu(II) \text{ species} \qquad 1.$$
$$\phantom{Cu(I) \text{ species}} (A) \qquad (B) \qquad\qquad (C)$$

$$Cu(II) \text{ species} + \text{polymerizable} \underset{K_3}{\overset{K_2}{\rightleftharpoons}} \text{complex} \qquad 2.$$
$$\phantom{Cu(II) \text{ species} +} \text{species}$$
$$(C) \qquad\qquad (D) \qquad\qquad (E)$$

$$\text{complex} \xrightarrow{K_4} \text{polymer} + Cu(I) \text{ species} \qquad 3.$$
$$(E) \qquad\qquad\qquad (F) \qquad\qquad (A)$$
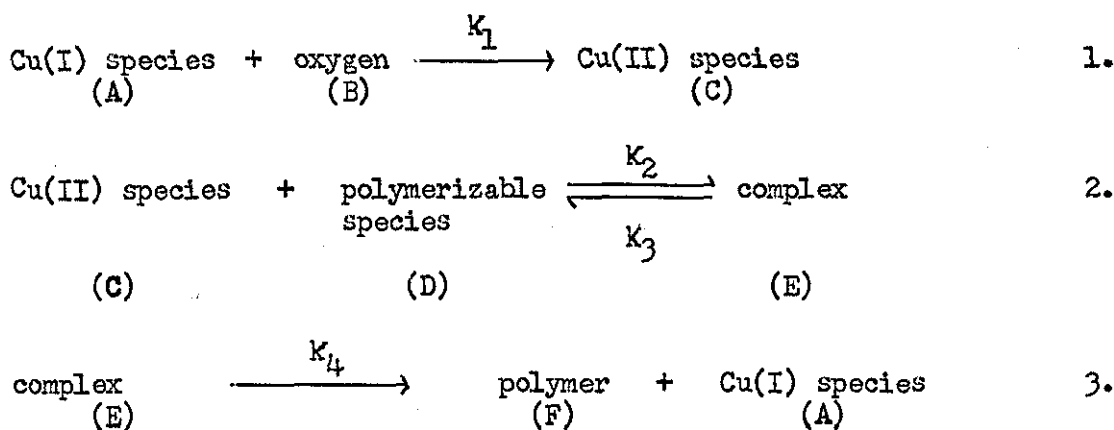
Scheme 2.3 Reaction mechanism proposed by Brooks.

The equilibrium of step 2 favoured E, thus making equation 3 the
rate determining step. Thus the rate of polymerization is given by

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equation 2.4.4.

Rate of polymerization $\quad \dfrac{- \, d \, [D]}{d \, t} = K_4 \, [A]_{t \, = \, 0}$ $\qquad$ (2.4.4)

where $[A]_{t \, = \, 0}$ is the initial concentration of copper (I) chloride.

This scheme accounts for the kinetics being first order with respect to the catalyst and zero order with respect to the monomer. Also from equation 2.4.4., one would expect the rate of polymerization to be zero order with respect to oxygen pressure, assuming conditions where the reaction rate was not mass transfer controlled. This, however, is not as was found by Finkbeiner et al.(24) and Price and Nakaoka (14), who, as previously reported (section 2.4.5) found the reaction rate to be of the order 1.33 and 1.0 respectively with respect to the oxygen pressure. Brooks did not study the effect of oxygen pressure on the kinetics. However, if it was assumed that step 1 (scheme 2.2) was the rate determining step and step 3 was a fast reaction, then most of the copper would be in the form of the Cu(I) species and would have a steady state concentration. This would give the following expression for the reaction rate:-

rate of polymerization $= K_1 \, [A] \, [B] = K_1 \, [Cu(I)] \, [O_2]$ (2.4.5)

This would account for kinetics of first order with respect to both catalyst concentration and oxygen pressure and zero order with respect to monomer concentration. Price and Nakaoka (14) showed that although the rate of polymerization was independent of monomer concentration, the rate did depend on the structure of the monomer. Thus in the above reaction mechanism, a monomer species needs to be coordinated to the copper (I) species, A, to be consistent with the

above experimental results.

Brooks (25) also reported the analogy between his oxidative coupling mechanism and enzyme reaction mechanisms.

Price and Nakaoka's Mechanism (14).

Price and Nakaoka suggested that the rate controlling step for oxidative coupling was the reaction of oxygen with a copper-phenol complex. This they deduced from their kinetics which showed that the rate of oxygen absorption was first order with respect to the oxygen pressure and catalyst concentration and independent of monomer concentration but dependent upon the structure of the monomer. For high ligand: Cu ratios they proposed the reaction mechanism given in Scheme 2.4. The slow step from C to D (also the rate controlling step), involving electron donation or transfer from Cu(I) to molecular oxygen, would be facilitated by enhanced electron availability at the Cu(I) in C. This would account for the favourable effect of electron-donor groups in the phenol. The increase in reaction rate arising from ortho substitution, they stated, may be due to steric hindrance which blocks excess coordination of bulkly solvent molecules at the Cu(I) in C, permitting more readily access for the small oxygen molecule. This scheme required that all the Cu(I) was rapidly and quantitatively converted to a form coordinated with phenol, C, so that the concentration of this species was dependent upon the concentration of the catalyst but not on the concentration of the phenol, provided that the concentration of phenol was large compared to the catalyst concentration.

Price and Nakaoka postulated that the phenomenon of a high ligand:

Scheme 2.4
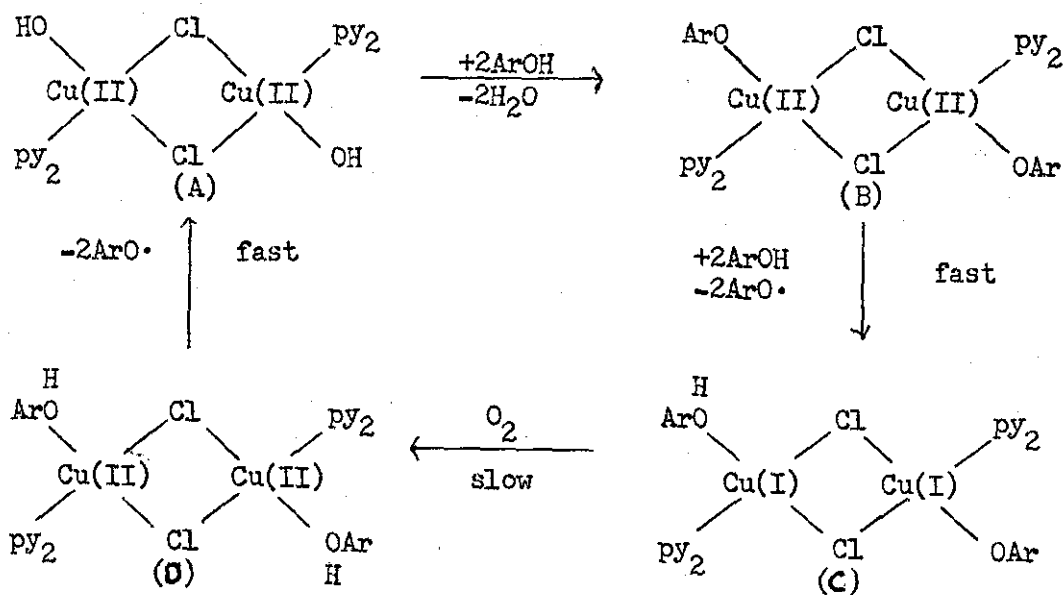
Reaction mechanism at high ligand : Cu ratios
(Price and Nakaoka)

Scheme 2.5
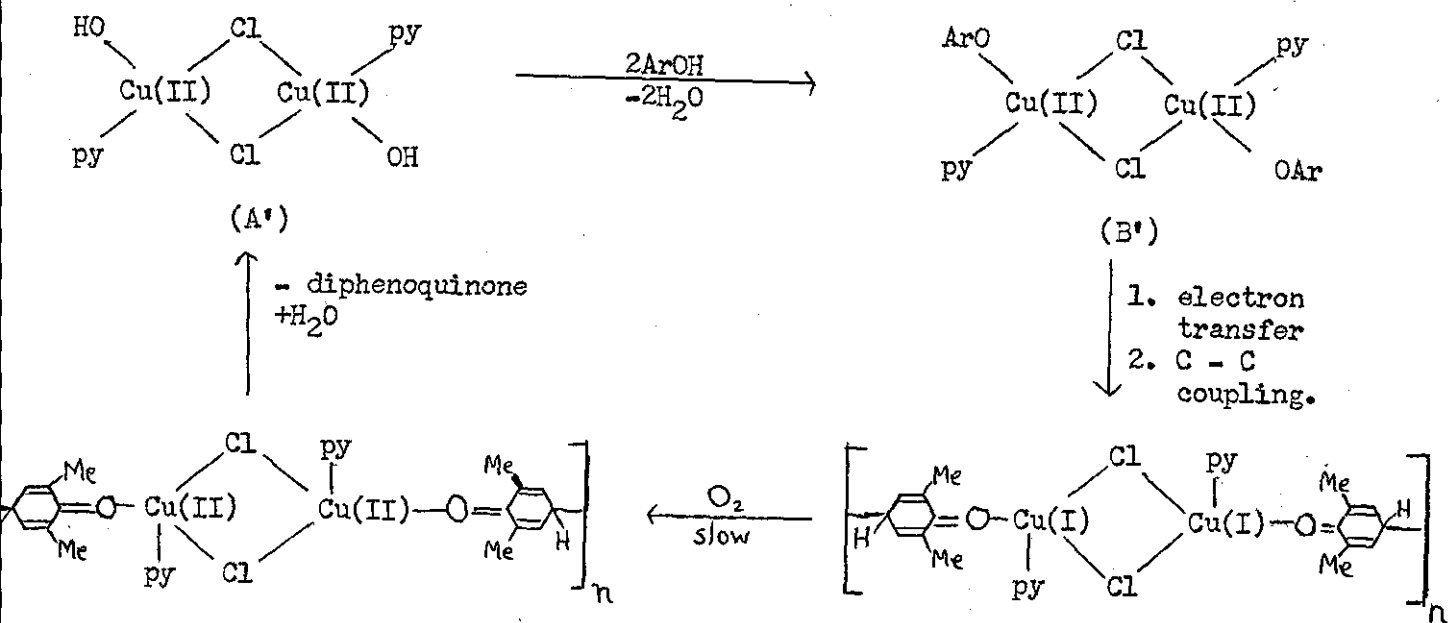
Reaction mechanism at low ligand : Cu ratios
(Price and Nakaoka).

Cu ratio promoting C - O coupling rather than C- C coupling may be dueto the decreased bond strength of the aryloxy radical to copper containing more ligands. Thus with two pyridines per copper the aryloxy radical would more readily dissociate as a "free" aryloxy radical to give the C - O coupling product, poly(phenylene oxide). They reported that with only one pyridine per copper, the aryloxy radical may not be so readily released. By remaining coordinated to Cu(I) it could then undergo C - C coupling to give C' (see Scheme 2.5). This would then react with oxygen to give D', which would give the diphenoquinone and regenerate the catalyst, A'.

Tsuchida et al. Mechanism (15).

The reaction mechanism proposed by Tsuchida et al. was very similar to the well-known enzyme reaction mechanism (27). Their mechanism can be represented schematically as follows (equation 2.4.6).

$$E \; + \; S \; \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} \; ES \; \overset{K_e}{\longrightarrow} \; ES' \; \overset{K_d}{\longrightarrow} \; E' \; + \; P \qquad (2.4.6)$$
$$\downarrow K_o$$
$$E$$
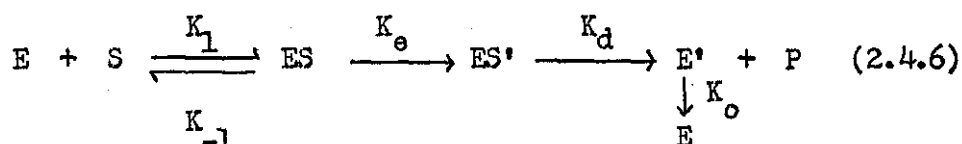
Where:-

E = copper (II) catalyst

S = monomer

ES = copper (II)-monomer species

ES' = copper (I)-monomer species

E = copper (I) catalyst

P = monomer radical from which the polymer is formed.

The complex ES' could, however, be oxidized directly as in equation 2.4.7., in which case the reoxidation step would not be an independent

reaction.

$$ES' \longrightarrow E + P \qquad (2.4.7)$$

Assuming steady states for the complexes ES and ES', the resulting rate equation from the reaction scheme was:-

$$\begin{aligned} v_d \\ \text{(rate of} \\ \text{polymerization)} \end{aligned} = K_d [ES'] = \frac{V_{max} \cdot [S]}{K_m + [S]} \qquad (2.4.8)$$

where

$$K_m = \left(\frac{K_{-1} + K_e}{K_1} \right) \left(\frac{K_d}{K_e + K_d} \right) \qquad (2.4.9)$$

and

$$V_{max} = K_2 \cdot [E]_o = \frac{K_e \cdot K_d}{K_e + K_d} \cdot [E]_o \qquad (2.4.10)$$

(where $[E]_o$ is the initial catalyst concentration).

Equation 2.4.7 is of the same form as the Michaelis-Menten equation for enzyme reactions. Plots of $1/v_d$ vs $1/[S]$ (Lineweaver-Burk plots) give linear relationships. Tsuchida et al. plotted the Lineweaver-Burk graphs for all their experimental results and obtained linear relationships from which they calculated the values V_{max}, K_m and K_2 (K_2 being the combination of steps K_e and K_d).

Effect of Ligand Ratio.

Tsuchida et al. explained the results of the effect of varying ligand:Cu ratios on the reaction rate (see Section 2.4.1) in terms of the rate constant K_2 and the equilibrium constant K_1^e (where $K_1^e = 1/K_m$). However, they did not explain why these constants should vary the way they did, except for reactions at very high ligand: Cu ratios. At very high ligand: Cu ratios, pyridine acts as a solvent and thus decreases the rate, as previously described in section 2.4.5.

The same authors suggested that it was the electronic state of the coordinated radicals which determined the type of coupling, C - O or C - C. They considered that C - O coupling occurred according to a coordinated radical mechanism. The carbon at the 4-position of the coordinated phenyl radical has a $\delta+$ property and is attacked by a coordinated phenoxy radical, giving C - O coupling. This theory is in contrast to other postulated theories (see section 2.5) of a free radical mechanism for C - O coupling. A suggested correlation between the coupling selectivity and K_1^e was the main evidence for the theory postulated by Tsuchida et al. The value of K_1^e was considered to be a measure of the affinity between the catalyst and the monomer. Consideration of their data for coupling selectivity and K_1^e shows that this correlation is questionable.

Effect of Oxygen Pressure.

Tsuchida et al.(28) suggested that the oxygen would participate in the activation of the monomer by forming a complex with the copper(II) catalyst and by acting as an electron acceptor. The coordinated oxygen, they reported, could promote either electron transfer (K_e) or the dissociation of the activated monomer (K_d) or both. In pyridine complexes, the coordinated pyridine could act as an electron acceptor giving high K_e values, and possibly also promote the K_d step, whereas aliphatic amines have no electron-acceptor properties. Hence the aliphatic amine complex catalyzed polymerization can only occur if oxygen, which acts as an electron acceptor, is coordinated to the complex.

Tsuchida et al.(28) suggested that oxygen could form a ternary complex (ESO_2') with any of the complexes, E, ES or ES'. The three

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possible mechanisms are shown in equations 2.4.11 to 2.4.13.

(a) $E + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} E.O_2$; $EO_2 + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ESO_2'\overset{K_e}{\longrightarrow} ESO_2' \overset{K_d}{\longrightarrow}$

$E.O_2' + S' \longrightarrow$ coupling. $\qquad\qquad$ (2.4.11)

$\downarrow$

E

(b) $E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES$; $ES + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} ESO_2 \overset{K_e}{\longrightarrow} ESO_2' \overset{K_d}{\longrightarrow}$

$E.O_2' + S' \longrightarrow$ coupling. $\qquad\qquad$ (2.4.12)

$\downarrow$

E

(c) $E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \overset{K_e}{\longrightarrow} ES'$; $ES' + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} ESO_2' \overset{K_d}{\longrightarrow}$

$E.O_2' + S' \longrightarrow$ coupling $\qquad\qquad$ (2.4.13)

$\downarrow$

E
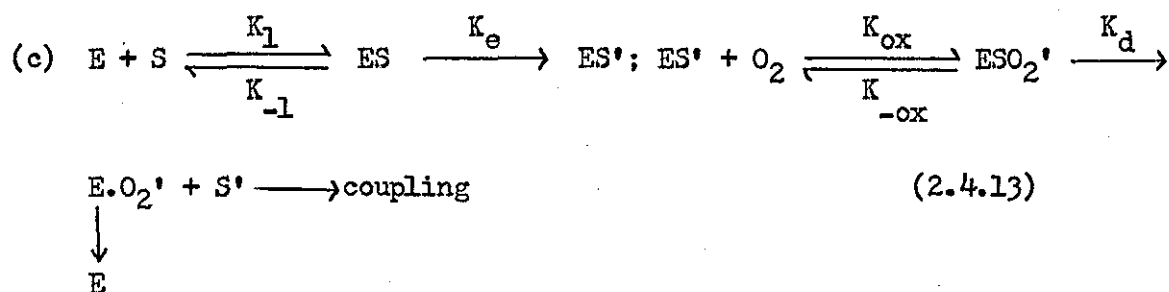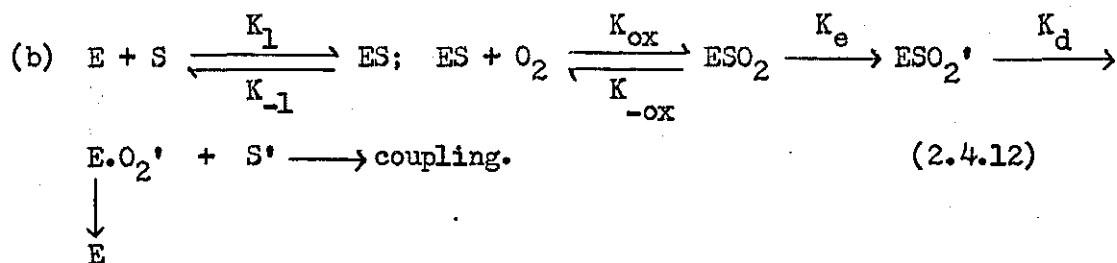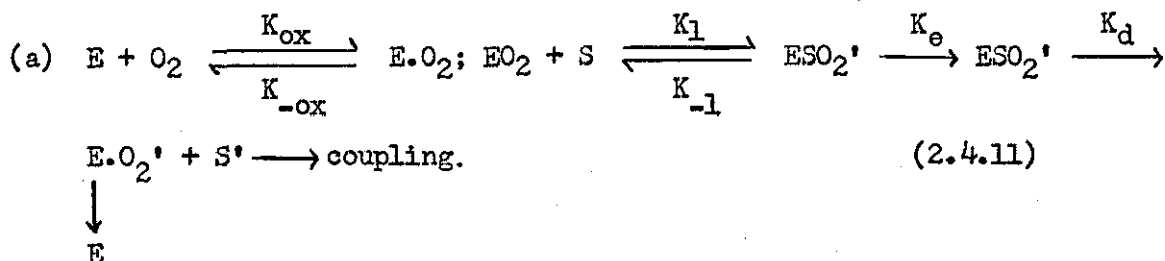
They derived equations giving the rate of polymerization for each of the above cases. These equations were derived on the assumption that only the oxygen complexes were active for the reaction. From these equations, the following expression was derived:-

$$\frac{1}{K_2} = \frac{B}{A} \cdot \frac{1}{[O_2]} + \frac{C}{A} \qquad\qquad (2.4.14)$$

(where A, B and C are constants and $[O_2]$ = the partial pressure of oxygen)

From their experimental results, they plotted graphs of $1/K_2$ against $1/[O_2]$. These gave linear relationships and thus supported equation 2.4.14. A mechanism in which the role of the oxygen was merely to oxidize the copper (I) complex, would show that K_2 was

proportional to the oxygen pressure and thus would not be consistent

with equation 2.4.14.

2.5 Mechanism of Polymer Growth in the Oxidative Coupling of Phenols.

The experimental work of this present project was concerned with

the oxidative coupling of thiols, amines and aminothiols, but not

phenols. Thus the mechanism of polymer growth for the oxidative

coupling of phenols has little or no direct relevance to this project

and therefore will be dealt with only very briefly. The majority of

proposed mechanisms (23, 29, 30, 31, 32 and 33) for polymer growth

of the phenols were formulated from the assumption that the dissociation

of the copper (I)-monomer complex produced a phenoxy radical, A.

A
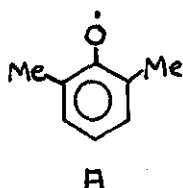
Various reaction schemes were considered whereby the radicals

of structure A react with each other to form poly(phenylene oxide).

Upon experimental evidence, Finkbeiner et al.(24) discounted a

simple aromatic substitution mechanism and suggested the following

two mechanisms :-

(a)   an "uncoupled" electron mechanism.

(b)   a quinol-ether rearrangement.

The uncoupled electron mechanism involved transmission of the

odd electron through the ether's oxygen to the end of the polymer-

chain radical. The quinol-ether mechanism is described later.

Blanchard et al.(33) and Butte and Price (29) gave evidence to

suggest that the uncoupled electron mechanism was used in polymer growth. However, Price in a later paper rejected this mechanism. The majority of authors (30, 32 and 14) investigating this mechanism gave conclusive evidence for the quinol ether mechanism.

Endres and Kwiatek (34), in their work on the oxidative coupling of 2,6-dimethylphenol found that the degree of polymerization rose sharply near the end of the reaction. This showed that the polymer growth was a stepwise mechanism, similar to condensation polymerization, whereby the growing polymer molecules react with each other as well as with the monomer.

Papers by Cooper et al (35) and Bolon (36) gave support to a quinol ether equilibration whereby two chain radicals of unit lengths x and y combine to form a quinol ether and then dissociate to form two aryloxy chain radicals of different lengths. This is shown by equation 2.5.1.

$$M_x + M_y \longrightarrow M_{x-1} + M_{y+1} \qquad (2.5.1)$$
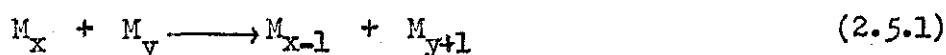
The basis of the quinol ether mechanism is given in Fig. 2.5.1. This mechanism is shown more fully in reference 24.
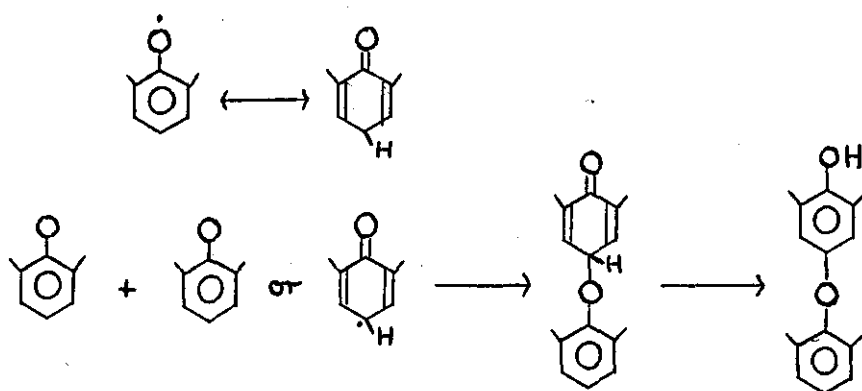
Fig. 2.5.1   Basis of the quinol-ether mechanism

2.6 Oxidative Coupling of Thiols.

In 1966 Hay (6) filed a patent describing the synthesis of disulphides from thiols and polydisulphides from dithiols. This was an oxidative coupling process using a copper (I) chloride pyridine complex as catalyst. No other product other than the disulphide or the polydisulphide was reported to have been formed. To the author's knowledge, no other paper concerning the development (mechanisms and kinetic studies) of this work has been published.

Thiols, however, can be oxidized to disulphides in aqueous solutions by gaseous oxygen using metal ions as catalysts. Tarbell(37) reviews the mechanisms and kinetics of the oxidation of thiols using various oxidizing agents. He reported that the contradictory nature of the reports concerning the mode of oxidation of various thiols did not allow an interpretation of the experimental data in terms of a unique mechanism. However any attempt to advance such a mechanism must take into account the following generalizations which emerge from a consideration of the past studies of the oxidation of thiols by oxygen:-

(a) The rates of oxygen uptake by aqueous thiol solutions appear to be independent of the thiol concentration.

(b) The rates of oxidation are proportional to the oxygen content of the reaction mixtures.

(c) The rates of oxygen uptake are accelerated by several metallic ions (e.g. Fe^{2+} and Cu^{2+}) and it appears that the formation of a metal ion-thiol complex is indispensable for the oxidation process.

Vigorous oxidizing conditions can convert the thiol or disulphide into more highly oxidized products, the most oxidized product being

the sulphonic acid R SO_3 H (where R = aryl or alkyl group). These products are listed by Savige and Maclaren (38).

2.7 Oxidative Coupling of Amines.

Preparation and Properties.

The oxidative coupling of aromatic amines to azo compounds in practically quantitative yield using a copper (I) chloride pyridine complex was first reported by Terent'ev and Mogilyanskii (13).

$$2 \ ArNH_2 \ \xrightarrow[\ O_2 \ ]{\ Cu(I) \ Cl/py \ } \ Ar \ N = NAr + 2H_2O \qquad (2.7.1)$$

(where Ar = aryl)
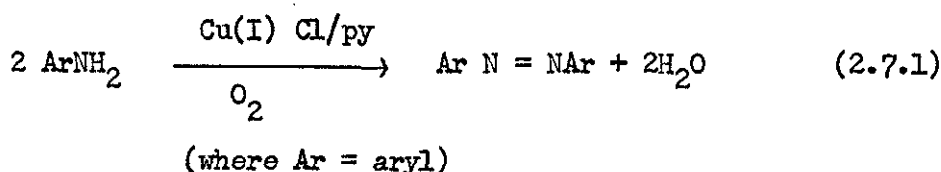
They reported that the oxidation of aniline using other catalyst systems had produced certain amounts of azo compounds in the product. However, because of side reactions, the yields of azo compounds were not very high and so these reactions did not find practical application for the preparation of azo compounds.

Bach and Black (8) discovered that azopolymers could be prepared by the oxidative coupling of aromatic diamines using the same catalyst.

$$n \ H_2N-Ar-NH_2 \ \xrightarrow[\ O_2 \ ]{\ Cu(I) \ Cl/py \ } \ (Ar-N=N-)_n \ + 2n \ H_2O \qquad (2.7.2)$$
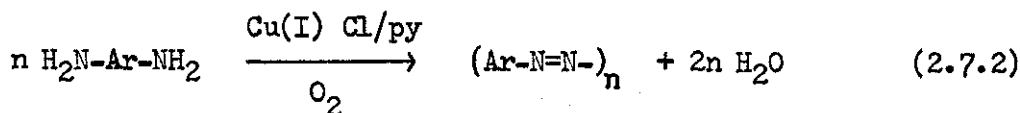
This reaction was also reported by Kotlyarevskii et al.(39).

Bach and Black (2) reported that polymers containing the azo linkage have been prepared by other methods, e.g. coupling of bisdiazonium salts with polyphenols, decomposition of bisdiazonium salts, hydrogen abstraction from aromatic diamines by free radicals

and polycondensation of azobenzene derivatives. However, these
methods impose limitations on the polymer structure because of one
or more of the following reasons:-

(a) specific substituents are required.

(b) a random incorporation of azo linkages is produced in
the polymer.

(c) very specific monomers are required.

By contrast, the catalyzed oxidative polymerization method is
generally applicable to primary aromatic diamines, an easily
accessible class of monomers.

From a study of the infrared spectra of azopolymers, Kotlyarevskii
et al (39) concluded that azoxy bonds ($_{-N} = \overset{\overset{\text{O}}{\|}}{N_-}$) were present in the
polymers. Bach and Black (2), however, from their infrared spectra
of azopolymers, concluded that azo links were formed exclusively.

In an experiment where p-phenylene diamine was "oxidized" under
an atmosphere of oxygen but with no catalyst, Bach and Black (2)
reported that the solution discoloured quickly but only a minimal
amount of oxygen was absorbed and no polymer was formed. The same
authors reported that the use of dimethylacetamide as solvent together
with pyridine, rather than pure pyridine, gave polymers of increased
molecular weight. This was because the polymers were more soluble
in dimethylacetamide than in pyridine.

Effect of Structure.

Terent'ev and Mogilyanskii (13) reported that, in the oxidative

coupling of aromatic amines, the presence of negative groups
(electron-withdrawing groups, such as -NO$_2$) decreased the yield
of the azo compound. In a later paper (40), the same authors
investigated the effect on the reaction rate of each of the substituents:
methyl; chloro; bromo and iodo in each of the positions: ortho;
meta and para of aniline. They found that for each of the substituent
atoms, a substituent in the ortho position produced the least
active aniline derivative. They claimed that this was because of the
formation of hydrogen bonds between the amino group and the
substituent atom in the ortho position. This could possibly be
true for the o-chloro-, o-bromo- and o-iodoanilines, but it is
certainly not the case for o-methylaniline.

Bach and Black (2) reported that the reactivity of a given amine
in oxidative coupling can be expected to be strongly dependent on the
availability of the lone electron pair on the amino nitrogen atom
for complex formation and electron transfer. The relative basicity
of the amine involved would also be related to this property, thus
possibly providing as easy way of predicting the suitability of a
given amine for oxidative coupling. They reported a fairly good
correlation between basicity, relative to pyridine, and reactivity
towards oxidative coupling. Bach and Hinderer (41) reported that
an unsymmetrical diamine, NH$_2$-Ar-Ar-NH$_2$' (where Ar = aryl group),
where the basicity of the NH$_2$ group was appreciably greater than that
of the NH$_2$' group, would, under certain conditions, selectively
dimerize as shown below.

$$NH_2\text{-Ar-Ar-NH}_2' \xrightarrow[O_2]{CuCl/py} NH_2'\text{-Ar-Ar-N=N-Ar-Ar-NH}_2' \qquad (2.7.3)$$
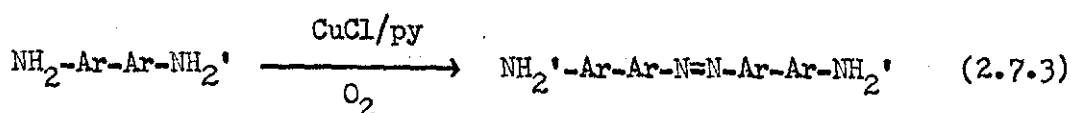
Increasing the temperature of the reaction mixture in situ at the end of the dimerization, would give a highly ordered block copolymer. A similar effect was reported by Kinoshita (22) who found that in the oxidative coupling of an equimolar mixture of aniline and p-anisidine, 4,4'-azoanisol was selectively obtained in the early stages of the reaction.

Oxidation of Hydroxyazo Compounds.

Kinoshita (22) reported that hydroxyazobenzene could be catalytically oxidized by a copper (I) chloride pyridine complex to azobenzene.

$$C_6H_5-NH-NH-C_6H_5 \xrightarrow[O_2]{CuCl/py} C_6H_5-N=N-C_6H_5 \qquad (2.7.4)$$
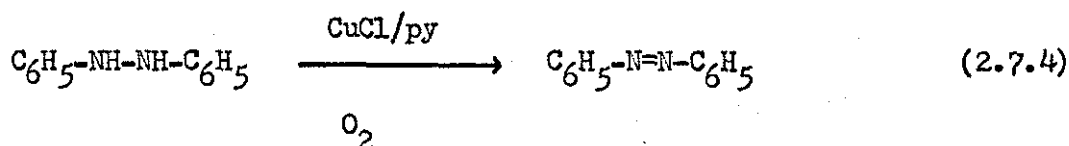
A similar reaction was reported by Terent'ev and Mogilyanskii (40), who demonstrated that N,N'-diaryhydrazines are dehydrogenated by the copper (I) chloride pyridine complex at a rate substantially faster than are the corresponding amines.

Reaction Mechanisms.

(a) Kinoshita (22) proposed the following scheme for the oxidative coupling of amines:-

$$C_6H_5NH_2 + Cu(II)Cl \longrightarrow C_6H_5NH_2Cu(II)^+Cl^- \qquad 1$$

$$C_6H_5NH_2Cu(II)^+ Cl^- + Cu(II)Cl \longrightarrow Cu(II)NHC_6H_5 \qquad 2$$

$$2 C_6H_5NH Cu(II) \longrightarrow C_6H_5NHNHC_6H_5 \qquad 3$$
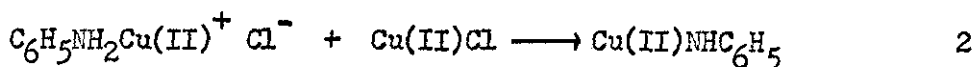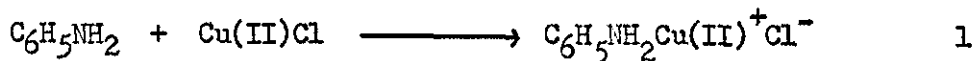
$$C_6H_5NHNHC_6H_5 \longrightarrow C_6H_5N=NC_6H_5 \qquad 4$$

Scheme 2.6   Reaction scheme for the oxidative coupling
of aniline   (Kinoshita).

Kinoshita was at a distinct disadvantage because at the time very little was known about the structure of the catalyst.

(b)   Bach and Black (2) postulated the following reaction mechanism:-

Complex
formation
$$ArNH_2 + Cu(II)OHCl \longrightarrow ArNH_2Cu(II)OHCl \qquad 1.$$

Electron
transfer
$$ArNH_2Cu(II)OHCl \longrightarrow ArNH_2^+ Cu(I)OHCl \qquad 2.$$

Coupling
$$2\ ArNH_2^+ Cu(I)OHCl \longrightarrow ArNHNHAr + 2\ Cu(I)Cl \qquad 3.$$

$$ArNHNHAr \xrightarrow[Cu(II)/py/O_2]{-2e\ -2H^+} ArN=NAr \qquad 4.$$

Catalyst
reoxidation
$$4\ Cu(I)Cl + O_2 + 2H_2O \longrightarrow 4\ Cu(II)OHCl \qquad 5.$$
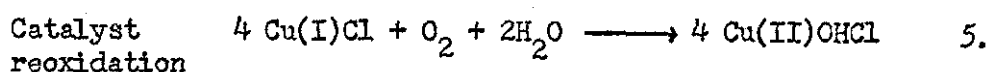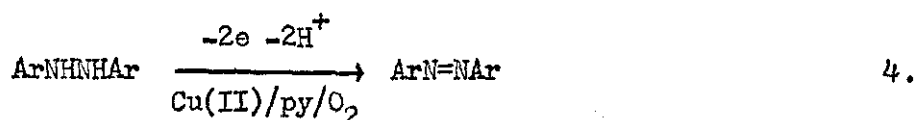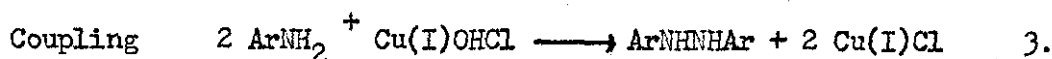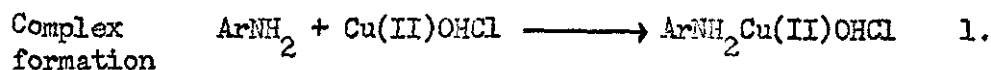
(the pyridine ligands have been omitted for the sake of clarity)

Scheme 2.7   Reaction scheme for the oxidative coupling
of amines (Bach and Black)

2.8 Mass Transfer Effects.

The study of mass transfer effects upon oxidative coupling reactions has been limited to brief comments in a few papers which describe the chemical kinetics of these reactions. The transfer of oxygen from the gaseous phase to the liquid phase is a necessary step of the reaction sequence where the catalyst is used in less than equivalent amounts. Thus under certain conditions, the reaction rate will be controlled by the mass transfer rate of the oxygen between the two phases.

Hay (21) reported that in the oxidative coupling of acetylene compounds using copper (I) chloride amine complexes as catalysts, the reactions were rapid enough at room temperature to be essentially diffusion controlled.

As stated previously (section 2.4.3), Brooks (25) reported experimental data which suggested that, under certain conditions, the reaction rate for the oxidative coupling of 2,6-dimethylphenol was controlled by the mass transfer of oxygen from the gas phase to the liquid phase.

Before studying the chemical kinetics of the oxidative coupling of 2,6-dimethylphenol, Price and Nakaoka (14) established conditions within which oxygen diffusion was not the rate controlling step. By varying the volume of reaction mixture at a fixed concentration of reactants, they found that below a certain volume of reaction mixture, the rate of oxygen absorption became independent of the rate of oxygen diffusion. When the partial pressure was reduced to 0.21

atmospheres, the results suggested that the diffusion of oxygen from the gas phase to the liquid phase had an appreciable effect on the reaction rate.

The data of Brooks (25) and Price and Nakaoka (14) cannot be effectively compared because they used different volumes of reaction mixture and the vessel dimensions and stirring characteristics were not reported.

3. MASS TRANSFER EFFECTS IN GAS-LIQUID REACTIONS.

3.1 Mass Transfer Theory of Gas-Liquid Systems.

A number of models have been suggested to represent the conditions in the region of the gas-liquid interface. These are now considered.

The earliest model was the "Two-Film" theory propounded by Whitman in 1923 (42).

(a) Two-Film Theory.

The basis of this theory is the assumption that the zones in which resistance to transfer lies can be represented by two hypothetical laminar layers, the gas film and the liquid film, in which the transfer is entirely by molecular diffusion (Fig. 3.1.1). Outside the laminar layers, turbulent eddies supplement the action caused by random movement of the molecules, and the resistance to transfer becomes negligible. Thermodynamic equilibrium is assumed to exist at the interface and therefore the relative positions of the points B and C are determined by the phase equilibrium relationship. Although this theory does not closely reproduce the conditions in most practical equipment, the mathematics of many gas-liquid systems can only be solved by using this model, and this is the reason why it is still extensively used. The average absorption rate per unit surface area, $\bar{V}_o$, is given by:-

$$\bar{V}_o = - D\left(\frac{\partial c_i}{\partial x}\right)_{x=0} \qquad (3.1.1)$$

where:-

D = diffusivity of the dissolved gas (cm^2/sec.)

X = distance from the interface (cm).
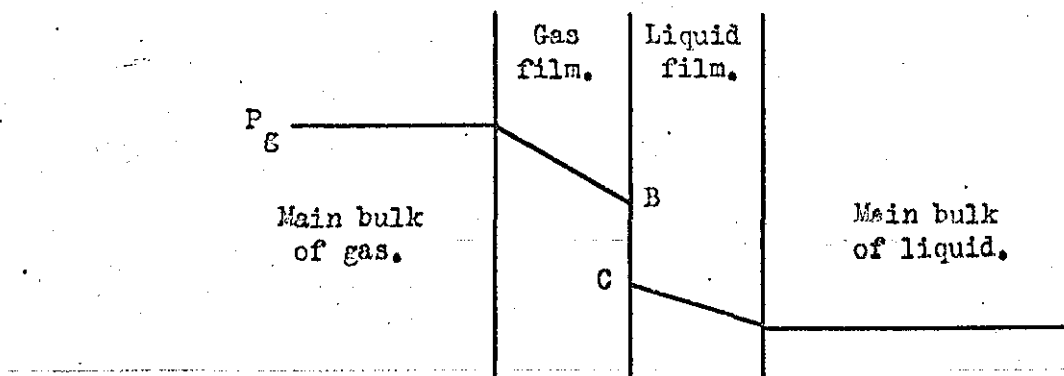
Fig. 3 .1.1. Concentration profile of the film theory.

Time function
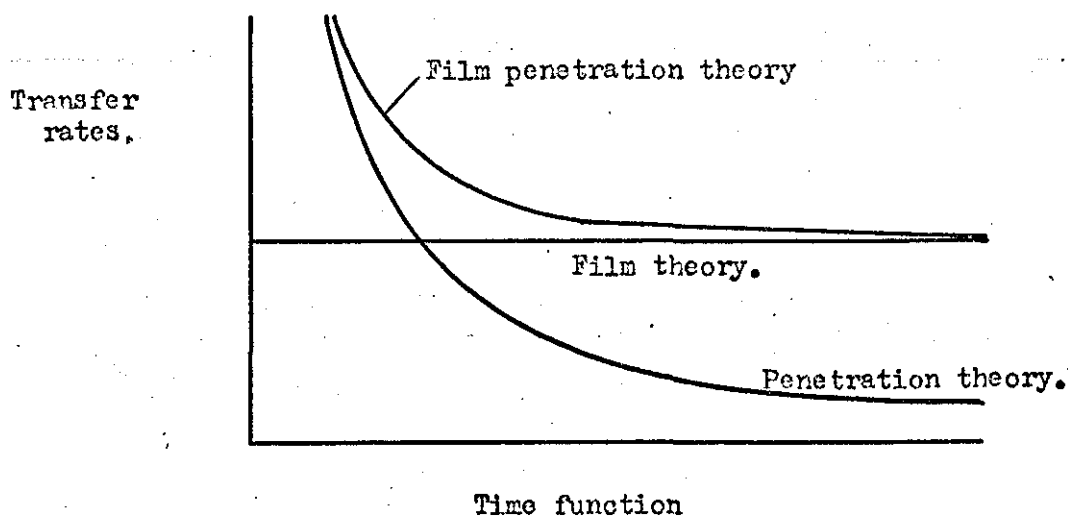
Fig. 3.1.2. Comparison of the film, the penetration and the film penetration theories.

c_i = concentration of component i

$\overline{V}_0$ = average absorption rate with no chemical reaction.

(b)   The Penetration Theory.

Higbie's Model (43).

The penetration theory was propounded in 1935 by Higbie. He suggested that the eddies in a fluid bring an element of the fluid from the bulk of the liquid to the interface where it is exposed to the second phase for a definite interval of time, after which the surface element is remixed with the bulk fluid. The initial composition of the surface element corresponds with that of the bulk liquid. It is assumed that equilibrium is immediately attained at the interface and a process of unsteady state diffusion then occurs until the element is remixed after a fixed interval of time. The differential equation representing the unsteady state molecular diffusion is given by (44):-

$$D \frac{\partial^2 c_i}{\partial x^2} = \frac{\partial c_i}{\partial t} \tag{3.1.2}$$

where t = time elapsed since surface renewal.

The boundary conditions associated with equation 3.1.2 are:-

$$t = 0, \quad c = c_0 \tag{3.1.3}$$

$$X = 0, \quad c = c_0' \tag{3.1.4}$$

$$x \longrightarrow \infty, \quad c = 0 \tag{3.1.5}$$

The average absorption rate is given by:

$$\overline{V}_0 = (c_0' - c_0) \cdot 2\sqrt{\frac{D}{\pi t}}^* \tag{3.1.6}$$

where

c_0' = concentration of c at the interface

c_0 = concentration of c in the bulk liquid

t* = life-time of the element

c = absorbent gas

Danckwerts' Model (45).

Higbie's model was modified by Danckwerts, who suggested that
each element of surface would not be exposed for the same length
of time, but a random distribution of ages would exist. Thus the
rate of disappearance of surface elements of any given age is prop-
ortional to the number of surface elements of that age which are
present. Equations 3.1.2 to 3.1.5 still apply, but the average
absorption rate is given by:

$$\overline{V}_o = \sqrt{Ds} \; (c_o{}' - c_o) \qquad\qquad (3.1.7)$$

where   s = rate of surface renewal (sec^{-1})

or 1/s = average life of a surface element.

(c)   The Film Penetration Theory (46).

Toor and Marchello proposed a "Film-Penetration" theory which
incorporated some of the principles of both the two-film theory and
the penetration theory. The whole of the resistance to transfer is
regarded as lying within a laminar film at the interface as in the
film theory. It is assumed that fresh surface is formed at intervals,
from fluid which is brought from the bulk of the liquid to the interface
by the action of eddy currents. Mass transfer then takes place as
in the penetration theory, with the exception that the resistance is
confined to the finite film, and the material which crosses the film
is immediately completely mixed with the bulk of the fluid. For short
times of exposure, when none of the material has reached the far side

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of the laminar layer, the process is identical to that postulated in the penetration theory. For prolonged periods of exposure when a steady state concentration has developed, conditions are similar to those considered in the film theory. The equations 3.1.2, 3.1.3 and 3.1.4 still apply, but the boundary condition of equation 3.1.5 is replaced by that in 3.1.8.

$$x = \lambda, \ c = c_o \qquad\qquad (3.1.8)$$

(where λ = depth of penetration, or thickness of region in which

molecular transfer is controlling).

It is assumed that at some distance below the surface, λ, the concentration remains constant at c_o, and that a freshly formed surface has this concentration. From solution of the equations, 3.1.2, 3.1.3, 3.1.4 and 3.1.8, Toor and Marchello derived equations for the average rate of absorption for short times and long times of surface element exposure; these equations corresponded to those applying to the penetration theory and the film theory respectively. Fig. 3.1.2 represents the comparison of the three theories.

(d) Dobbins' Model (47).

The model proposed by Dobbins was similar to the film-penetration theory. A film of liquid at the interface is assumed to be present, as for the film theory. The liquid of which this film is composed is considered to be continuously exchanged for liquid from layers beneath the surface. The model combines the concepts of a random exchange function with the boundary conditions of a liquid film of finite thickness, λ. Using the same boundary conditions as for the film-penetration theory (equations 3.1.3, 3.1.4 and 3.1.8, together

with the differential equation 3.1.2, Dobbins produced the expression

shown below for the physical absorption coefficient, k_L^o.

$$k_L^o = \sqrt{Ds} \; \coth \sqrt{\frac{s\lambda}{D}} \qquad\qquad (3.1.9)$$

$$\left(\text{where } \coth(y) = \frac{e^y + e^{-y}}{e^y - e^{-y}} \right)$$

The following relationship can be derived from equation 3.1.9:-

$$k_L^o \propto D^n \qquad\qquad (3.1.10)$$

The value of n varies with varying values of λ and s. It was

shown by Astarita, that for the film theory:-

$$k_L^o \propto D \qquad\qquad (3.1.11)$$
$$\text{i.e. } n = 1.0$$

and for the penetration theory:-

$$k_L^o \propto \sqrt{D} \qquad\qquad (3.1.12)$$
$$\text{i.e. } n = 0.5$$

Toor and Marchello did not report any expression for k_L^o.

In equation 3.1.10 :-

(a)   as $s \longrightarrow 0$, $k_L^o \longrightarrow \frac{D}{\lambda}$, i.e. n = 1.0

this corresponds to the film theory.

(b)   as $s \rangle 3.0$, $k_L^o \longrightarrow \sqrt{Ds}$, i.e. n = 0.5

this corresponds to the penetration theory.

By means of experimental work, Dobbins (47) showed that as the

value of s increased, the value of n decreased. For a gas-liquid

system where k_L^o and D are fixed, he showed that as the value of s

increased (by increased mixing of the liquid), the value of λ

decreased. This is as would be expected.

It is difficult to conceive a sudden change from the laminar conditions within the film to the turbulent conditions immediately below it. There is undoubtedly a gradual change from conditions at the interface where the molecules have the same general orientation, to conditions within the liquid mass, where they are completely random.

Other postulated models have been discussed by Danckwerts, however, in practice, the mathematics of many gas-liquid systems can only be solved for the much simplified, but less realistic models.

3.2 Theory of Mass Transfer with Chemical Reaction of Gas-Liquid Systems.

The differential equation which represents the phenomenon of simultaneous diffusion and chemical reaction in a liquid phase may be written as :-

$$D \frac{\partial^2 c_i}{\partial x^2} = \frac{\partial c_i}{\partial t} + r \qquad (3.2.1)$$

(where r = chemical reaction rate)

This neglects velocity gradients in the liquid film, which means that during its life, the surface element behaves as a rigid body, but it does not imply that its position in space does not vary. The general equation 3.2.1 cannot be solved, nevertheless a number of asymptotic solutions can be found when simple expressions for r are considered. The above equation has only been applied to the film and the penetration theories. These theories generally give results that are of sufficient accuracy for practical application. The use of the more realistic, but more complex, theories, leads to expressions, the mathematics of which are, in most cases, impossible to solve.

The film theory model assumes that the phenomenon considered is in steady state conditions so that equation 3.2.2 applies.

$$\frac{\partial c_i}{\partial t} = 0 \qquad\qquad (3.2.2)$$

Thus equation 3.2.1. becomes:-

$$D \frac{\partial^2 c_i}{\partial x^2} = r \qquad\qquad (3.2.3)$$

Boundary Conditions.

The following boundary conditions need to be specified in order to solve equations 3.2.1. and 3.2.3 for given expressions of r.

(a) Film Theory.

$x = 0, \quad c = c'_o$

$x = \delta, \quad c = c_o$ and $b = b_o$ \qquad\qquad (3.2.4)

where b_o = bulk liquid concentration of the liquid phase reactant.

δ = film thickness.

(b) Penetration Theory.

$t = 0, \quad b = b_o$ and $c = c_o$

$x = 0, \quad c = c'_o$ \qquad\qquad (3.2.5)

$x \rightarrow \infty, \quad c = c_o, \quad \frac{\partial c}{\partial x} = 0, \quad b = b_o, \quad \frac{\partial b}{\partial x} = 0$

The above conditions for the penetration theory apply both to Higbie's and Danckwerts' models.

Astarita (44) and Danckwerts (48) have published works giving a comprehensive treatment of the theory of mass transfer with chemical reaction. Both these works are now considered.

3.2.2. Astarita's Treatment.

Astarita made use of the following two concepts:-

(a) Diffusion Time. Diffusion time, t_d, was difined by equation 3.2.6.

$$t_D = \frac{D}{(k_L^o)^2} \qquad (3.2.6)$$

The physical meaning of diffusion time was the average life of surface elements.

(b) Reaction Time. Reaction time, t_r, was defined by equation 3.2.7.

$$t_r = \frac{c - c'}{r} \qquad (3.2.7)$$

where c' = equilibrium concentration of absorbent gas.

Astarita described the physical meaning of the reaction time as the amount of time which is required in order that the reaction may proceed to an appreciable extent.

The theory of mass transfer with chemical reaction was described under the following regimes:-

(A) Slow Reaction Regime (where $t_D \ll t_r$).

There is negligible reaction occuring during the life of a surface element of liquid. This means that :-

$$k_L = k_L^o \qquad (3.2.8)$$

(where k_L = chemical absorption coefficient.)

This regime was further sub-divided into:-

(1) The diffusional regime, where the rate controlling phenomenon is diffusion. The effect of the chemical reaction is to keep the bulk liquid concentration of gas, c_o, down to its equilibrium value, c'.

(2) The kinetic regime, where the liquid is completely saturated with gas and the rate controlling phenomenon is the chemical reaction.

(B) Fast Reaction Regime (where $t_D \gg t_r$).

The reaction is fast enough to take place appreciably during the life of the surface elements.

(C) Transition from Slow to Fast Reaction.

This is a consideration of the general case, where the concentration of the liquid phase reactant is assumed constant throughout the liquid.

(D) Instantaneous Reaction.

This is where the absorbing component and the liquid phase reactant, b, cannot coexist. A concentration profile is shown in Fig. 3.2.1. The position of the reaction plane, λ, changes with time. The average absorption rate is proportional to the physical absorption rate. The effect of the chemical reaction is to enhance the absorption rate by a factor which is independent of the reaction kinetics.

(E) Transition from Fast to Instantaneous Reaction.

This was a consideration of the most general case in which the concentrations of both the absorbing component and the liquid phase reactant were variable. This situation leads to very complex differential equations for which rigorous solutions are not known.

In general, for a chemical absorption process, the total absorption
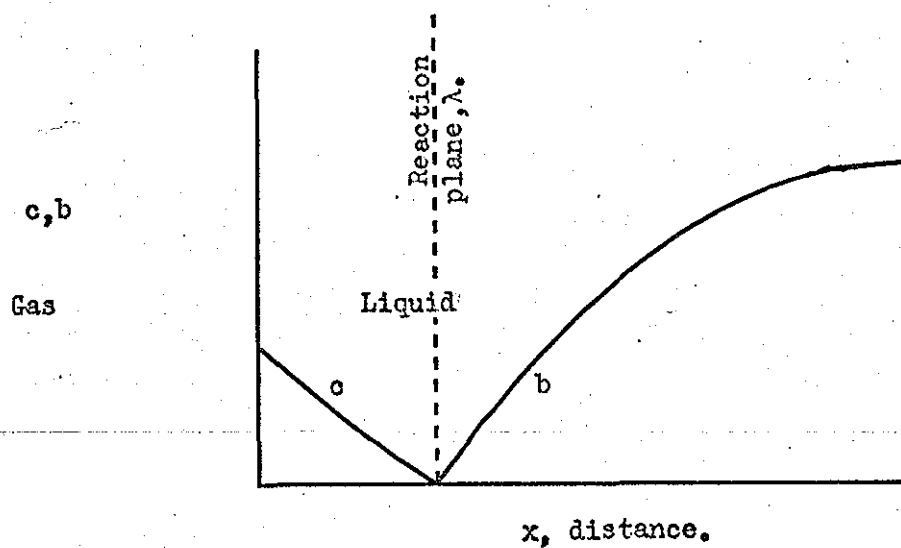
Fig. 3.2.1. Concentration profile of an
instantaneous reaction.
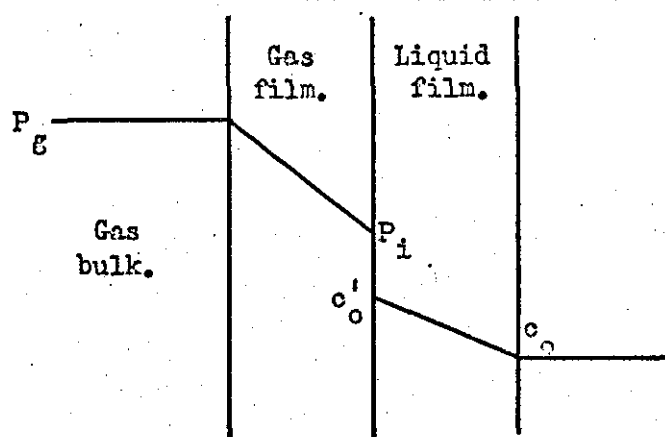
Fig. 3.2.2. Concentration profile of a gas-liquid
interface showing a gas film resistance.

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rate is given by:-

$$\overline{V}_a \propto a^{\varepsilon_1} . (\phi a)^{\varepsilon_2} . k_L^{\varepsilon_3} . r^{\varepsilon_4} . c_0'^{\varepsilon_5} \qquad (3.2.9)$$

where a = interfacial area.

ϕ = volume of liquid per unit interface.

The four regimes of chemical absorption (diffusional, kinetic, fast and instantaneous reaction regimes) are identified by their dependence upon the variables: a; ϕa; k_L; r and c'_0, and by a set of values of the five parameters ε_1 to ε_5. These are summarized in table 3.1. Thus by comparing experimental results with the above table, the applicable regime(s) can be identified.

3.2.3. Danckwerts Treatment.

Danckwerts considered the subject of mass transfer with chemical reaction in a similar manner to that of Astarita's. The relevant differences and additions are now considered.

Use was made of the concept of the "enhancement factor," E'. This was defined as follows:-

$$E' = \frac{\text{amount of gas absorbed in a given time into a reacting liquid.}}{\text{amount of gas absorbed in the same time in the absence of a reaction.}} \qquad (3.2.10)$$

Danckwerts derived general equations for 1st, 2nd and mth order reactions which were applicable to all regimes, except the instantaneous reaction regime. The instantaneous reaction regime was considered as a special case. The complex general equations could be simplified by considering limiting cases. For each of these limiting cases, a

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Regime	ε_1	ε_2	ε_3	ε_4	ε_5
Kinetic	0	1	0	1	n
Diffusional	1	0	1	0	1
Fast reaction	1	0	0	$\frac{1}{2}$	$\frac{n+1}{2}$
Instantaneous reaction	1	0	1	0	0

n = order of reaction with respect to c'_o

Table 3.1.

Values of the parameters ε_1 to ε_5 for the various regimes of mass transfer with chemical reaction.

specific regime was identified, similar to those identified by Astarita.

An important phenomenon considered by Danckwerts was the gas-side resistance.

Gas-Side Resistance.

When a soluble or reacting gas is mixed with an insoluble or non-reacting gas, it must diffuse through the latter to reach the surface. As a result, the partial pressure of the soluble gas at the interface is generally less than that in the bulk. This phenomenon is termed "gas-side resistance". This can be considered as a stagnant film of gas of finite thickness across which the soluble gas is transferred by molecular diffusion alone, while the bulk of the gas has uniform composition (see Fig. 3.2.2). This is exactly analogous to the film model of the processes occurring on the liquid side of the interface. The interfacial concentration, c'_o, is in equilibrium with the interfacial partial pressure, p_i.

Concentration profiles are shown in Fig. 3.2.3 for instantaneous reactions with varying concentrations of liquid phase reactant, b.

Fig. 3.2.3(a). This corresponds to the general case where there are finite concentrations of both reacting gas and liquid phase reactant in the liquid phase at the interface.

Fig. 3.2.3(b). This describes the special case where the liquid phase reactant diffuses to the interface at exactly the same rate (in chemical equivalents) as the reacting gas diffuses to the interface.
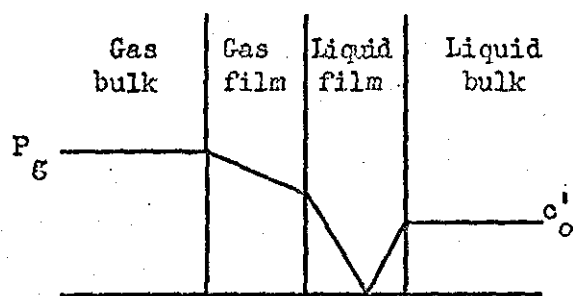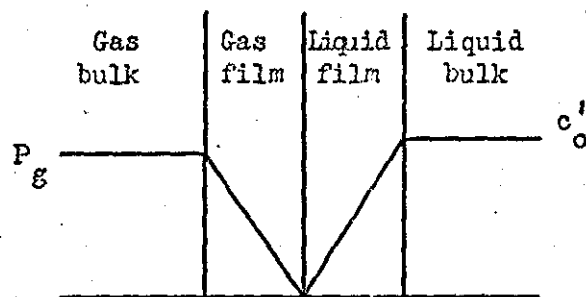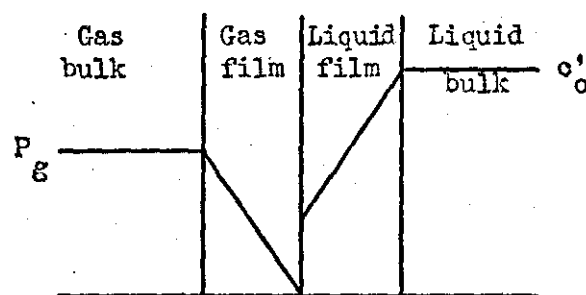
Fig. 3.2.3. Three possible concentration profiles
for the instantaneous reaction regime.

Fig. 3.2.3(c). In this case, the absorption process is entirely controlled by the transport of the reacting gas across the gas film.

It is thought that when a pure gas is used, there would be no gas side resistance, i.e. there would be no concentration gradient in the layers of gas immediately adjacent to the interface. Because of the high diffusivities of gases, the gas-side resistance becomes important only for instantaneous or very fast reactions.

Danckwerts also considered the following:-

(a) Consecutive reactions, where the initial product of a gas-liquid reaction reacts further with the liquid reactant.

$$a + b \longrightarrow P_1$$
$$P_1 + b \longrightarrow P_2$$

(3.2.11)

where P_1 = initial product

P_2 = secondary product.

(b) The rise in temperature at the surface of the liquid arising from the heat of absorption and the heat of reaction (if exothermic).

(c) Selectivity, both in the absorption of two gases or when the initial product reacts further with the gas, as shown below.

$$a + b \longrightarrow P_1$$
$$P_1 + a \longrightarrow P_2$$

(3.2.12)

Certain sections of the work of Astarita and Danckwerts, which are relevant to the experimental work of this present project are discussed more fully in section 6.

3.3 Industrial Absorbers.

Treybal (49) gave a comprehensive description of equipment used for gas-liquid operations. The main features are discussed below.

(a) The Packed Tower.

The most common type of absorption equipment is the packed tower. It consists of a vertical cylindrical shell filled with one of numerous types of inert packing material.   Fig. 3.3.1 shows a typical packed tower. The operation is usually countercurrent, the solvent being distributed over the packing at the top of the tower and passing down over the packing in thin liquid films, giving a large interfacial area, while the gas passes up through the free space between the wetted particles of packing. Special care must be taken to ensure proper initial distribution of gas and liquid flow through the packing. In a tall tower it may be necessary to divide the packing into several sections, with a device above each which will collect fluid from the wall and redistribute it to the packing. The various types of packing used in such towers are described in the Encyclopedia of Chemical Process Equipment (50).

(b) The Plate Tower.

Fig. 3.3.2. shows a diagram of a typical plate column. The gas to be treated enters at the bottom, passing up the tower and bubbling through the liquid on each plate. The solvent is fed at the top and overflows from plate to plate. Usually each plate has a number of small (3 - 6 inches) caps on each plate. The gas from below enters the caps, depressing the liquid level inside the caps and escapes into the liquid on the plate through the notches or slots in the periphery

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Fig.3.3.1. Packed tower.

GAS OUT

LIQUID IN

gas gas gas

GAS IN

LIQUID OUT
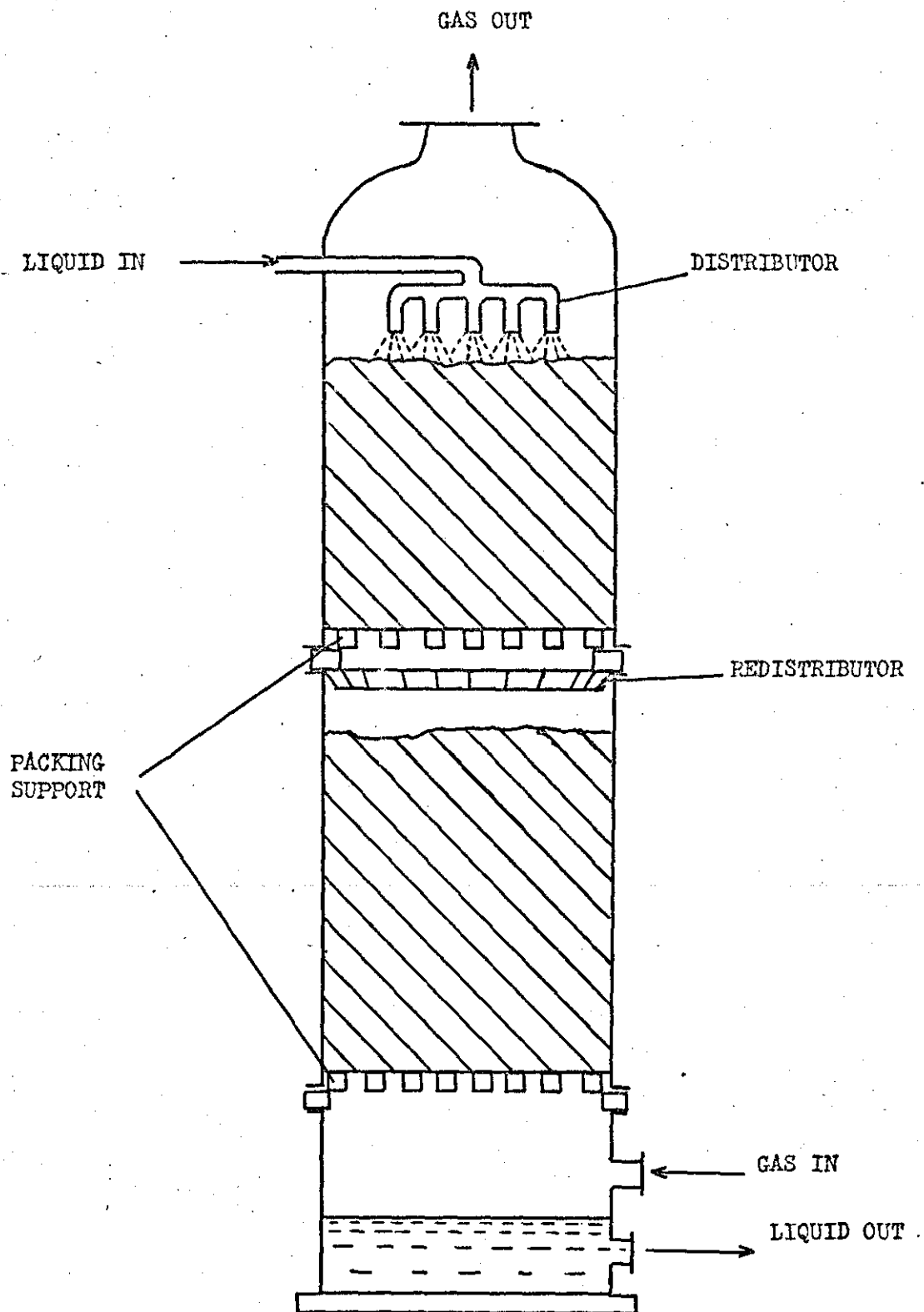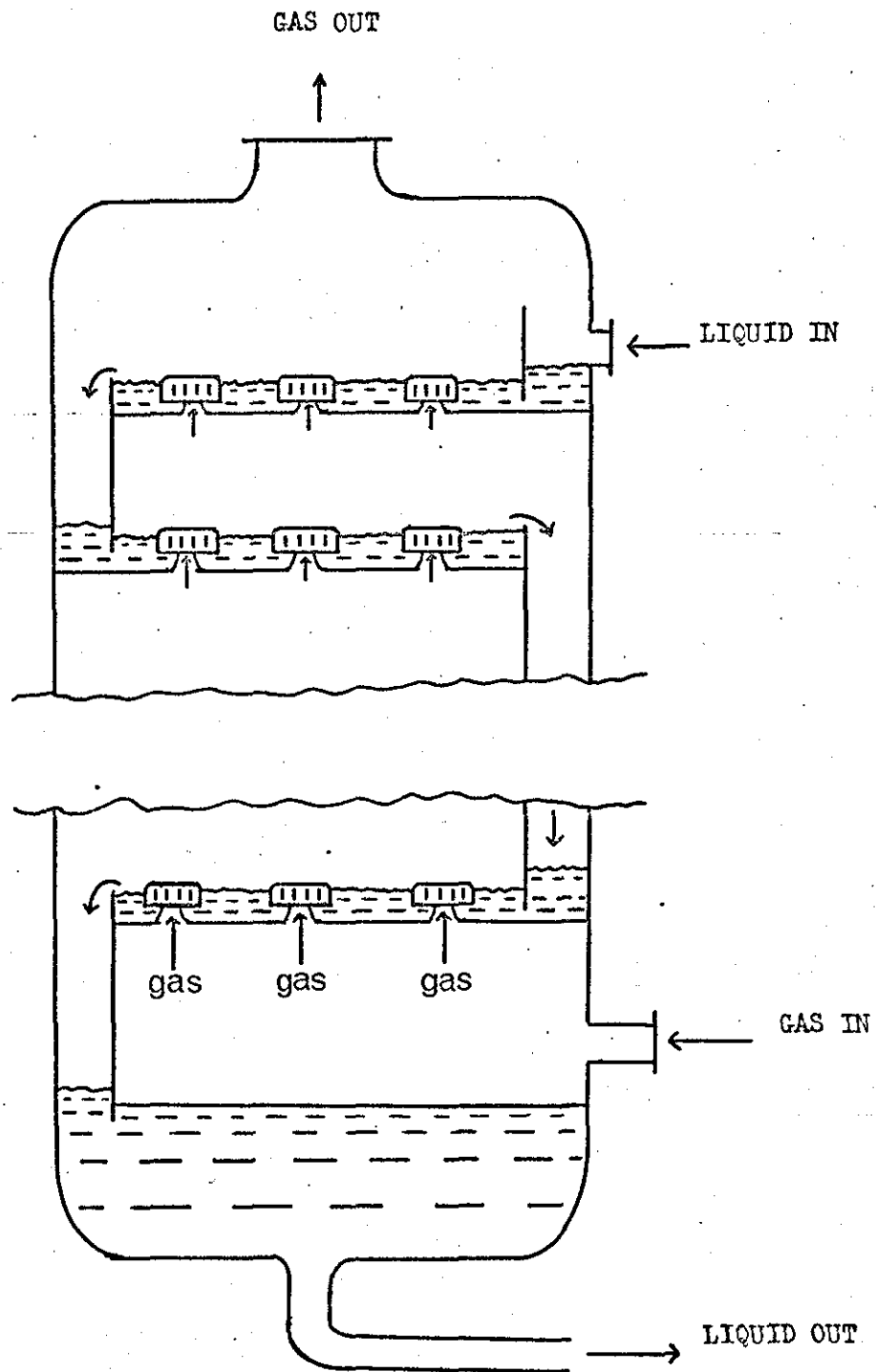
Fig. 3.3.2. Plate tower.

of each cap. The gas passes through these notches or slots at high
speed and passes into and up through the liquid pool in the form of
irregular bubbles of all shapes and sizes. When the gas velocity
is high, the resultant violent agitation of the liquid and the escape
of gas from its surface causes considerable foam and splashing so that
the space between the plates may operate as a spray chamber.

In addition to bubble caps, various types of sieves, and porous
plates may be used to obtain a similar bubbling action.

(c) The Spray Tower.

Fig. 3.3.3 shows a diagram of a typical spray tower. Sprays are
usually produced by forcing the liquid stream through a nozzle or
nozzles under pressure. The gas stream usually flows up from the
bottom of the tower, whereas the liquid may be sprayed either up or
down the tower. The problem of designing an efficient spray tower
reduces to that of providing sufficient interfacial area in the spray
chamber in the form of liquid drop sizes suitable for easy handling
in the gas stream.

(d) Stirred Vessels.

A diagram of a typical stirred vessel is shown in Fig. 3.3.4.
The degree of dispersion and consequently the rate of absorption of
the gas is optimized by introducing the gas from the open end of
tubes located just below a spinning impeller. The hooded ring
surrounding the impeller aids in projecting the stream downwards and
therefore provides a longer time of contact between the gas and the liquid.

GAS OUT

Fig. 3.3.3. Spray tower.

SPRAY MANIFOLD

NOZZLE

GAS IN

LIQUID IN

LIQUID OUT

Fig. 3.3.4. Stirred vessel.

TURBINE IMPELLER

GAS OUT

HOODED RING

GAS IN

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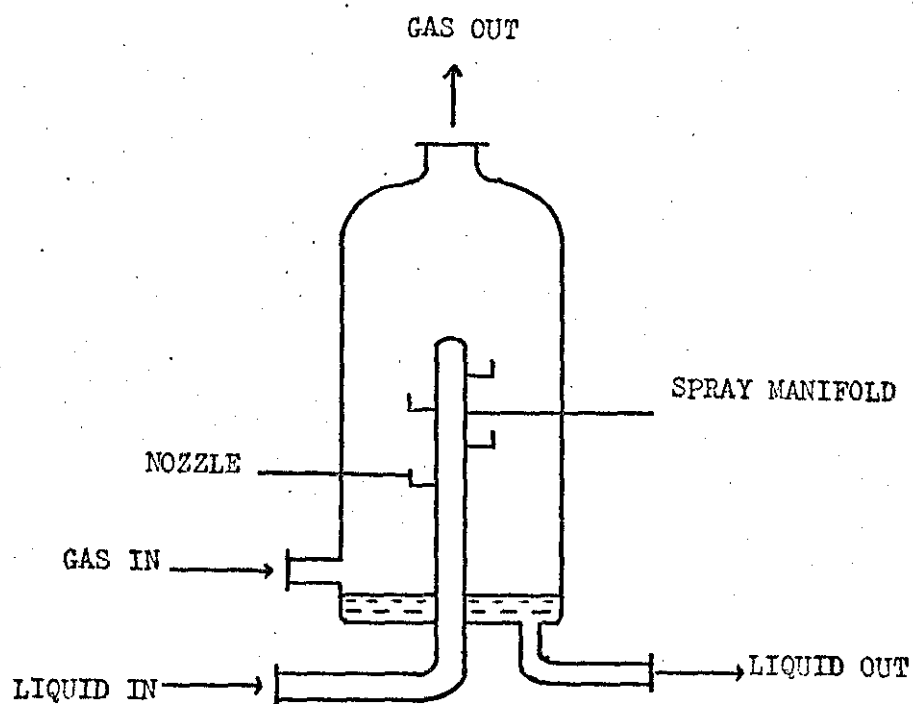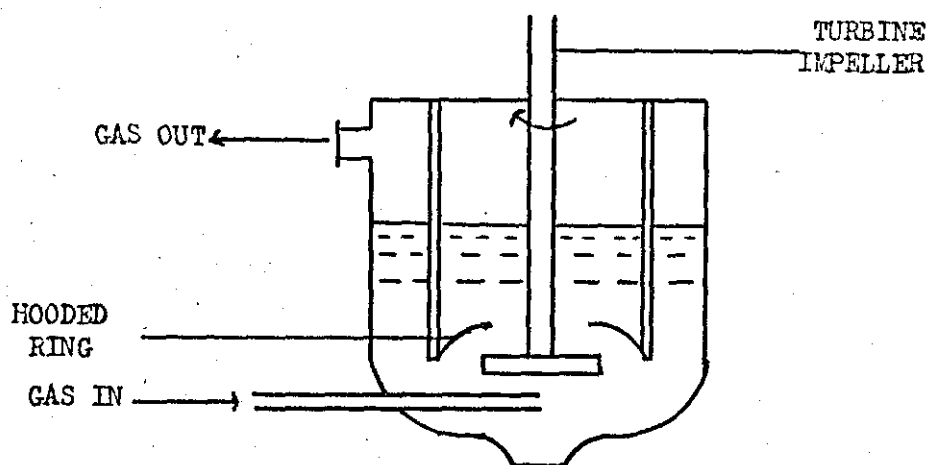
Equipment of this type usually operates batchwise. Packed towers and plate columns are normally capable of promoting greater rates of absorption than stirred vessels. However, stirred vessels are especially useful when a slurry or emulsion must be treated with a gas or when, as in several cases in this project, the product (e.g. a polymer) may precipitate out of solution. In such cases, the use of packed or plate towers would present numerous difficulties in the handling of materials.

4. METHOD OF APPROACH TO THE PROJECT

As stated in the introduction, the purpose of this project
was to develop the kinetics of oxidative coupling reactions which
use copper-amine catalysts; it was thought that this would involve the
study of mass transfer effects of these gas-liquid systems, together
with the kinetics involved in these catalytic oxidation reactions.

The general direction and subsequent course of this project
can be attributed to an interesting phenomenon encountered during a
preliminary investigation of the oxidative coupling of 2-aminothiophenol.
The phenomenon encountered was the consumption of more oxygen than
that which would be expected from the reaction postulated below. From
knowledge of the oxidative coupling of thiols and amines, the oxidative
coupling of 2-aminothiophenol using a copper (I) chloride pyridine
catalyst may be expected to proceed as follows:-

$$2n \, \langle\bigcirc\rangle\text{-SH} \xrightarrow[\text{CuCl/Py}]{\frac{3n}{2} O_2} \left[\langle\bigcirc\rangle\text{-N=N-}\langle\bigcirc\rangle \right]_n + 3n \, H_2O \quad (4.1)$$
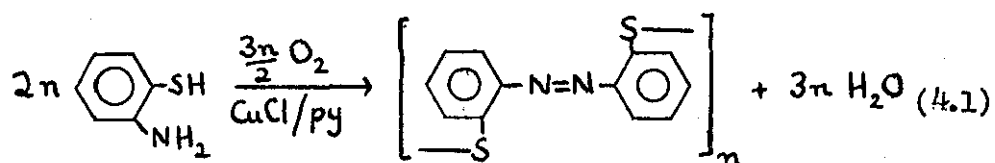
In this reaction 2n moles of 2-aminothiophenol would require
3n/2 moles of oxygen for complete polymer formation. It was found
that an additional 50% oxygen was consumed. No such phenomenon as
this had previously been reported for oxidative coupling reactions
using the copper-amine catalyst; thus it was decided that this
phenomenon required further investigation. The resulting black
"polymer" was not soluble in any of the common organic solvents,
concentrated sulphuric acid being the only solvent in which it would
dissolve. Because of this property, the polymer may prove to be useful.

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Three possible explanations for the extra oxygen consumption are as follows:-

(a)   Oxidation of the benzene ring.

(b)   Further oxidation of the thiol or disulphide groups.

(c)   Further oxidation of the amine or azo groups.

(a)   The benzene ring is usually stable in vigorous oxidizing conditions and thus it is very unlikely that it would be oxidized in the relatively mild oxidizing conditions of the copper (I) chloride pyridine catalyst system.

(b)   Further oxidation products of disulphides obtained in hydrolytic solvents are described by Savige and Maclaren (38). These are: disulphide monoxide or thiolsulphinate (RSOSR); disulphide dioxide or thiolsulphonate (RSO_2SR); disulphide trioxide (RSO_2SOR); disulphide tetroxide (RSO_2SO_2R); sulphenic acid (RSOH); sulphinic acid (RSO_2H) and sulphonic acid (RSO_3H) (where R is an alkyl or aryl group).

(c)   Oxidation products of aniline, obtained under various oxidizing conditions are discussed by Ginsburg (51). He reported that there are two modes of oxidation of the aniline molecule:-

(1)   Certain oxidizing agents supply oxygen to the aniline molecule and certain monomolecular and dimolecular products are obtained. These are: Phenylhydroxylamine (C_6H_5NOH); Nitrosobenzene (C_6H_5NO); Nitrobenzene ($C_6H_5NO_2$); p-Benzoquinone (OC_6H_4O); Azobenzene ($C_6H_5N=NC_6H_5$); Azoxybenzene ($C_6H_5 \overset{\underset{|}{}}{N}=NC_6H_5$, with O) and Phenylquinonediimine (Fig. 4.1).

$$C_6H_5N = \langle \rangle = NH$$
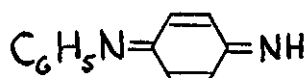
Fig. 4.1 Phenylquinonediimine

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(2)   The majority of oxidizing agents, however, abstract a
hydrogen atom from aniline leading to radical formation.   These products
include azobenzene phenylquinonediimine, benzoquinone and deeply-
coloured azopolymers ("aniline black").

It was decided to investigate more fully the oxidative coupling
of thiophenol and also of aniline, paying particular attention to mass
transfer effects.   This would serve as a good basis from which to study
the oxidative coupling of aminothiophenols.   Aniline and thiophenol
were reported to give azobenzene and diphenyl disulphide respectively
as the only products of oxidative coupling using the copper (I) chloride
pyridine complex (see sections 2.6 and 2.7).

It was found that under certain conditions, diphenyl thiolsulphinate
(PhSOSPh) as well as diphenyl disulphide was formed in the oxidative
coupling of thiphenol.   The effect of mass transfer on both the oxidation
rates and selectivity of the reaction was then studied.   In 1962,
Monsanto Chemicals Limited (53) reported that thiolsulphinates were
not at present used commercially as antioxidants, however, the discovery
of a relatively cheap method of their production could regenerate
interest in their use as such.   The synthesis of thiolsulphinates by
this oxidative coupling reaction could well be a relatively cheap
process.   Thus the extensive study in this present project, of the
oxidative coupling of thiophenol may be useful not only as a basis
for the study of the oxidative coupling of aminothiophenols, but also
as a synthetic method of producing thiolsulphinates.

No other product, other than azobenzene was detected in the

product of the oxidative coupling of aniline.

The kinetics of the oxidative coupling of 4-aminothiophenol together with the related diamines and dithiols, were then investigated further. 4-aminothiophenol was used rather than 2-aminothiophenol, to eliminate any possible steric effects.

5. EXPERIMENTAL METHOD.

5.1 Reaction Rate Measurements
for Oxidative Coupling Reactions.

5.1.1. Materials.

Cuprous chloride was prepared by bubbling sulphur dioxide through dilute acetic acid containing a cuprous chloride/cupric chloride mixture (B.D.H. supply). The off-white sludge of cuprous chloride was filtered, washed successively with water, methanol and petroleum ether and dried in an oven at $50^{\circ}C$. The powder could be kept in a sample tube in a desiccator for several months without losing its off-white colour.

Pyridine (Fison's Analar) was redistilled from sodium hydroxide pellets and dried over molecular sieves. Thiophenol (B.D.H) was redistilled before use; p-phenylenediamine (Fison's Laboratory Reagent) was recrystallised from benzene. Fresh supplies of aniline (B.D.H. Analar), 2-aminothiophenol(Ralph Emmanuel), 4-aminothiophenol (Ralph Emmanuel) and toluene-3,4-dithiol were used without further purification. Commerical grade oxygen (B.O.C., 99.5% purity) was used.

5.1.2 Apparatus.

The usual method employed to determine the rates of oxidative coupling reactions has been the measurement of the rate of oxygen absorption, measuring the volume change at constant pressure (14,17,25). As previously stated (section 2.4.6) a gas burette connected to a U-tube manometer is the conventional apparatus used for these measurements. Brooks (25), however, used a gas burette inside which was a hollow glass plunger containing mercury. The gap between the plunger and the burette was sealed with mercury, which was supported

on a "lip" around the edge of the plunger. This system, he reported, was near to being a "frictionless piston" and provided a good means of following oxygen consumption. This sytem was developed further and used in this present project.

Precision bore tubing (0.8 cm diameter $\pm$ 0.01 mm) was used for the gas burette and the plunger was made of stainless steel, of the shape shown in Fig. 5.1.1; it was carefully machined on a lathe to just fit into the tubing. Mercury was used to obtain an airtight seal between the plunger and the walls of the burette. A meter rule was placed behind the gas burette in order to obtain readings of the distance moved by the float.

The gas burette was kept in chromic acid when not in use. "Brasso" was used to polish the stainless steel plunger; this gave a very smooth surface, reducing the friction between the plunger and the walls.

Magnetic Stirrer Apparatus (Fig. 5.1.1.).

Fig. 5.1.1 shows a diagram of the "magnetic stirrer" apparatus used for most of the experiments. A suba-seal cap was inserted at A and the substrate was then injected through this using a hypodermic needle. Alternatively an arrangement shown in Fig. 5.1.2 was used in some experiments. To start the reaction using this arrangement, the tube C was rotated about the ground glass joint D, thus adding the substrate solution to the catalyst solution. It was thought that this method would be advantageous in that there would be no change in the closed volume of the reaction chamber and thus any initial absorption or evolution of gas could be detected (see section 6.1.1. (b)).

RUBBER
BUNG

WATER OUTLET
(RETURNED TO
WATER BATH)

METER RULE

STAINLESS STEEL
PISTON

GAS BURETTE

MERCURY
SEAL

METAL SPRING

FLEXIBLE JOINT

GLASS SEAL

WATER JACKET

MERCURY TRAP

B

A

GAS
INLET

GLASS SEAL

WATER INLET
(FROM CONSTANT
TEMPERATURE
WATER BATH)

CATALYST
SOLUTION
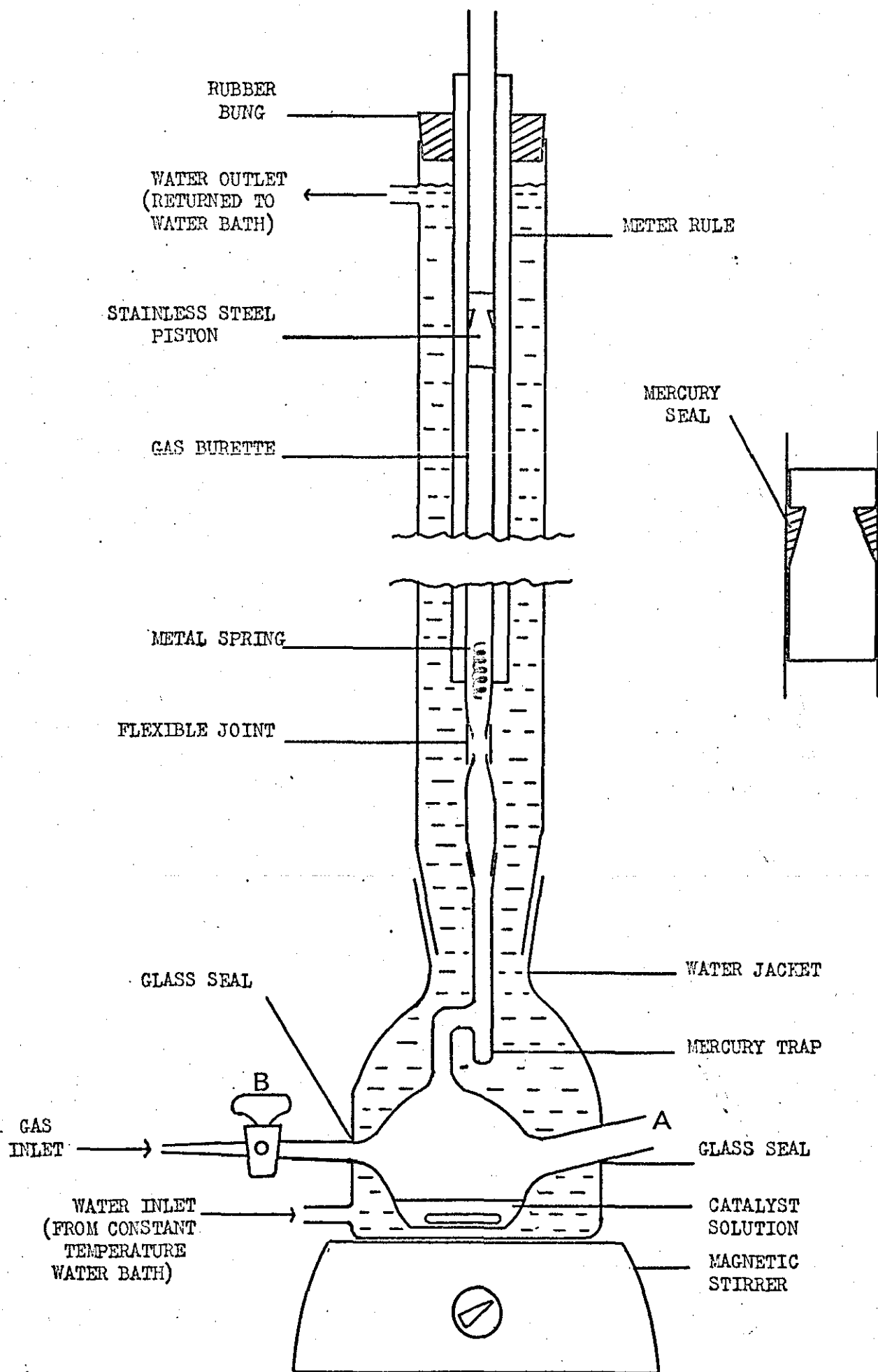
MAGNETIC
STIRRER

Fig. 5.1.1. Magnetic stirrer apparatus.
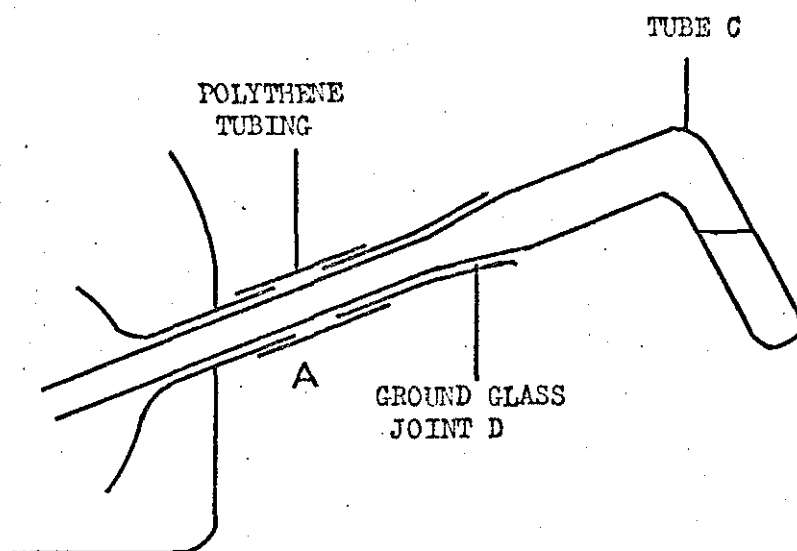
Fig. 5.1.2. Arrangement for adding the substrate
solution to the catalyst solution.
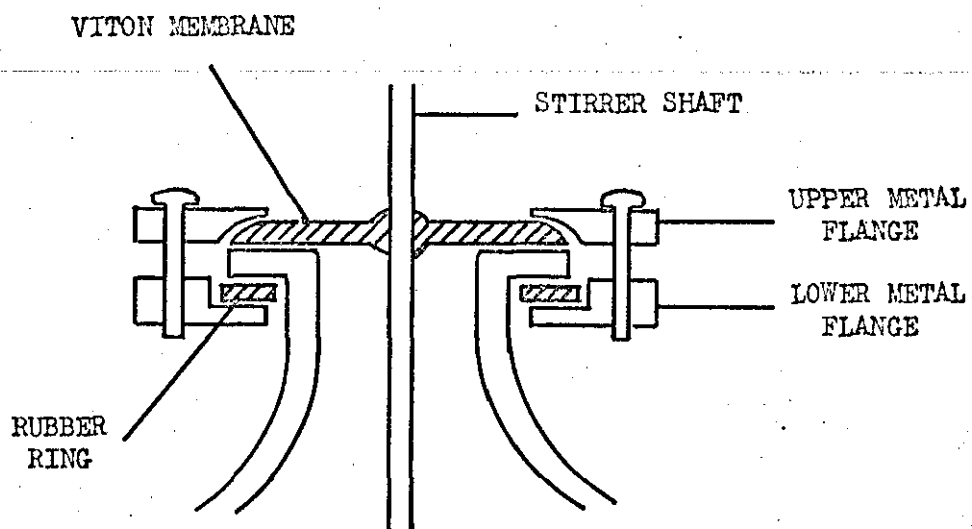
Fig. 5.1.4. Membrane sealing unit.

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A suba-seal cap was used for experiments when it was required to remove samples from the reaction mixture during the course of a reaction. A syringe with a 5 inch hypodermic needle was used for sampling. The metal spring acted as a cushion if the stainless steel plunger was accidently allowed to drop by opening the gas tap. The complete apparatus was kept at a constant temperature by means of an integrated water jacket through which water was circulated from a thermostatically controlled water bath. The apparatus was similar to a gas thermometer and was very sensitive to small changes in temperature, even responding to the small variations in temperature ($\pm$ 0.25°C) of the water bath.

5.1.3. Procedure.

After addition of the catalyst solution to the reaction flask, the apparatus, including tube C, when used, was flushed out with oxygen, the plunger not having as yet been inserted. Gas tap B was then closed and either the suba-seal or the arrangement of Fig. 5.1.2 was inserted at A. The gas tap B was opened momentarily to allow the plunger to drop to a suitable level. About 15 - 30 minutes was allowed for the apparatus to reach thermal equilibrium; this had been attained when the plunger registered a steady reading. On addition of the substrate solution, the stop-watch was started and readings were taken at suitable intervals during the course of the reaction. Stirring was provided by means of a magnetic stirrer, set at a constant speed of revolutions for all reactions.

To eliminate the tedious procedure of removing and replacing the plunger between sucessive experiments the following method was adopted. At the end of an experiment, the plunger was lowered to the bottom

of the gas burette and the apparatus was then flushed out with oxygen.
The suba-seal cap, or tube C, was subsequently inserted at A and more
oxygen was passed into the apparatus through gas tap, B, in order
to raise the plunger to a suitable level. This meant that the section
of the apparatus from C to D was probably not completely flushed out
with oxygen. However, since this section of the apparatus represented
less than 5% of the reactor volume, it was assumed that this would
have a negligible affect on the results. The significance of this
assumption is discussed further in section 6.2.1.

The catalyst solution was prepared by dissolving a known weight
of copper (I) chloride in pyridine. If necessary, the required
concentration was obtained by sucessive dilution of a stock solution.

In the experiments of section 6.1.3., where the substrate
(thiophenol) concentration was varied over a wide range, the volume
of oxygen consumed in these reactions obviously also varied over a
wide range. This necessitated slight alterations to the procedures
for measuring the oxygen consumption. At low substrate concentrations,
small bore diameter (1.5 mm) tubing was used for the gas burette,
with a bead of mercury being used instead of the piston. This modification
was considerably more accurate than the original arrangement. At
high substrate concentrations, the volume of oxygen consumed was equal
to several times the volume of the gas burette. In these experiments
each time the piston almost reached the bottom of the gas burette,
additional oxygen was injected into the system, via gas tap B, to pump
the piston up to the top of the burette. By extrapolating the readings
just before and just after the injection of additional oxygen, the
interim readings could be accurately estimated.

At a certain stage in the experimental work, it was desirable to increase the gas-liquid mixing by the use of a "vibromix" stirrer. This necessitated the designing of a new piece of apparatus to incorporate this stirrer. A diagram of the vibromix apparatus is shown in Fig. 5.1.3. Fig. 5.1.4 shows a diagram of the membrane sealing unit used to obtain an airtight seal around the stirrer shaft. The lower metal flange had to be cut in half in order to mount it onto the sealing unit. The upper and lower flanges are shown in Fig. 5.1.5.

The Vibromix Stirrer.

The vibromix stirrer consists of a vibratory motor driving a shaft up and down in short strokes at mains frequency (50 cycles/sec). The shaft does not rotate and thus a membrane containing a central orifice through which runs the shaft provides a good seal. The amplitude of vibration can be regulated from zero to $1/16$ inch. At the bottom of the shaft is a glass disc containing a number of holes tapered downwards (Fig. 5.1.6); these force the liquid and/or gas down against the bottom of the flask and provide a good dispersion of bubbles in the liquid. The disc is situated on the surface of the liquid to give optimum gas-liquid mixing. Both the shaft and the disc were of pyrex glass.

The action of the vibromix stirrer caused some of the reaction mixture to be sprayed onto the sides and ceiling of the reaction flask, and thus a P.T.F.E. sleeve, rather than silicone grease was used to provide an airtight seal at the ground glass joint. In a separate experiment, it was discovered that silicone grease discoloured the

GAS BURETTE

WATER OUTLET
(RETURNED TO
WATER BATH)

METER RULE

STAINLESS
STEEL
PISTON

STIRRER
SHAFT

METAL SPRING

FLEXIBLE
JOINT

MEMBRANE
SEALING
UNIT

P.T.F.E.
SLEEVE

A'

OUTLET E
(RUBBER
BUNG)

B'

MERCURY
TRAP

WATER INLET
FROM CONSTANT
TEMPERATURE
WATER BATH)

CATALYST   FLEXIBLE
SOLUTION   JOINT
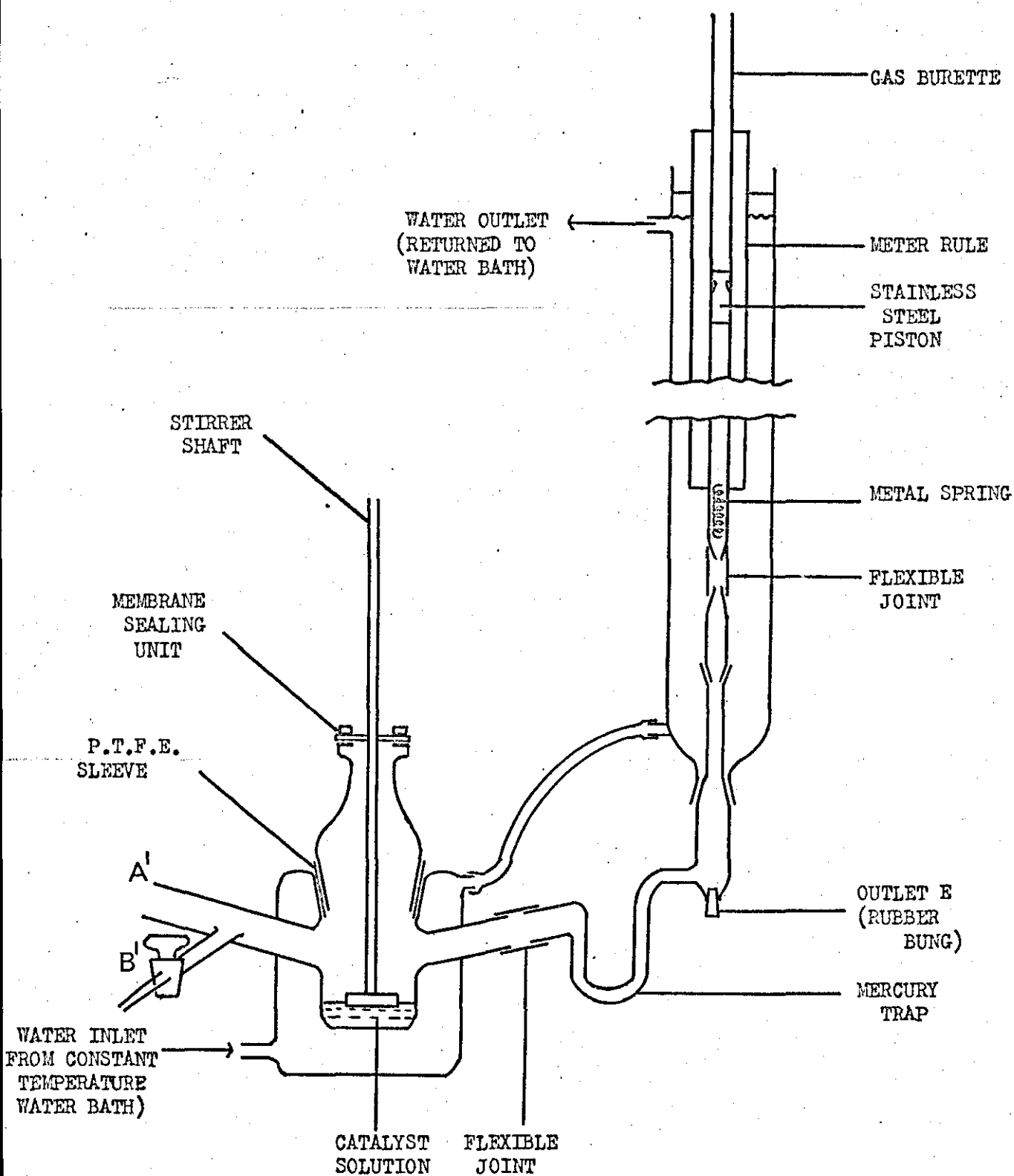
Fig. 5.1 .3. Vibromix stirrer apparatus.
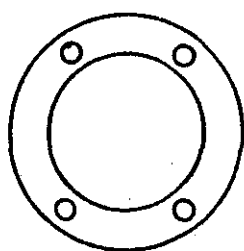
<table>
<tr><td>a</td><td>b</td></tr>
<tr><td>Upper metal
flange.</td><td>Lower metal
flange.</td></tr>
</table>
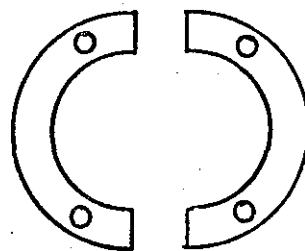
Fig. 5.1.5.   Metal flanges used on the membrane
sealing unit.
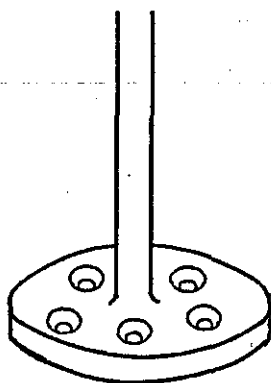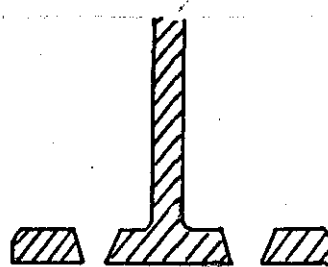
a   b

Fig. 5.1.6. Vibromix stirrer disc.

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catalyst solutions and thus this was unsuitable for use on this joint. To minimize the heat loss, lagging was used on all parts of the apparatus that were not surrounded by the water jacket.

The experimental procedure used was similar to that used for the magnetic stirrer apparatus. As for the magnetic stirrer apparatus, the tedious process of removing and replacing the plunger between sucessive experiments could be eliminated. To do this the piston was lowered to the bottom of the gas burette; the suba-seal or tube C was inserted at A' and the rubber bung was removed from outlet E. The apparatus was then flushed out with oxygen, after which the rubber bung was replaced and more oxygen was passed into the apparatus to raise the plunger to a suitable height. In an attempt to produce consistent stirring characteristics for a series of experiments, the apparatus was not dismantled between experiments. A syringe together with several 5 inch hypodermic needles, the tips of which were bent at various angles, were used to rinse the inside of the flask with solvent. Analar acetone was used for the final rinse after which a stream of oxygen was passed through the flask to remove all traces of the solvent.

The above experimental procedure was used for all oxidative coupling reactions reported in this present project.

From the readings of the distance moved by the plunger, the rates of oxygen absorption (moles/litre/sec) and the percentage oxygen consumption for a given reaction could be calculated (see appendix B).

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5.2 Determination of Diphenyl Thiolsulphinate Concentration.

The concentration of diphenyl thiolsulphinate was determined iodometrically by the method described by Barnard and Cole (54). In glacial acetic acid under anaerobic conditions, thiolsulphinates liberate an equivalent amount of iodine from iodide ions.

Procedure.

At the completion of the thiophenol oxidation reaction, the copper chloride pyridine catalyst was deactivated by adding a known volume of glacial acetic acid or 880 ammonia to the reaction mixture. A suitable aliquot of the reaction mixture was then taken and added to the glacial acetic acid containing excess iodide. The iodine thus liberated was then titrated, under an atmosphere of carbon dioxide, against standard 0.01 N sodium thiosulphate, using starch indicator to detect the end point. From this titration reading, the percentage thiolsulphinate in the product could be calculated (see appendix C).

Copper-Ion Interference.

In the above determination of thiolsulphinate, iodine is liberated by the oxidation of iodide by copper (II) ions in addition to the iodine liberated by the thiolsulphinate.

$$2\ Cu^{2+} + 2\ I^{-} \longrightarrow 2\ Cu^{+} + I_2 \qquad (5.2.1)$$

$$I_2 + 2\ Na_2S_2O_3 \longrightarrow 2I^{-} + 4\ Na^{+} + S_4O_6^{2-} \qquad (5.2.2)$$
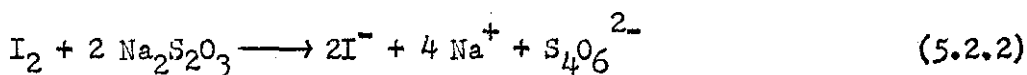
Thus the thiolsulphinate titration needed to be corrected to compensate for the copper (II) ion interference. The calculations for

this correction are also given in appendix C. In practice, this interference was negligible for catalyst concentrations below 0.005 g copper (I) chloride per 5.0 ml pyridine.

5.3 Determination of Thiophenol Concentration.

The thiophenol concentration was determined by the method described by Tamele et al (55). This was a potentiometric titration with silver/silver sulphide and glass electrodes using an alcoholic titration solution containing sodium acetate as the buffer. The titrant, silver nitrate, reacts with thiophenol to form a silver mercaptide precipitate.

$$PhSH + AgNO_3 \longrightarrow PhSAg + H^+ + NO_3^-$$
$$\text{white precipitate}$$
$$(5.3.1)$$
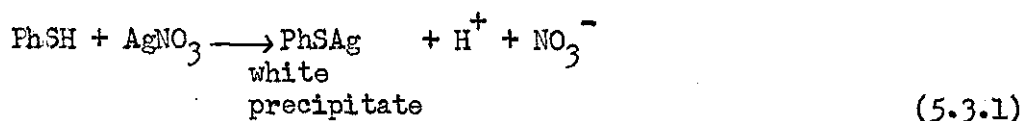
The silver/silver sulphide electrode consisted of a 2 x 1 cm section of silver foil electrolytically coated with silver sulphide by a preliminary titration of sodium sulphide. Fig. 5.3.1. shows a diagram of the apparatus used. Stirring was provided by means of a magnetic stirrer. A digital voltmeter was used to measure the e.m.f of the titration cell. The end point was detected by a marked change in potential (shown in Fig. 5.3.2) which occurred when the precipitation was complete.

Procedure for the Thiophenol Determination of Samples Taken During the Course of the Thiophenol Oxidation Reaction.

At certain times during the course of the thiophenol oxidation reaction, a suitable aliquot of the reaction mixture was removed from the reaction flask. This aliquot was added to about 150 ml. of
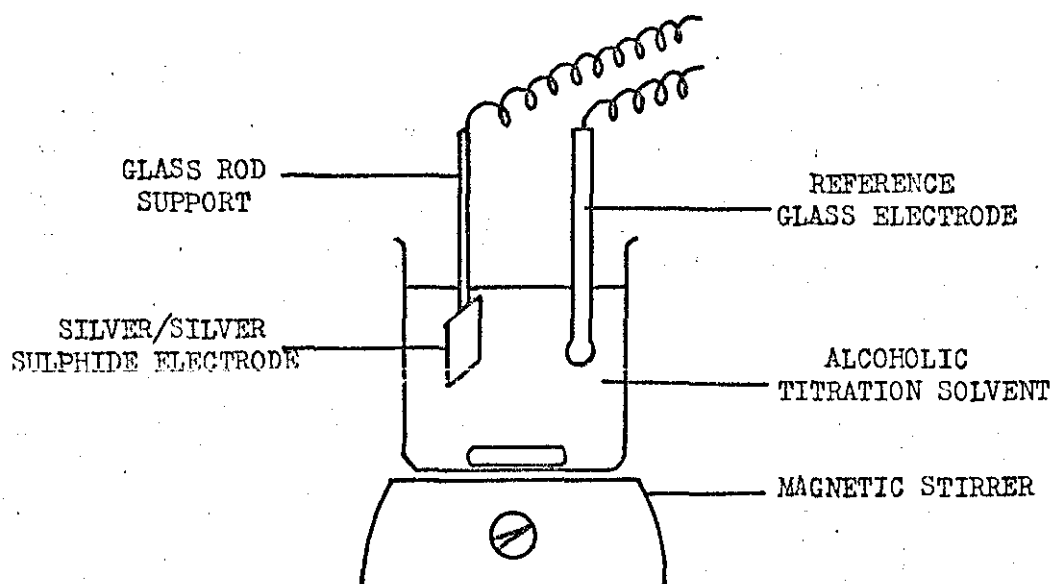
Fig. 5.3.1. Apparatus used for the thiophenol titrations.
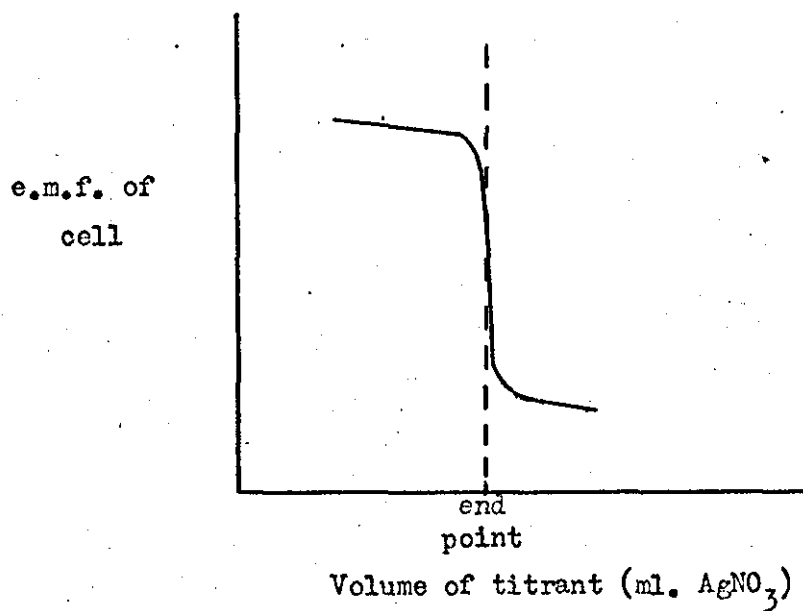
Fig. 5.3.2. e.m.f. of cell vs volume of titrant for the thiophenol titration.

titration solvent in the titration cell and immediately titrated against standard 0.01 N alcoholic silver nitrate. If the sample was left any length of time, further oxidation of thiophenol might occur.

Preliminary experiments with known amounts of thiophenol gave consistently low results; average readings were 94% of the theoretical values. No explanation has been found for these low results. The experimental work of Tamele et al was confined to alkyl thiols; no mention was made concerning the application of this method to aromatic thiols. Further investigation into the reason of these low results and the development of this method for aromatic thiols was considered to be outside the scope of this present project. However, since all the results were consistently low, the true values could be determined with sufficient accuracy by multiplying the experimental results by a correction factor (^{1}/0.94).

Normally, in potentiometric titrations, small portions of titrant are added to the titration cell and after each addition, sufficient time is allowed for the cell to reach a constant potential. The burette reading and the e.m.f are then recorded. Near the end point, smaller portions of the titrant are added to give greater accuracy. The end point is determined from a graph of e.m.f. vs volume of titrant added (Fig. 5.3.2). However, this is a lengthy procedure if, as in the thiophenol titration, an appreciable length of time is required after each addition to allow the cell to reach a constant e.m.f. When samples are taken out of the reaction mixture at different times during the course of one reaction run, the limited time between sucessive sampling did not allow such a lengthy procedure. However,

after considerable experience, it was possible to perform the titration
by observing only the initial behaviour of the unsteady cell potential
immediately after each addition of silver nitrate solution. A sufficiently
accurate end-point ($\pm$ 0.1 ml) could be obtained by this method. From
the titration reading the concentration of thiophenol in the sample
could be calculated (see appendix D).

5.4 Work-Up Procedure for obtaining poly(p-aminothiophenol).

Unless stated otherwise, all the oxidative coupling reactions of
p-aminothiophenol were commenced in an afternoon and left to proceed
throughout the night, the final reading being taken the following
morning. The reactions in which the vibromix stirrer was used were
terminated within three hours reaction time; this was because of the
vibromix stirrer motor overheating.

To precipitate the polymer out of solution, the reaction mixture
was added to a large volume of water acidified with dilute hydrochloric
acid; this produced a black suspension of the polymer. Much of the
polymer had already precipitated out of solution during the course of
the oxidation reaction. This precipitate was removed from the
reaction flask by mechanical means. The aqueous solution containing
the polymer suspension was neutralised with dilute hydrochloric acid.
Upon standing the polymer coagulated and was filtered; it was then
washed sucessively with dilute hydrochloric acid, water and acetone.
The polymer was dried in an oven at $40^{\circ}C$ for several hours.

5.5 Molecular Weight Determinations of Poly(p-aminothiophenol).

A Hewlett Packard 302 B vapour pressure osmometer was used for

molecular weight determinations. Dimethylacetamide was used as the solvent at an operating temperature of 65°C. Benzil was used to calibrate the instrument for this solvent.

5.6 Elemental Analyses of Poly(p-aminothiophenol).

The polymer samples were sent to Mikroanalytisches Laboratorium, Beller, Gottingen, Germany for elemental analyses for carbon, hydrogen, nitrogen and sulphur.

5.7 Infrared Spectra.

Infrared spectra of the polymers were recorded on a Perkin-Elmer 257 Spectrometer. Potassium bromide discs of the samples were prepared and used for obtaining these infrared spectra.

6 THIOPHENOL OXIDATION.

6.1 Results

6.1.1 Stirring Characteristics.

(1) Magnetic Stirrer Apparatus.

(a) No Stirring.

With 5.0 ml. of liquid contained in the magnetic stirrer apparatus, the interfacial area, with no stirring, was calculated to be 18.1 cm^2 and the depth of the liquid was 0.3 cm.

(b) With Stirring.

With stirring the profile of the reaction mixture was similar to that shown in Fig. 6.1.1.(b). This could be approximated to the profile given in Fig. 6.1.1.(c), in which case the interfacial area was 19.2 cm^2. Thus it can be seen that the magnetic stirrer provided no appreciable increase in the interfacial area. However, it gave an increased rate of surface renewal, provided agitation of the liquid and also probably contributed towards the mixing of the gas directly above the surface of the liquid.

(2) Vibromix Stirrer Apparatus.

(a) No stirring.

With 5.0 ml of liquid contained in the vibromix stirrer apparatus, the interfacial area was 12.6 cm^2 and the depth of liquid was 0.4 cm.

(b) With Stirring.

The use of vibromix stirrer provided a good dispersion of small bubbles within the bulk of the liquid and thus it was virtually impossible to estimate the interfacial area to any degree of accuracy.
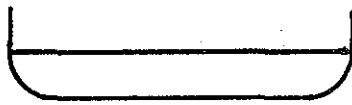
a

No stirring.

b

With stirring.
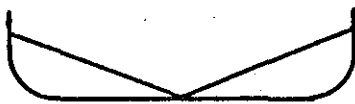
c

Approximate profile of (b)

Fig. 6.1.1. Profiles of the reaction mixture in the
magnetic stirrer apparatus.

6.1.2 Explanation of the Apparent Initial Absorption of a Small Amount of Gas Upon Mixing the Reactants.

From the tables of results (appendix A), it can be seen that upon adding the substrate solution to the catalyst solution, there appeared to be an immediate absorption of a very small amount of gas. It was thought that this may have arisen from the fact that the substrate solution was at a lower temperature than the catalyst solution (since it was not enclosed in the water jacket). Upon mixing of the reactants, the temperature of the reaction mixture would be depressed, thus slightly cooling the surrounding gas which would cause a contraction in the total volume giving the apparent absorption of a small amount of gas. This theory was tested by replacing the catalyst and substrate solutions by pure pyridine samples and mixing them under the same conditions used in a normal oxidation experiment. Upon mixing, the piston again dropped slightly, suggesting the absorption of a small amount of gas. However, after a while, the piston gradually moved up the burette to approximately the original position. This would be due to the water jacket reheating the cooled reaction mixture to the temperature of the initial catalyst solution. It was thus shown that the initial drop of the piston upon mixing the reactants was not in fact due to the absorption of gas but the effect resulting from a temperature difference between the catalyst and the substrate solutions.

6.1.3 Dependence of the Kinetics Upon Copper (I) Chloride Concentration.

(a) Use of the Magnetic Stirrer.

A series of preliminary experiments in which the rates of oxygen absorption were measured were conducted at various catalyst concentrations keeping the rest of the reaction conditons constant; the magnetic

stirrer was used. The equivalent amount of oxygen (100% oxygen consumption[1]) was consumed for reactions using relatively high catalyst concentrations. By decreasing the catalyst concentration progressively more oxygen was consumed. This suggested that a further oxidation product of thiophenol, other than the disulphide was being produced. As stated previously, Savige and Maclaren (38) reported that thiolsulphinates (RSOSR) and thiolsulphonates (RSO$_2$SR) are formed by the mild oxidation of disulphides. Thus it was thought that either one or both of these compounds may have been formed, in which case their formation might account for the extra oxygen consumed. Barnard and Cole (54) reported methods of the detection and estimation of these two compounds. The use of the given method for detecting the thiolsulphonates showed that this compound was not present in the final reaction mixture. However, an iodine test for detecting the presence of thiolsulphinate was positive, iodine being liberated from iodide ions in acidic solution by the thiolsulphinate according to equation 6.1.3.1.

$$PhSOSPh + 2I^- + 2H^+ \longrightarrow PhSSPh + I_2 + H_2O \qquad (6.1.3.1)$$
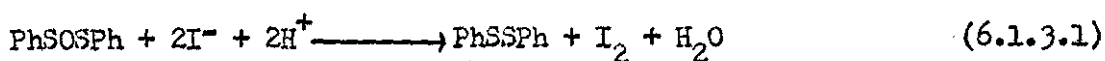
A quantitative determination of thiolsulphinate by the method given by Barnard and Cole for the product of a thiophenol oxidation reaction, showed that the extra oxygen that would be required to form the thiolsulphinate corresponded, within a few percent to the extra oxygen consumed in the reaction. Equations 6.1.3.2 and 6.1.3.3 show the stoichiometric requirements for the formation of these two products.

$$2 PhSH + \tfrac{1}{2}O_2 \longrightarrow PhSSPh + H_2O \qquad (6.1.3.2)$$

$$2 PhSH + O_2 \longrightarrow PhSOSPh + H_2O \qquad (6.1.3.3)$$
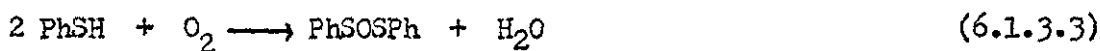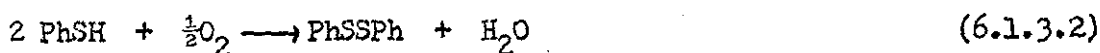
/ 1 See later in this same section /

The series of experiments at variable catalyst concentrations was then repeated; this time, in addition to measuring the rates of oxygen absorption, the product was analysed quantitatively for thiolsulphinate.

Typical graphs of the total oxygen consumption against time are shown in Fig. 6.1.3.1. No appreciable induction periods were detected. The term "100% oxygen consumption" is used to denote the stoichiometric amount of oxygen which is required to oxidize thiophenol to diphenyl disulphide. Thus the consumption of $\frac{1}{4}$ mole of oxygen in the oxidation of one mole of thiophenol to diphenyl disulphide is termed "100% oxygen consumption". Similarly in the oxidative coupling of aniline, diamines, dithiols and aminothiophenol, the term 100% oxygen consumption is used to denote the amount of oxygen which is required to form a product containing only disulphide and/or azo bonds.

The gradients of the graphs in Fig. 6.1.3.1. represent the rates of oxygen absorption. Table 6.1 gives experimental data showing the dependence of the initial rate of oxygen absorption upon the catalyst concentration. Also given in table 6.1 are the dependence of the initial rate of thiophenol consumption, the total oxygen consumption and the percentage thiolsulphinate in the product, upon the catalyst concentration. The method of calculation of the initial rate of thiophenol consumption is given in section 6.1.6.a. The percentage thiolsulphinate is defined as follows:-

$$\% \text{ PhSOSPh} = \frac{\text{moles of thiophenol which are consumed to produce the thiolsulphinate present at the end of the reaction}}{\text{total number of moles of thiophenol consumed in the reaction}}$$

(6.1.3.4)

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Oxygen consumption (moles/litre x 10^2).

16

D

C

12

B

E

8

A

F

A   0.05 grms   CuCl

B   0.005 grms   CuCl

4   C   0.0005 grms   CuCl

D   0.00005 grms   CuCl

E   0.00002 grms   CuCl

F   0.00001 grms   CuCl

0   600   1200   1800

Time (sec.)
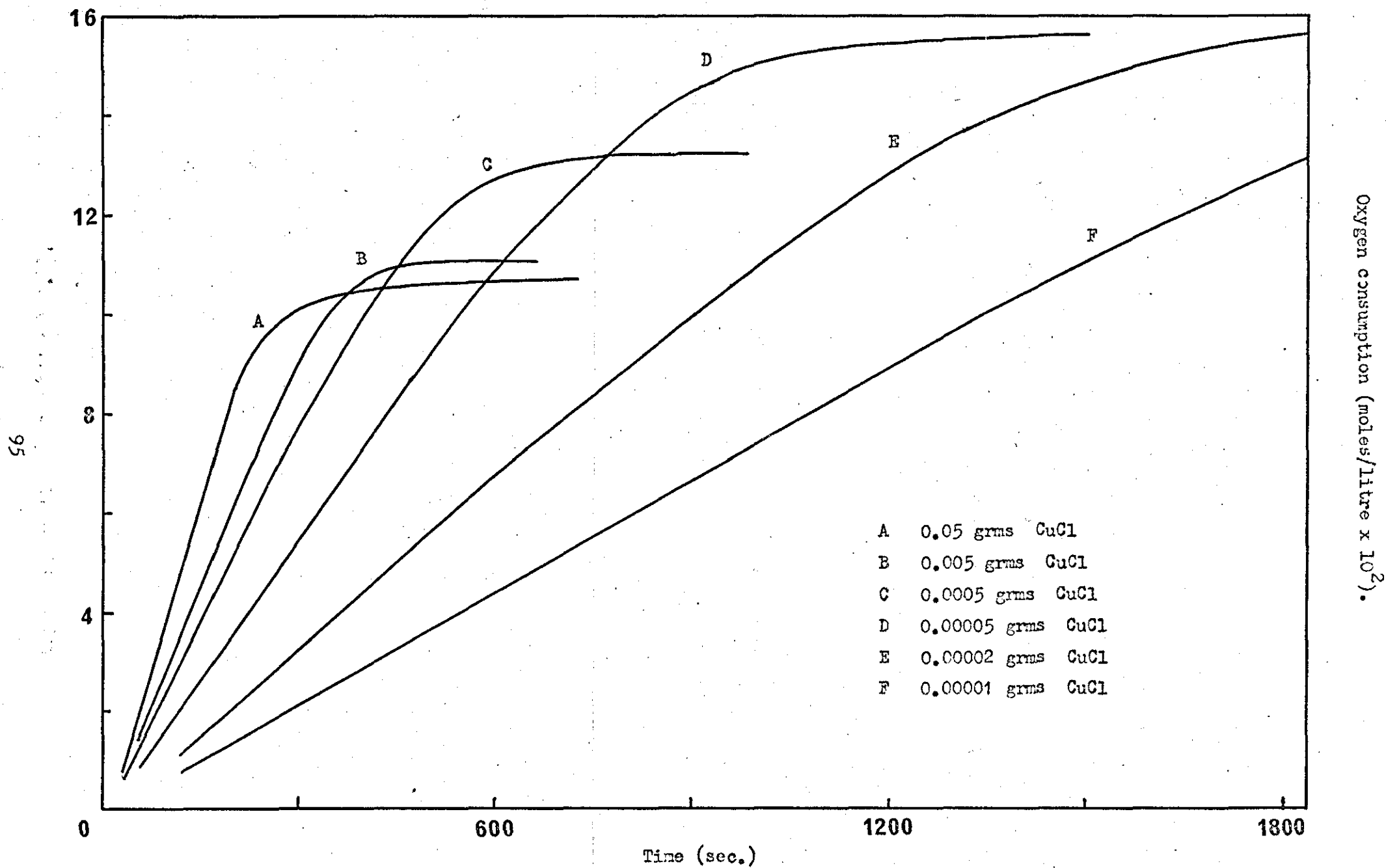
Fig. 6.1.3.1.   Oxygen consumption vs time.

Weight of CuCl (grm/5 ml. py)	$[CuCl]$	% Oxygen consumption	%PhSOSPh	$\dfrac{-d[O_2]}{dt}$ (X 10^4)	$\dfrac{-d[PhSH]}{dt}$ (X 10^4)
0.050	0.1010	96	$\langle 2$	4.50	1.13
0.0050	0.0101	97	$\langle 2$	3.30	0.825
0.00050	0.00101	111	4	2.58	0.630
0.00010	0.00020	131	32	2.36	0.495
0.00005	0.00010	138	32	1.76	0.370
0.00002	0.00004	143	41	1.14	0.225
0.00001	0.00002	143	47	0.80	0.155
0.000005	0.00001	143	31	0.50	0.110

The reaction conditions were: 5.0 ml pyridine (solvent); 0.25 g thiophenol (equivalent to 0.453 moles/litre); 25°C ; "pure" oxygen at atmospheric pressure.

Table 6.1

Results: dependence of the reaction upon the catalyst concentration using the magnetic stirrer.

Fig. 6.1.3.2 shows the graph of log (initial rate of oxygen absorption) vs log (catalyst concentration). This graph falls into two sections, A'B' and B'C'. It was possible that the region A'B' may have been a region where the rate controlling step of the reaction was determined by the chemical kinetics of the reaction, and the region B'C' may have been a region where the rate controlling step was the mass transfer of oxygen from the gas phase to the liquid phase. This theory would be supported by the findings of Brooks (25) who, as previously reported, suggested that at high catalyst concentrations, the oxidative coupling of phenols was controlled or modified by the mass transfer of oxygen from the gas phase to the liquid phase. Proof of this theory was sought by repeating the series of experiments under identical conditions but using different modes of stirring in order to either increase or decrease the rates of mass transfer. These experiments are described in section 6.1.3(b). If the region A'B' was a "kinetic control" regime then the graphs which might be expected from changing the mass transfer rates by using other modes of stirring are as shown in Fig. 6.1.3.3.

From table 6.1, it can be seen that the extra oxygen consumed corresponded, within a few percent, to the extra oxygen required for the formation of the thiolsulphinate. A plot of percentage thiolsulphinate vs log (copper (I) chloride) is shown in Fig. 6.1.3.4. These results together with other results in section 6.1 will be discussed in further detail in section 6.2.

(b) Use of Different Modes of Stirring.

A series of experiments at various catalyst concentrations were repeated under identical conditions to those described in section

97
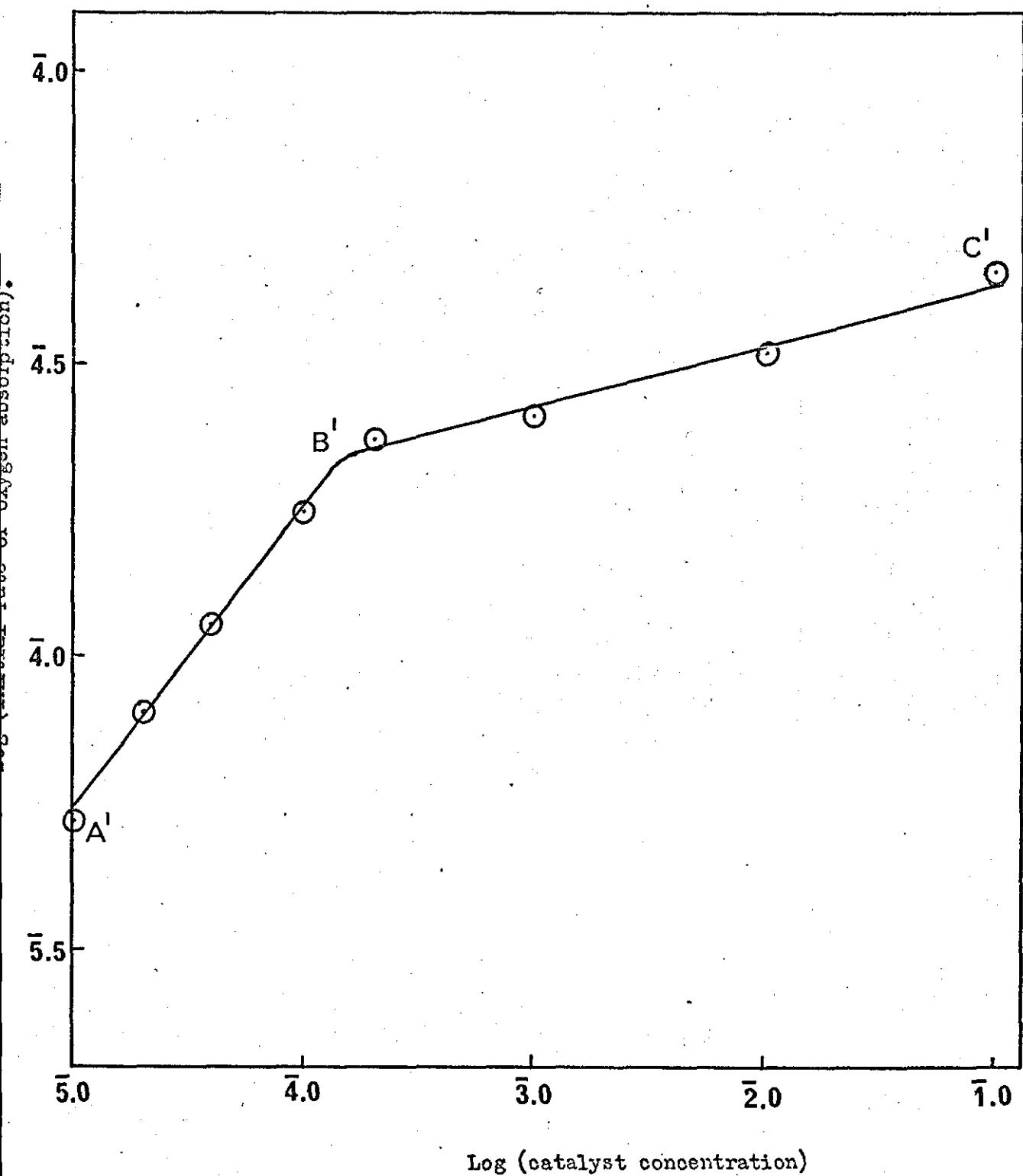
Fig. 6.1.3.2. Log (initial rate of oxygen absorption)
vs log (catalyst concentration).

98
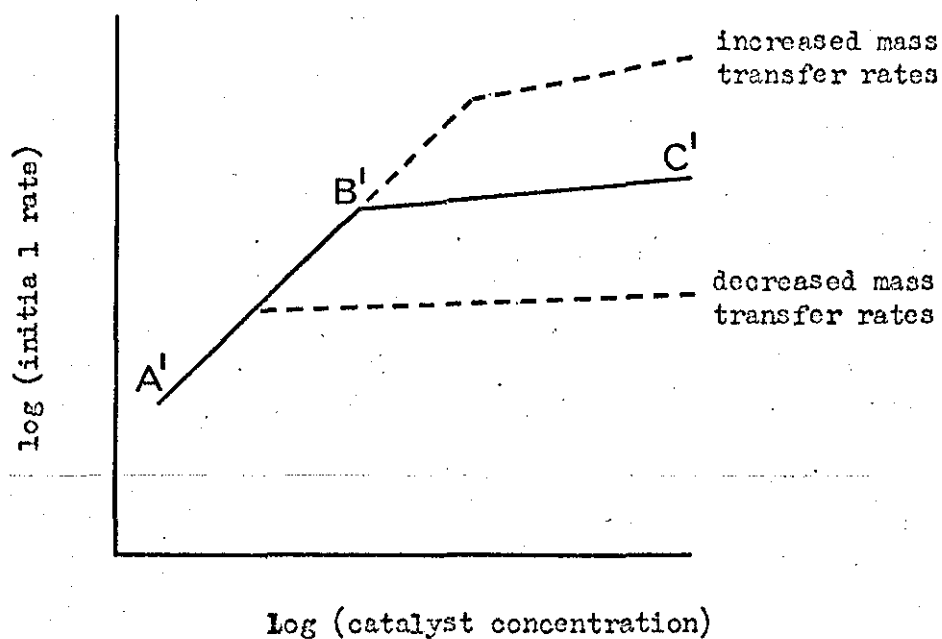
Fig. 6.1.3.3. Graphs which might be expected for
different modes of stirring.
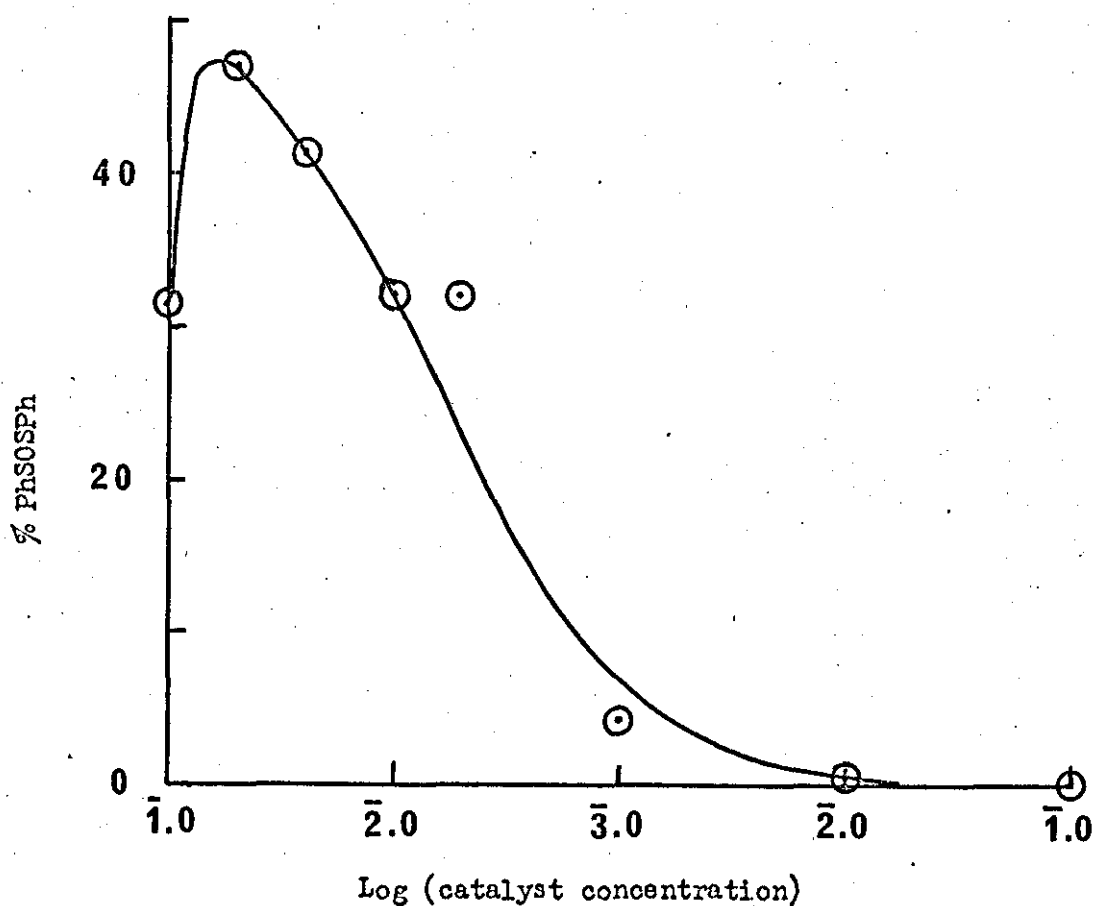
Fig. 6.1.3.4. % Thiolsulphinate vs log (catalyst
concentration).

6.1.3 (a), using the following modes of stirring:-

(1) Vibromix Stirring. This increased the gas-liquid mixing and thus increased the mass transfer rates.

(2) No Stirring, but using the magnetic stirrer apparatus. The magnetic stirrer was used for the first 15 seconds of the reaction (to mix the reactants) and then it was switched off.

Tables 6.2 and 6.3 summarize the results of the experiments using the vibromix stirrer and no stirring respectively. The graphs for all the three modes of stirring of log (initial rate of oxygen absorption) vs log (catalyst concentration) and percentage thiolsulphinate vs log (catalyst concentration) are shown in Figs. 6.1.3.5 and 6.1.3.6 respectively. Consideration of the graphs in Fig. 6.1.3.5 leads to the conclusion that the general regions AB and BC cannot be described as purely mass transfer and kinetic control regions respectively. The interpretation of these graphs will be discussed further in section 6.2.1.

(C)   Use of a Oxygen/Nitrogen Atmosphere.

The series of experiments at various catalyst concentrations were also repeated under the same conditions, using a magnetic stirrer but replacing the atmosphere of "pure" oxygen by an atmosphere consisting of 88% oxygen and 12% nitrogen. These results are summarized in table 6.4. The graphs of log (initial rate of oxygen absorption) vs log (catalyst concentration), and percentage thiolsulphinate vs log (catalyst concentration) are plotted together with the similar graphs of Figs. 6.1.3.2 and 6.1.3.4 in Figs. 6.1.3.7 and 6.1.3.8 respectively.

6.1.4 Dependence of the Kinetics on Thiophenol Concentration

A series of experiments was conducted at varying thiophenol concentrations keeping the rest of the reaction parameters constant. The results are summarized in table 6.5. These experiments were conducted at a very low catalyst concentration which, at a thiophenol concentration of 0.25 g/5.0 ml of pyridine, would fall in the middle of the region A'B' of Fig. 6.1.3.2. The graphs of log (initial rate of oxygen absorption) vs log

Weight of CuCl (grms/5 ml. py)	[CuCl]	% oxygen consumption	%PhSOSPh	$-\dfrac{d[O_2]}{dt}$ $(\times 10^4)$	$-\dfrac{d[PhSH]}{dt}$ $(\times 10^4)$
0.050	0.1010	111	$\langle 2$	22.8	5.70
0.0050	0.0101	114	4	11.3	2.77
0.00050	0.00101	133	25	6.10	1.34
0.00010	0.00020	152	35	4.43	0.915
0.00005	0.00010	159	47	3.08	0.590
0.00002	0.00004	151	53	1.39	0.255
0.00001	0.00002	167	51	0.57	0.105
0.000005	0.00001	142	12	0.24	0.055

Table 6.2.

Results: dependence of the reaction upon

the catalyst concentration using the

vibromix stirrer.

Weight of Cu Cl (grms/5 ml. py)	[Cu Cl]	% Oxygen consumption	%PhSOSPh	$-\dfrac{d[O_2]}{dt}$ $(\times 10^4)$	$-\dfrac{d[PhSH]}{dt}$ $(\times 10^4)$
0.0050	0.0101	101	⟨2	0.64	0.160
0.00050	0.00101	102	⟨2	0.49	0.125
0.00016	0.00032	105	2	0.43	0.105
0.00005	0.00010	107	5	0.38	0.095
0.000032	0.000064	107	6	0.27	0.065
0.00002	0.00004	116	12	0.24	0.055
0.00001	0.00002	120	14	0.165	0.040

Table 6.3.

Results: dependence of the reaction

upon catalyst concentration using

the magnetic stirrer.
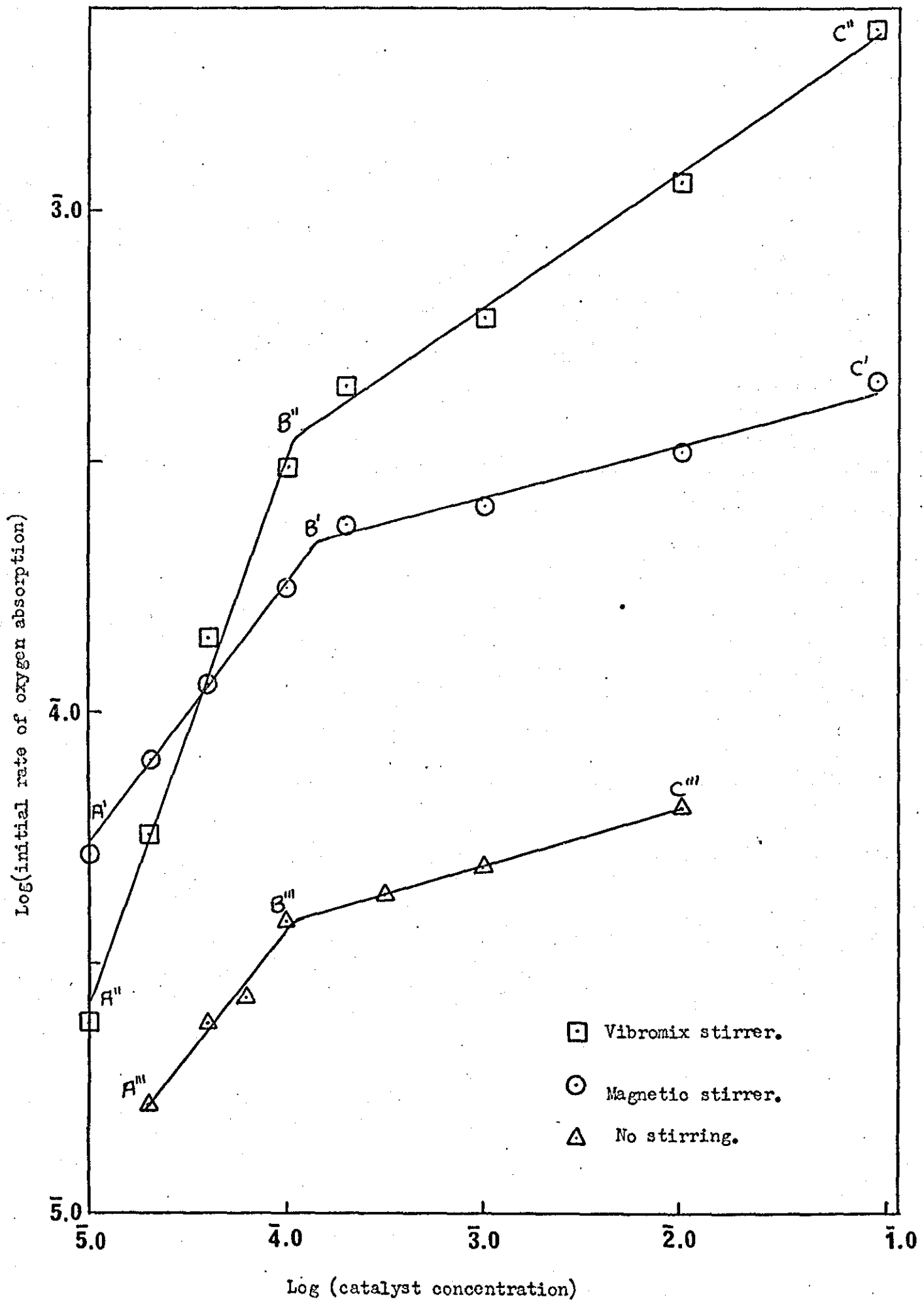
Fig.6.1.3.5. Log (initial rate) vs log (catalyst concentration) for three different modes of stirring.
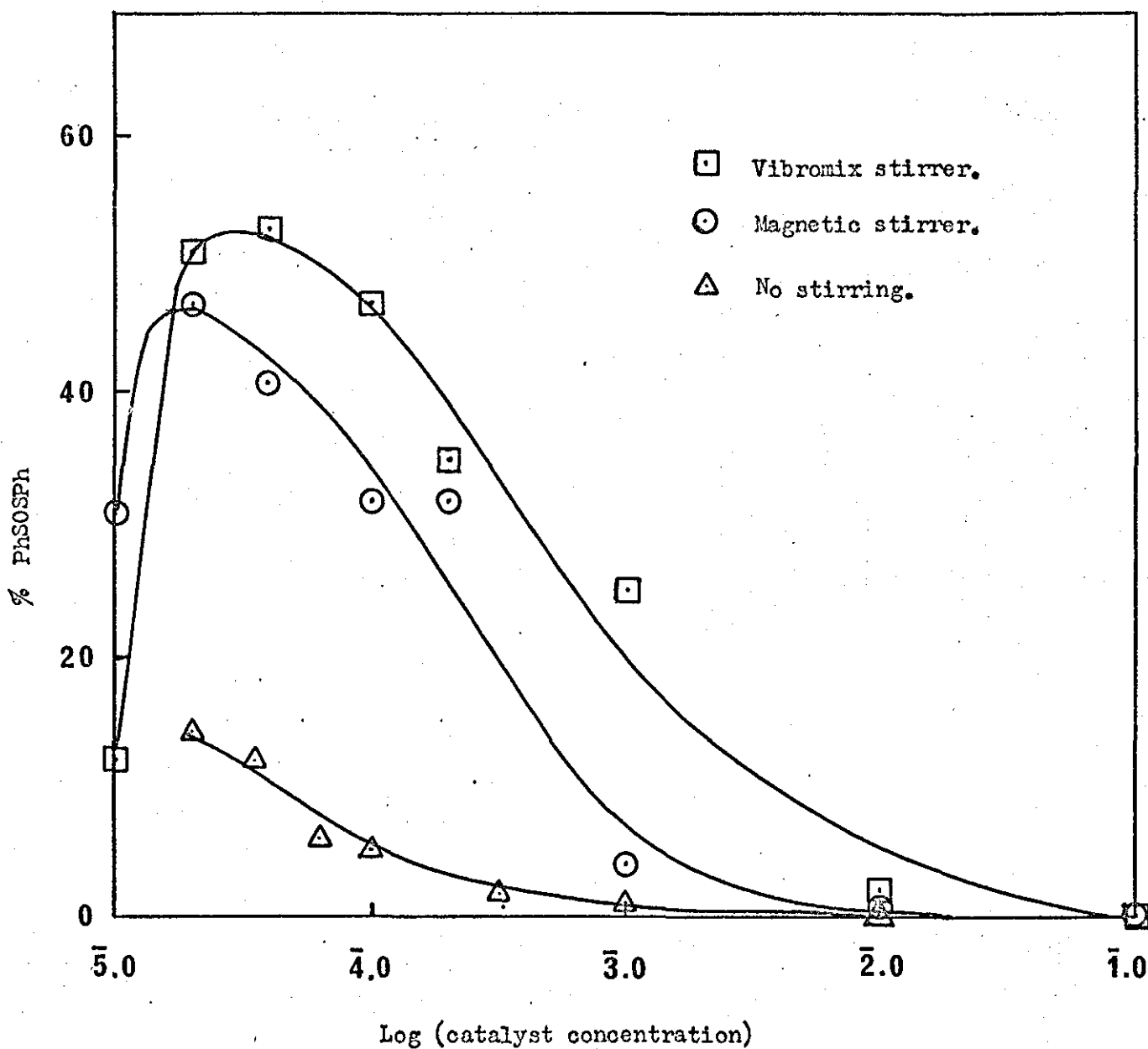
Fig. 6.1.3.6. % PhSOSPh vs log (catalyst concentration) for
three different modes of stirring.

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Weight of Cu Cl (grms/5 ml. py)	[Cu Cl]	% oxygen consumption	%PhSOSPh	$-\dfrac{d[O_2]}{dt}$ $(\times 10^4)$	$-\dfrac{d[PhSH]}{dt}$ $(\times 10^4)$
0.0050	0.0101	108	⟨2	2.24	0.560
0.00050	0.00101	111	5	1.88	0.460
0.00010	0.00020	129	24	1.81	0.400
0.000025	0.00005	137	32	1.15	0.240
0.00001	0.00002	144	39	0.63	0.125
0.000005	0.00001	144	n.d.	0.50	n.c.
0.0000025	0.000005	n.d.	n.d.	0.345	n.c.

(n.d. = not determined;   n.c. = not calculated.)

Table 6.4.

Results: dependence of the reaction upon the

catalyst concentration using a magnetic stirrer

and an oxygen/nitrogen atmosphere.
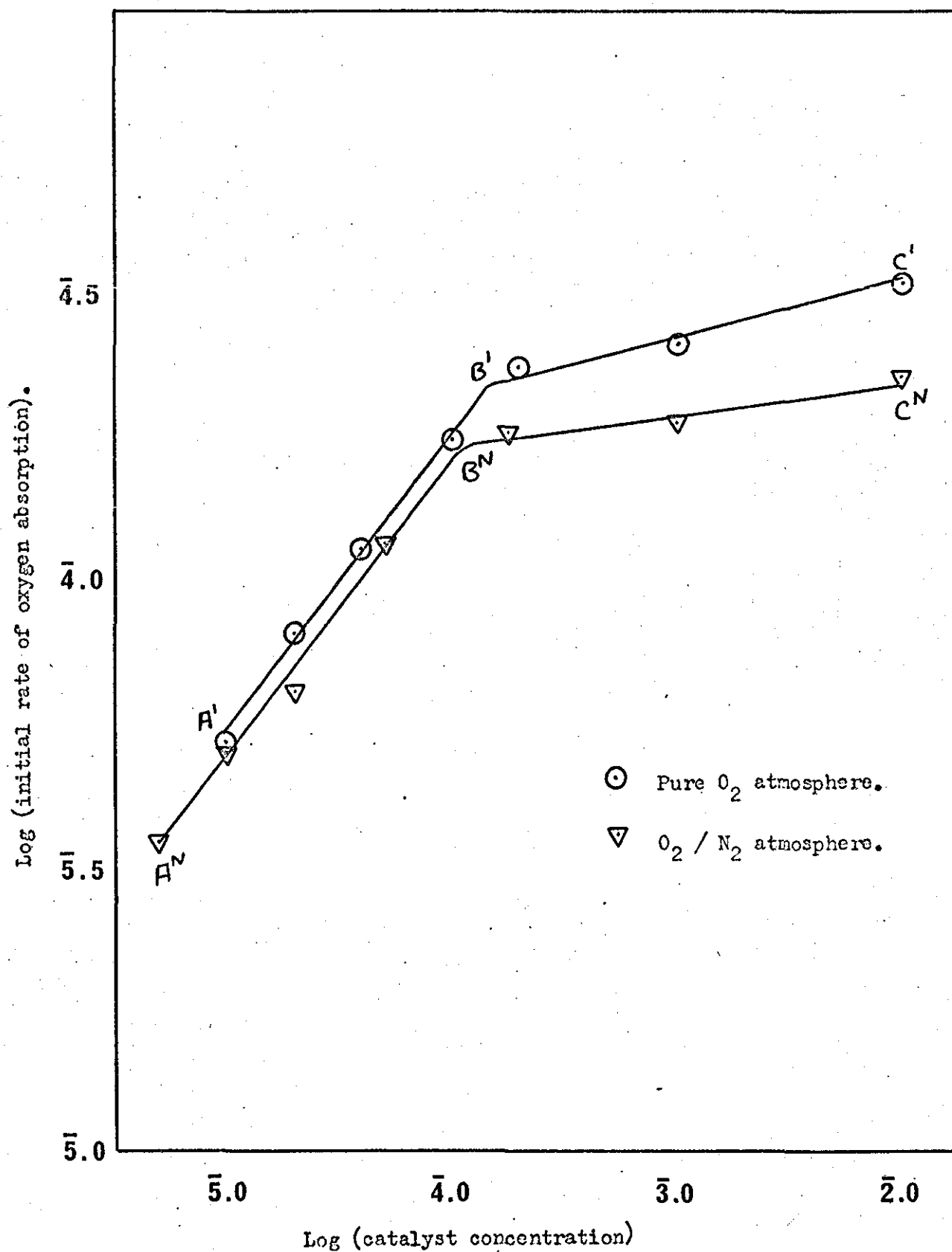
Fig. 6.1.3.7. Log (initial rate) vs log (catalyst concentration) for different atmospheres.

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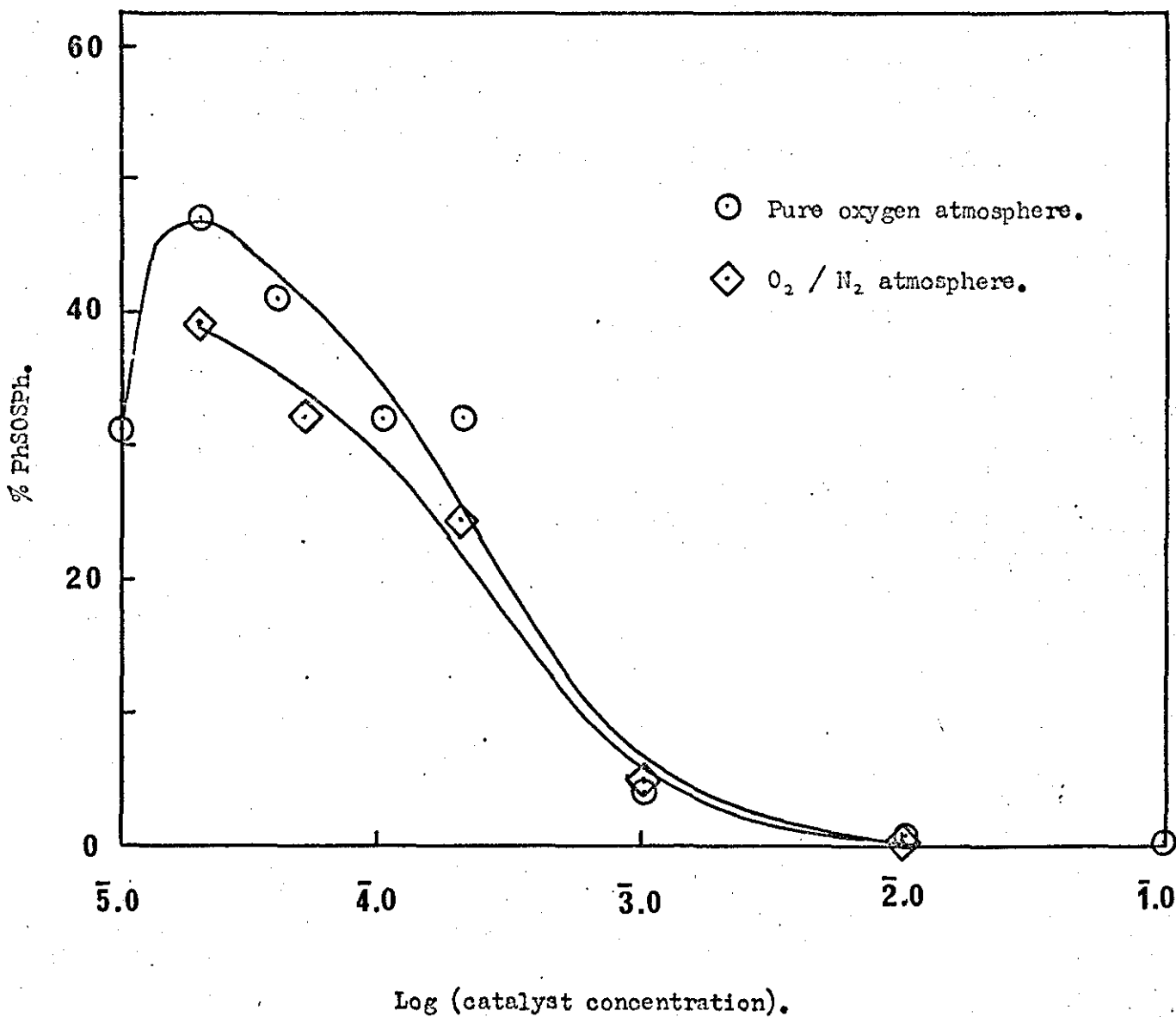
Fig. 6.1.3.8. % PhSOSPh vs log (catalyst concentration) for different atmospheres.

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(initial concentration of thiophenol) and percentage thiolsulphinate vs log (initial concentration of thiophenol) are shown in Figs. 6.1.4.1 and 6.1.4.2 respectively.

6.1.5 Dependence of the Kinetics on Temperature.

The effect of the reaction temperature on the kinetics of the thiophenol oxidation was studied. The conditions of oxidation together with the results are shown in table 6.6.

6.1.6 Analysis of Samples Taken During the Course of the Thiophenol Oxidation Reaction

In all previous investigations by other workers into the kinetics of oxidative coupling reactions, the rate of removal of the substrate has been directly proportional to the rate of oxygen consumption, only. e.g. For the oxidative coupling of 2,6-dimethylphenol (DMP):-

$$- 2 \left(\frac{d[DMP]}{dt} \right) = - \frac{d[O_2]}{dt} \qquad (6.1.6.1)$$

However, in the case of thiophenol oxidation where both the disulphide and the thiolsulphinate are produced, the rate of oxygen absorption is a function of two variables, the rate of thiophenol consumption and another variable whose value is dependent upon the selectivity of the reaction. If, however, it could be proved that the selectivity for thiolsulphinate was constant throughout the reaction, then it can be shown that the following relationship exists:-

$$- \frac{d[O_2]}{dt} = \left(- \frac{d[PhSH]}{dt} \right) x \quad f \qquad (6.1.6.2)$$

where f, a correction factor is a function of the selectivity, ϕ, of the reaction for thiolsulphinate and thus its value varies for varying reaction conditions. By considering the equations 6.1.3.2 and 6.1.3.3.

Weight of PhSH (grms/5 ml.py)	[PhSH]	% oxygen consumption	%PhSOSPh	$-\dfrac{d[O_2]}{dt}$ $(\times 10^4)$	$-\dfrac{d[PhSH]}{dt}$ $(\times 10^4)$
0.0079	0.0134	128	n.d.	0.185	n.c.
0.0095	0.0163	129	n.d.	0.215	n.c.
0.0131	0.0238	190	43	0.27	n.c.
0.0192	0.0349	155	42	0.37	0.073
0.0308	0.0559	148	48	0.52	0.099
0.0474	0.0861	153	48	0.64	0.122
0.0733	0.133	154	47	0.83	0.159
0.119	0.216	151	46	0.94	0.181
0.148	0.268	151	43	1.07	0.210
0.229	0.416	145	39	1.13	0.227
0.399	0.724	135	32	1.26	0.265
0.776	1.409	118	20	1.35	0.304
1.246	2.263	115	12	1.33	0.313
2.491	4.522	105	4	1.32	0.310

(n.d.= not determined; n.c. = not calculated)

Reaction Conditions: 0.00002 g CuCl (equivalent to 0.00004 moles/litre); 5.0 ml. pyridine; 25°C, oxygen atmosphere at atmospheric pressure.

<u>Table 6.5.</u>

Results: Dependence of the reaction upon the initial thiophenol concentration using the magnetic stirrer.
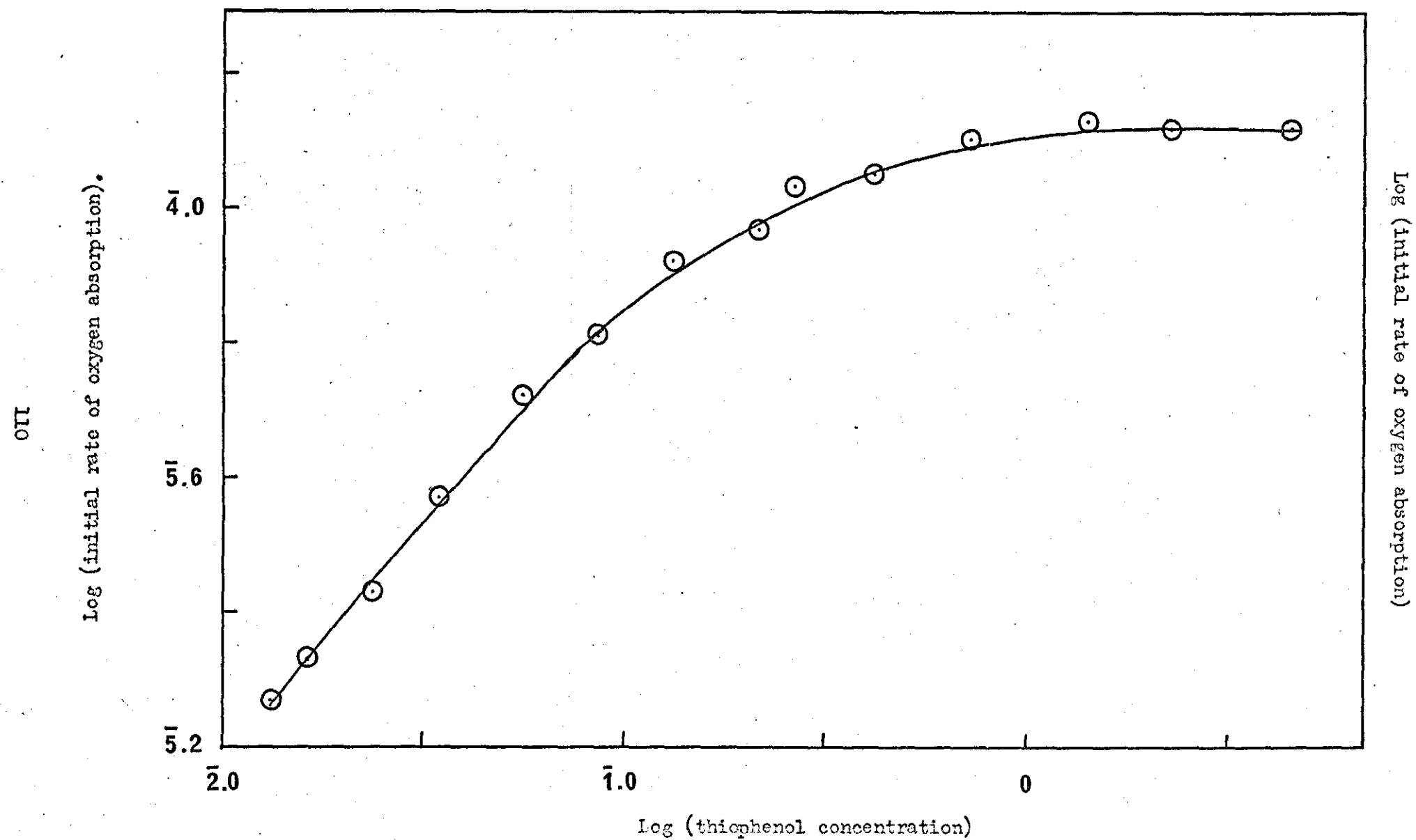
Fig. 6.1.4.1. Log (initial rate of oxygen absorption)   vs   Log (thiophenol concentration).
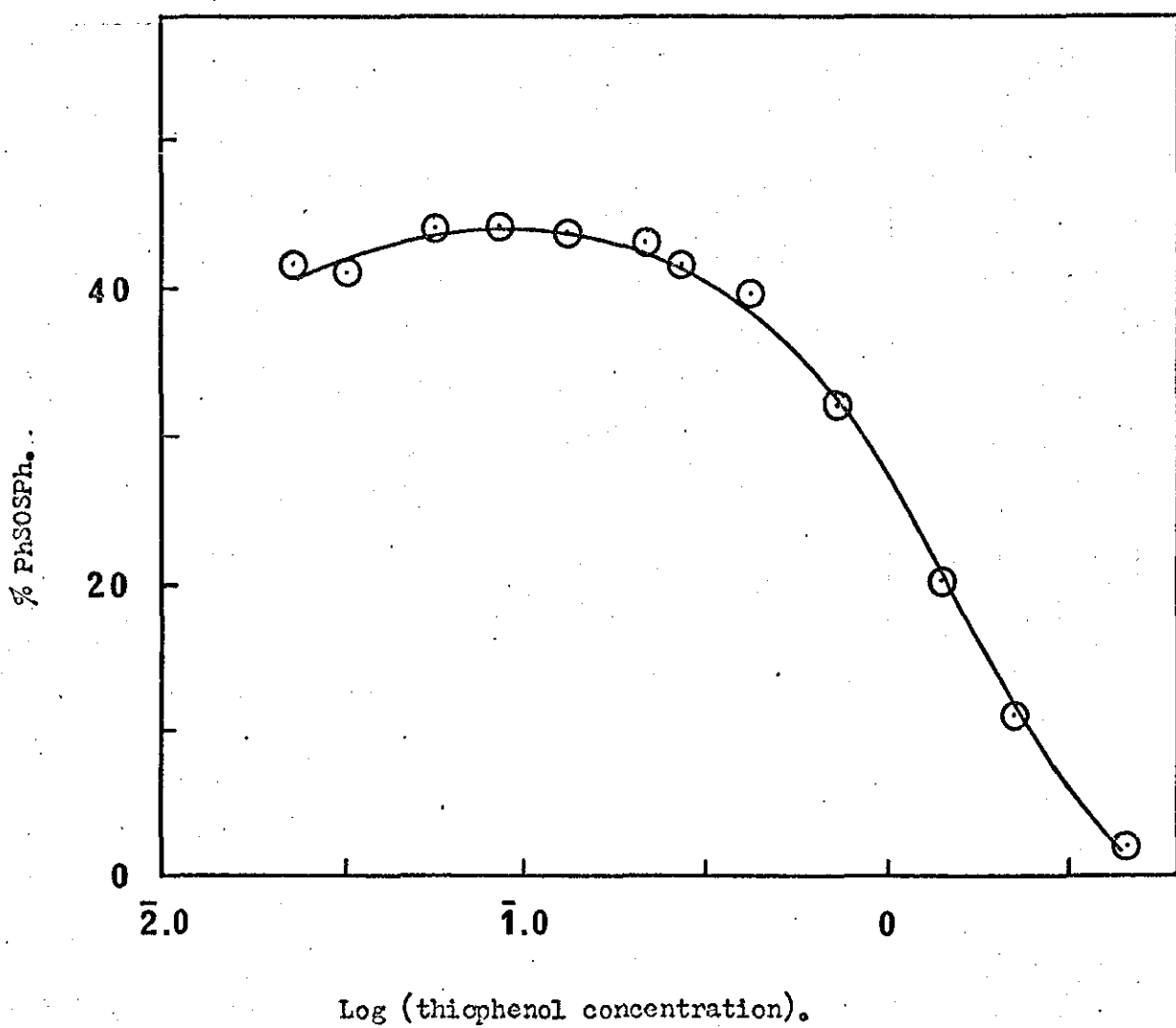
Fig. 6.1.4.2.   % PhSOSPh vs Log (thiophenol concentration).

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Reaction Temperature (^{o}C)	$-\dfrac{d[O_2]}{dt}$	% oxygen consumption	% PhSOSPh	$\dfrac{-d[PhSH]}{dt}$
10	1.07	170	59	0.188
25	1.14	143	41	0.227
40	1.11	112	8	0.266

Reaction conditions: 0.00002 g Cu Cl;   0.25g thiophenol;

5.0 ml. pyridine;   oxygen atmosphere at atmospheric

pressure; magnetic stirrer.

Table 6.6

Dependence of the reaction upon temperature.

$$2PhSH + \tfrac{1}{2}O_2 \longrightarrow PhSSPh + H_2O \qquad\qquad (6.1.3.2)$$

$$1-\phi \quad \tfrac{1}{4}(1-\phi) \qquad\qquad \tfrac{1}{2}(1-\phi)$$

$$2PhSH + O_2 \longrightarrow PhSOSPh + H_2O \qquad\qquad (6.1.3.3)$$

$$O \qquad \tfrac{1}{2}\phi \qquad\qquad \tfrac{1}{2}\phi$$
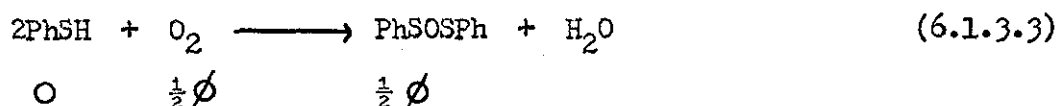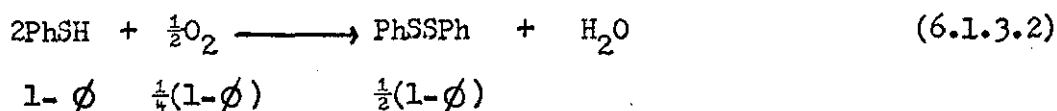
it can be shown (appendix F) that f is defined by the following
expression:-

$$f = \tfrac{1}{4}(1+\phi) \qquad\qquad (6.1.6.3)$$

$$\text{where } \phi = \frac{\text{moles of PhSH consumed to produce PhSOSPh}}{\text{moles of PhSH consumed to produce PhSSPh and}} \qquad (6.1.6.4)$$
$$\text{PhSOSPh}$$

The fact that very small concentrations of catalyst were used
in comparison to the concentration of the thiophenol used, and the
fact that in most of the reactions, the rate of oxygen absorption
was virtually constant for over 90% of the reaction, suggests that
the selectivity of the reaction was probably constant throughout the
reaction, in which case equations 6.1.6.2, 6.1.6.3 and 6.1.6.4 would
apply. Proof of this constant selectivity throughout the course of
the reaction was sought by the following investigation into the
composition of the reaction mixture during the course of the reaction.

From data of the oxygen consumption and the quantitative
determination of the thiolsulphinate concentration at any time, t,
during the course of the reaction, it was thought that the concentrations
of all the three species (PhSH, PhSSPh and PhSOSPh) present in the
reaction mixture, at that time, t, could be calculated (see appendix F).

Unfortunately, the presence of thiophenol in the samples interfers with the iodometric titration for thiolsulphinate. The thiolsulphinate concentration was previously determined by the quantitative oxidation of iodide ions in acidic conditions by the thiolsulphinate according to equation 6.1.3.1. However, thiophenol reduces iodine according to equation 6.1.6.5.

$$2PhSH + I_2 \longrightarrow PhSSPh + 2I^- + 2H^+ \qquad (6.1.6.5)$$
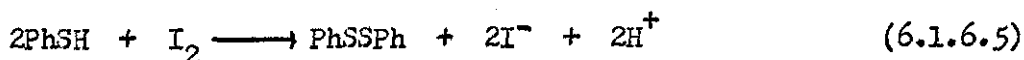
Thus the iodine liberated by the thiolsulphinate is immediately reduced by any thiophenol which may be present. It was thought, at first, that this problem could be overcome by the addition of a known excess of iodine to the titration solution so that there would always be iodine remaining after completion of the two opposing reactions given in equations 6.1.3.1 and 6.1.6.5. From the determination of the net iodine liberated, or consumed, as a result of these two opposing reactions, together with the data of oxygen consumption, it was thought that the concentrations of the three species present could be found. However, it was found that the net amount of iodine that would be liberated or consumed in the titration was dependent only upon the amount of oxygen absorbed up to the time, t, when the sample was taken, and was independent of the relative concentrations of the three species, PhSH, PhSSPh and PhSOSPh. This is shown in further detail in appendix F. Thus this modification to the method for thiolsulphinate analysis could not be used as a means of providing information about the composition of the reaction mixture at any time, t, during the course of the reaction. In previous thiolsulphinate titrations, this problem of thiophenol interference had not been encountered since the samples for titration were taken from the completely oxidized raction

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mixture, which obviously contained no thiophenol.

An alternative method of investigating the composition of samples taken during the course of the thiophenol oxidation reaction was by the quantitative determination of either thiophenol or diphenyl disulphide, together with the oxygen consumption data. As previously reported (section 5.3), Tamele et al (55) published a paper describing the determination of thiols by a potentiometric titration method. This method proved acceptable for the determination of thiophenol concentration in the samples taken. From the results of these titrations, together with data for the oxygen consumption, the concentrations of the three species present in the reaction at any time, t, could be calculated (see appendix G). Suitable concentrations of the substrate and catalyst were chosen to give not only appreciable concentrations of thiolsulphinate in the product, but also long reaction times so that there was sufficient time, between taking samples, to perform a thiophenol titration. Four such experiments were undertaken, two ((a) and (b)) using the magnetic stirrer and two ((c) and (d)) using the vibromix stirrer. The results are shown in table 6.7. All the experiments were conducted at 25°C in an oxygen atmosphere at atmospheric pressure. The value of F is defined as follows:-

$$F = \frac{\text{moles of thiophenol which are consumed in producing the thiolsulphinate which is present at time, t.}}{\text{moles of thiophenol which are consumed in producing the disulphide and the thiolsulphinate which is present at time, t.}} \quad (6.1.6.6)$$

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Sample	% Extent of the Reaction	F	$\frac{F}{F_f}$	Experiment
1	16	–	–	
2	37	0.56	0.95	
3	56	0.33	0.56	(a)
4	80	0.37	0.63	

Final % oxygen consumption = 168%
Final % PhSOSPh = 47%
$F_f = 0.59$

Sample	% Extent of the Reaction	F	$\frac{F}{F_f}$	Experiment
1	9	–	–	
2	18	0.82	1.67	
3	38	0.61	1.24	(b)
4	64	0.61	1.24	
5	80	0.47	0.96	

Final % oxygen consumption = 155%
Final % PhSOSPh = 43%
$F_f = 0.49$

Sample	% Extent of the Reaction	F	$\frac{F}{F_f}$	Experiment
1	20	–	–	
2	43	0.47	0.94	(c)
3	79	0.38	0.78	

Final % oxygen consumption = 156%
Final % PhSOSPh = 34%
$F_f = 0.39$

Sample	% Extent of the Reaction	F	$\frac{F}{F_f}$	Experiment
1	22	–	–	
2	50	0.44	1.13	(d)
3	68	0.31	0.80	
4	85	0.34	0.87	

Final % oxygen consumption = 146%
Final % PhSOSPh = 34%
$F_f = 0.39$

Table 6.7.

Results: analysis of samples taken during the course of
the thiophenol oxidation reaction.

It may appear that the value of F is always equal to ϕ

(equation 6.1.6.4), which may be defined more fully as:

$$\phi = \frac{\text{moles of thiophenol which are consumed in producing all}}{\text{the thiolsulphinate which was generated up to time, t.}}$$
$$\frac{}{\text{moles of thiophenol which are consumed in producing the}}$$
disulphide and thiolsulphinate which is present at
time, t.

(6.1.6.4)

However, as is shown later (section 6.2.1.4) it is necessary

to make a distinction between ϕ and F. Clearly the denominators for

both ϕ and F are identical. However, if some of the thiolsulphinate

which is generated by the thiophenol oxidation reaction is destroyed

by a side reaction, then it can be seen that the value of the

numerator of F (and thus the value of F itself) will be smaller than

that of ϕ . In the tables of results, table 6.7, the value of F

was used, since the amount of thiolsulphinate determined was the

actual amount of the thiolsulphinate which was present in the reaction

mixture (the amount of thiolsulphinate generated, less any thiolsulphinate

which was destroyed by a side reaction) at the time when the sample

was taken, as opposed to the total amount of thiolsulphinate which

had been generated up to this time.

F_f is defined as the value of F at the completion of the reaction.

The value of F_f is slightly different from the previously defined

term "percentage thiolsulphinate", which was a measure of the amount

of thiolsulphinate present in the reaction mixture at the end of the

reaction compared to the total amounts of thiolsulphinate, disulphide

and any other oxidation products of thiophenol which were formed

(see equation 6.1.3.4).

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The titration readings for thiophenol of the first sample in each of the four reactions gave results which suggest that a higher concentration of thiophenol was present in the first sample than that in the reaction mixture at the start of the reaction. This obviously cannot be so. One possible explanation for this is that there is another product formed in the initial stages of the reaction which causes very high readings for the thiophenol titration. The nature of this product as yet is unknown.

At these low catalyst concentrations, the difference between the oxygen that would be consumed to give the disulphide and the thiolsulphinate only, and the oxygen which is actually consumed is quite appreciable. This fact was taken into consideration in calculating the value of F, which is a measure of the amount of thiolsulphinate present in the reaction mixture as compared to the total amount of the disulphide and thiolsulphinate present (see equation 6.1.6.6). The method of calculating F is given in appendix G.

Fig. 6.1.6.1 and 6.1.6.2 show graphs of F/F_f vs percent extent of the reaction for experiments with the magnetic stirrer and vibromix stirrer respectively. These results are discussed in section 6.2. It will be shown that although the experimental evidence does not exactly prove that the selectivity of the reaction is constant throughout the reaction, the assumption of this constant selectivity is consistent with the above experimental results.

6.1.7 Calculation of the Rate of Removal of Thiophenol.

Fig. 6.1.7.1 shows graphs of the log (initial rate of thiophenol consumption) vs log (catalyst concentration) and Fig. 6.1.7.2 shows
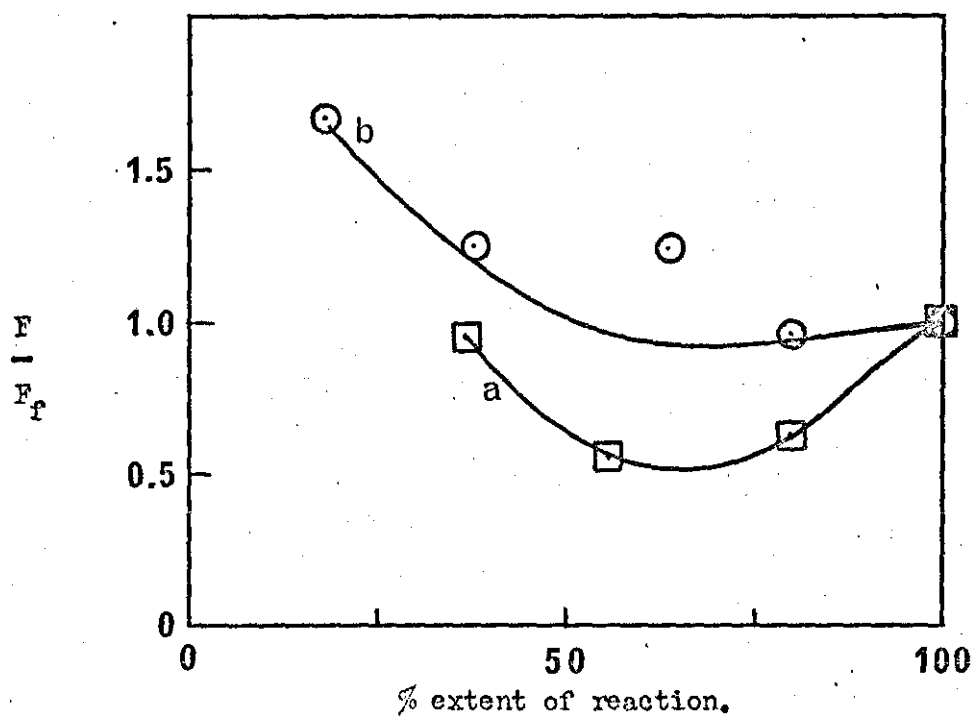
Fig. 6.1.6.1. F / F_f vs % extent of
reaction.
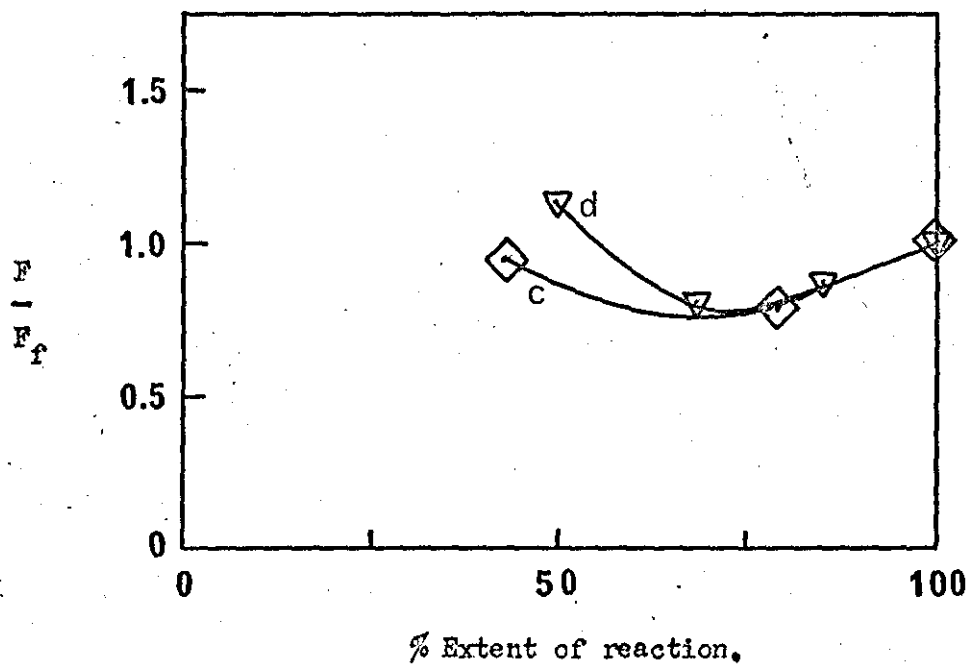
Fig. 6.1.6.2. F / F_f vs % extent of
reaction.

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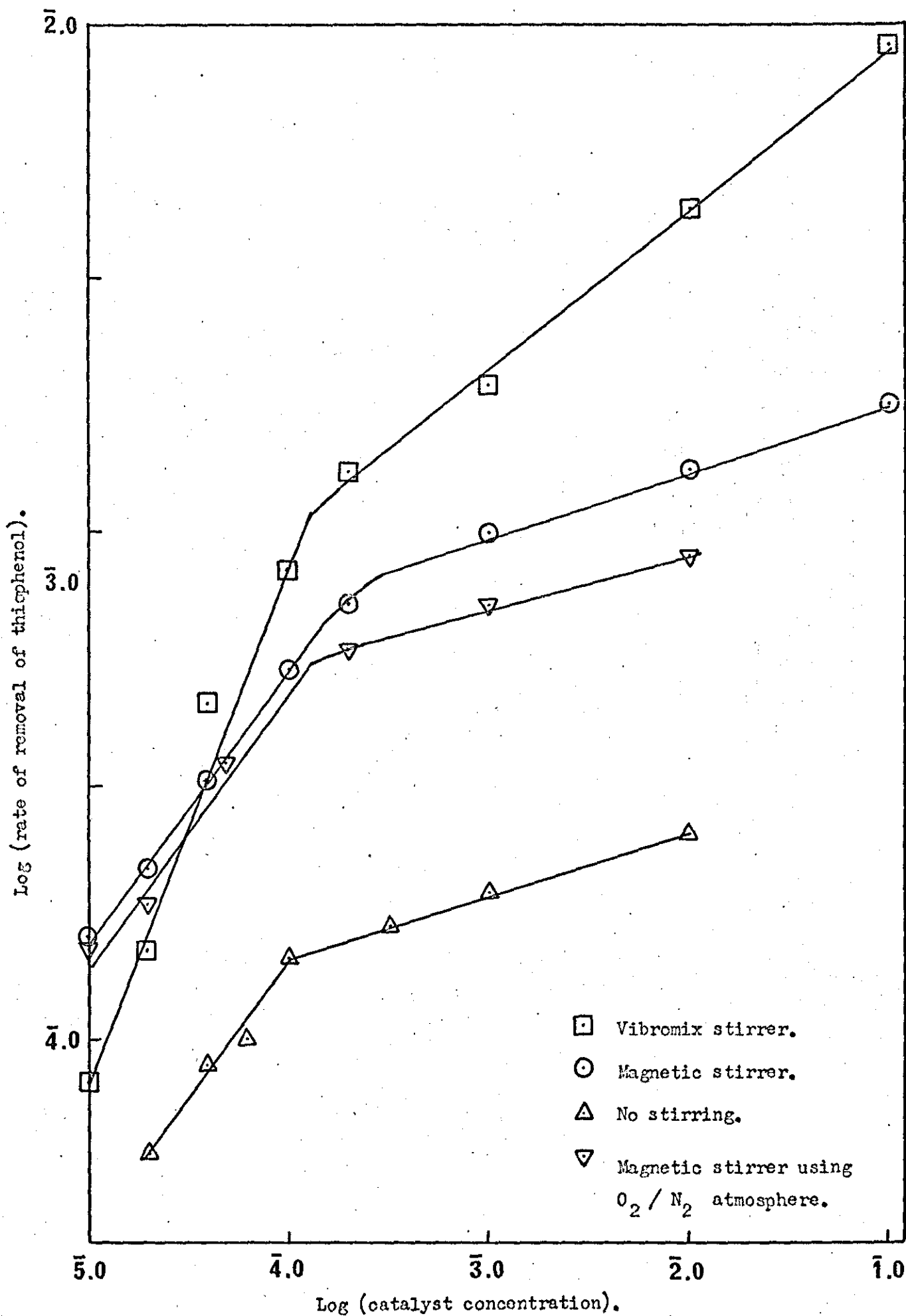
Fig. 6.1.7.1. Log (rate of removal of thiophenol) vs
log (catalyst concentration).

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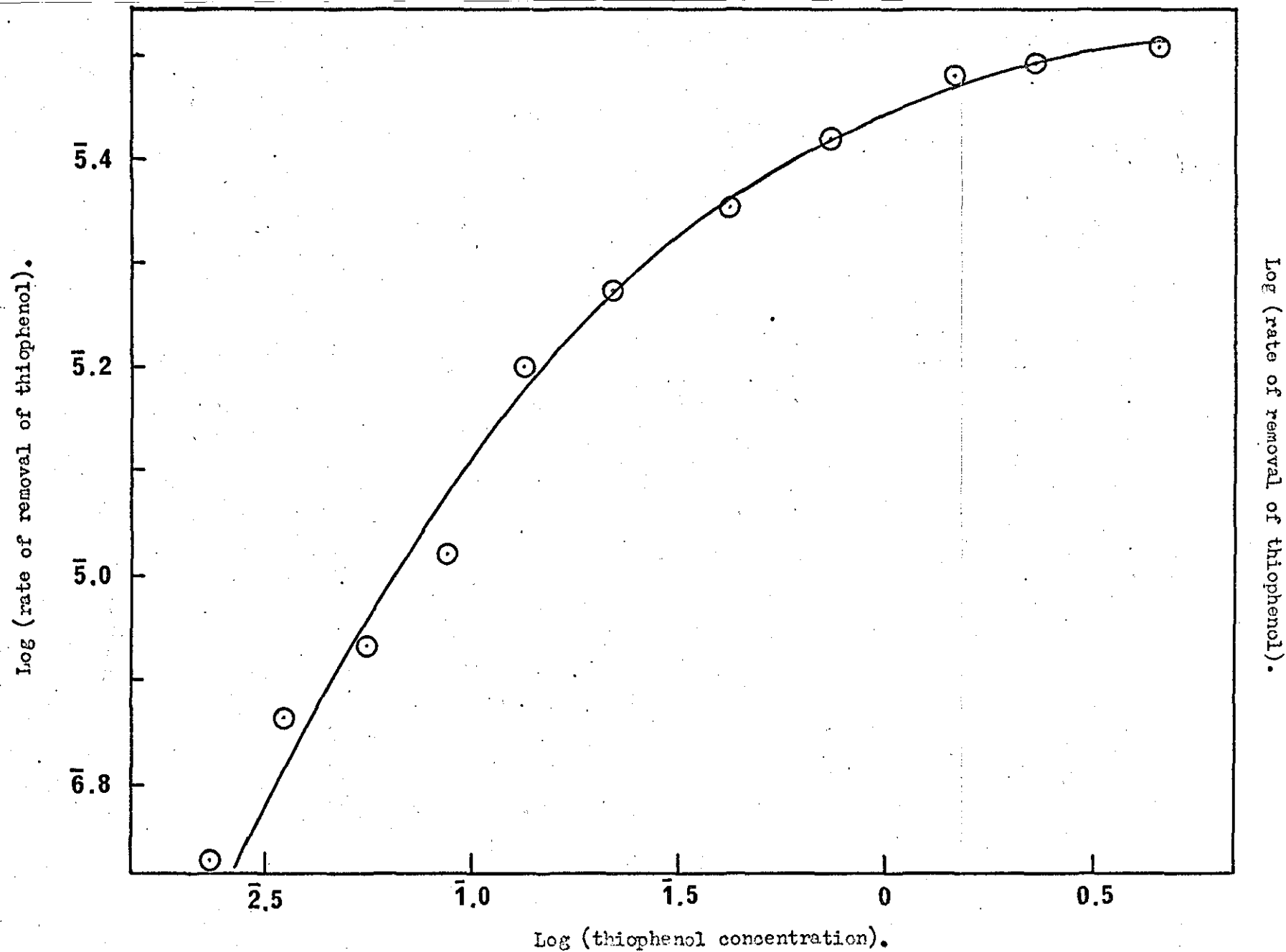
Fig. 6.1.7.2.   Log (rate of removal of thiophenol) vs log (initial
thiophenol concentration).

a graph of log (initial rate of thiophenol consumption) vs log

(thiophenol concentration). In each case, in order to calculate the

rate of thiophenol consumption, the assumption has been made that

the selectivity of the reaction throughout the reaction is equivalent

to the relative yields of the two products at completion of the

oxidation. This assumption is probably correct for high catalyst

concentrations, but is only approximately correct for low catalyst

concentrations. The rate of removal of thiophenol was calculated

using equations 6.1.6.2 and 6.1.6.3. The value of ϕ was taken as

being equal to % PhSOSPh/100. This usually gave a good approximation.

The greatest errors were incurred in the following cases:-

(1) for experiments at low catalyst concentrations (and thus with

long reaction times) where there would be an appreciable amount of

the thiolsulphinate decomposed by a side reaction with thiophenol

(see equation 6.2.1.6). The true value of ϕ would then be greater

than the value of %PhSOSPh/100.

(2) for experiments where there was an appreciable difference

between the actual amount of oxygen consumed and that which would

be consumed in the formation of the disulphide and the thiolsulphinate.

Again the true value of ϕ would be greater than the value of

%PhSOSPh/100.

It can be seen from a comparison of Figs. 6.1.3.5 and 6.1.7.1

that, for these experiments, there is no significant difference in

the shapes or slopes of the graphs when the rate of thiophenol

consumption is substituted for the rate of oxygen absorption.

6.1.8 Pretreatment of the Catalyst.

It was noticed during the experimental work that the colour of
the catalyst solutions changed upon ageing or as a result of a change
in temperature. It was possible that the catalytic activity of the
catalyst also changed. A series of experiments was undertaken,
during the early stages of the experimental work, at constant reaction
conditions but for each experiment the catalyst was pretreated before
use in different ways. Table 6.8 shows the effects of the various
pretreatment processes upon both the rates of oxygen consumption and
the percentage thiolsulphinate formed. It can be seen from the results,
that although there is a statistical spread of results, these show no
definite trends. Thus it can be concluded that, within the reaction
conditions studied, the pretreatment of the catalyst by heating or ageing
has no effect either upon the rate of oxygen absorption or on the
relative yields of products.

6.1.9 Attempted Oxidation of Diphenyl Disulphide.

There are two possible routes for the oxidation of thiophenol
to the thiolsulphinate; these are via AB or via C as shown in
equation 6.1.9.1.

$$
\begin{array}{ccc}
& A & \\
\text{PhSH} \xrightarrow{\hspace{2cm}} & & \text{PhSSPh} \\
\diagdown & & \downarrow B \\
& C & \text{PhSOSPh}
\end{array}
\qquad (6.1.9.1)
$$
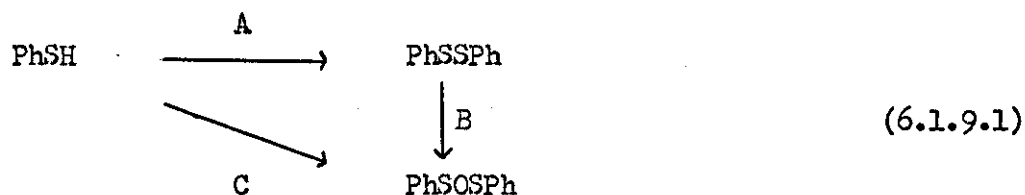
If the thiolsulphinate was formed via the route AB, then one
would expect that at the completion of the thiophenol oxidation that
the thiolsulphinate would be the only product. Thus the fact that
thiolsulphinate is not the only product present at the end of the
reaction shows that it must be formed directly from thiophenol via

Pretreatment	$\dfrac{-d[O_2]}{dt}$ $(\times 10^4)$	% oxygen consumption	%PhSOSPh
1. Normal Run*	1.14	143	41
2. Dilute Solution left $3\frac{3}{4}$ hours	1.13	145	41
3. Stock solution left for the following times:-			
(a) $3\frac{1}{4}$ hours	1.18	138	35
(b) $17\frac{1}{2}$ hours	1.13	142	37
(c) $22\frac{1}{2}$ hours	1.16	132	31
(d) 2 days	1.14	143	39
(e) 7 days	1.11	143	40
(f) 9 days	1.11	145	39
4. Stock solution heated for $\frac{1}{2}$ hour at the following temperatures:-			
(a) $45^{\circ}C$	1.17	147	43
(b) $52.5^{\circ}C$	1.11	146	36
(c) $60^{\circ}C$	0.81	141	34
(d) $67.5^{\circ}C$	1.12	144	39
(e) $75^{\circ}C$	1.07	142	37
(f) $90^{\circ}C$	1.14	142	38
5. Stock solution heated at $45^{\circ}C$, diluted at $45^{\circ}C$	1.14	142	39

Reaction Conditions: 0.00002 g CuCl; 0.25 g Thiophenol; 5.0 ml pyridine; $25^{\circ}C$; oxygen atmosphere at atmospheric pressure; magnetic stirrer.

* Previous experiments were conducted using a standard pretreatment of the catalyst, the catalyst solutions being kept at $25^{\circ}C$ and the reactions were started 1 hour after making up the stock solution.

The "stock" solution was the catalyst solution at a concentration 0.040 g CuCl/5.0 ml pyridine, which was sucessively diluted to give the solution of the required concentration.

Table 6.8.

Results: Effect of varying pretreatment of the catalyst.

route C. This was confirmed experimentally by the attempted oxidation of diphenyl disulphide, when it was found that no oxygen was consumed. The reaction conditions were: 0.0001 g. Cu Cl; 0.258 g. diphenyl disulphide; 5.0 ml. pyridine; 25°C; oxygen atmosphere at atmospheric pressure using the vibromix stirrer.

6.2 DISCUSSION.

6.2.1 Qualitative Discussion and Interpretation of the Results.
6.2.1.1 Variable Catalyst Concentrations.

(a) Rate Curves (Figs. 6.1.3.5 and 6.1.3.7)

As reported in section 6.1.3, the consideration of the graphs in Figs. 6.1.3.5 and 6.1.3.7 leads to the conclusion that the general regions AB and BC cannot be described solely as kinetic control and mass transfer control regions respectively.

(1)   The Region A" B" (Vibromix Stirrer).

In comparison with the corresponding regions A'B', $A^{N}B^{N}$ and A''' B''', the region A" B" shows a very unusual dependence upon the catalyst concentration (Fig. 6.1.3.5). For catalyst concentrations below 3.2×10^{-5} moles/litre copper (I) chloride, the rates of oxygen absorption were lower than the corresponding rates when the magnetic stirrer was used. It was thought that this anomalous effect was unlikely to be caused directly by the increased rates of mass transfer of the oxygen from the gas phase to the liquid phase. A more probable explanation is that the increased mass transfer rates caused the formation of a more highly oxidized product of thiophenol, compound X, which either deactivated the catalyst, or interfered with the oxidation reaction in some other way, and thus decreased the rates of oxygen

absorption. It was stated in section 2.3.5 that various acids deactivate the copper catalysts; thus if one or more of the acids: benzene sulphenic acid (PhSOH); benzene sulphinic acid (PhSO$_2$H) and benzene sulphonic acid (PhSO$_3$H) was formed, it may possibly deactivate the catalyst. A further condition which is required so that this theory is consistent with the experimental results is that the compound X is produced only in the initial stages (1 - 2%) of the reaction. If it was produced throughout the reaction the reaction rate would be continuously reduced, and if sufficient of the compound X was formed the reaction would eventually stop. In this case a plot of oxygen consumption vs time would not give a linear relationship. A logical explanation can be given for the attainment of these conditions.

Before addition of the thiophenol solution to the catalyst, the whole of the catalyst solution would be saturated with oxygen. After the addition of the thiophenol solution, the concentration of oxygen within the bulk of the liquid would decrease to about zero. This would be true for all regimes of mass transfer with chemical reaction except for the kinetic regime. Thus in the initial stages of the reaction there would be a relatively high concentration of oxygen within the bulk of the liquid; this may cause the initial formation of compound X which may interfere with the oxidation reaction giving the anomalous results. It might be argued that this effect should also be present when the magnetic stirrer apparatus was used. However, in this case the rate of decrease of the oxygen concentration in the bulk of the liquid would be faster than that obtained when the vibromix stirrer was used. This is because the vibromix stirrer, which gives increased mass transfer rates would maintain a high concentration of oxygen

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within the liquid for a longer period of time. This effect may be similar to that shown in Fig. 6.2.1.1. At high catalyst concentrations, the rate of decrease of the oxygen concentration in the bulk of the liquid would be much faster and thus there would be much less compound X formed. Also for a given amount of compound X, the interference would be comparatively smaller as the concentration of the catalyst increased. Thus at higher catalyst concentrations this effect would be negligible.

Support for the above theory was sought from an experiment, the details of which are given in appendix A.1.5. For this thiophenol oxidation experiment using a magnetic stirrer, small quantities of benzene sulphonic acid in pyridine were added to the reaction mixture at various stages of the reaction. The amount of acid added was roughly equivalent to the amount which might be produced in the initial stages of a thiophenol oxidation reaction using the vibromix stirrer. The graph of oxygen consumption vs time is given in Fig. 6.2.1.2. From this graph it can be seen that the added acid had no effect upon the reaction rate. This proves that even if a small quantity of benzene sulphonic acid was produced in the reaction, it would not deactivate the catalyst or interfere in the oxidation. Thus this experiment did not support the above theory, although it did not exactly disprove it. There may still have been a product, other than benzene sulphonic acid, formed in the initial stages of the reaction when the vibromix stirrer was used. This compound X, although not an acid may have either deactivated the catalyst or interfered in the oxidation reaction in some other way.

Mass transfer effects in the general regions AB and BC are now
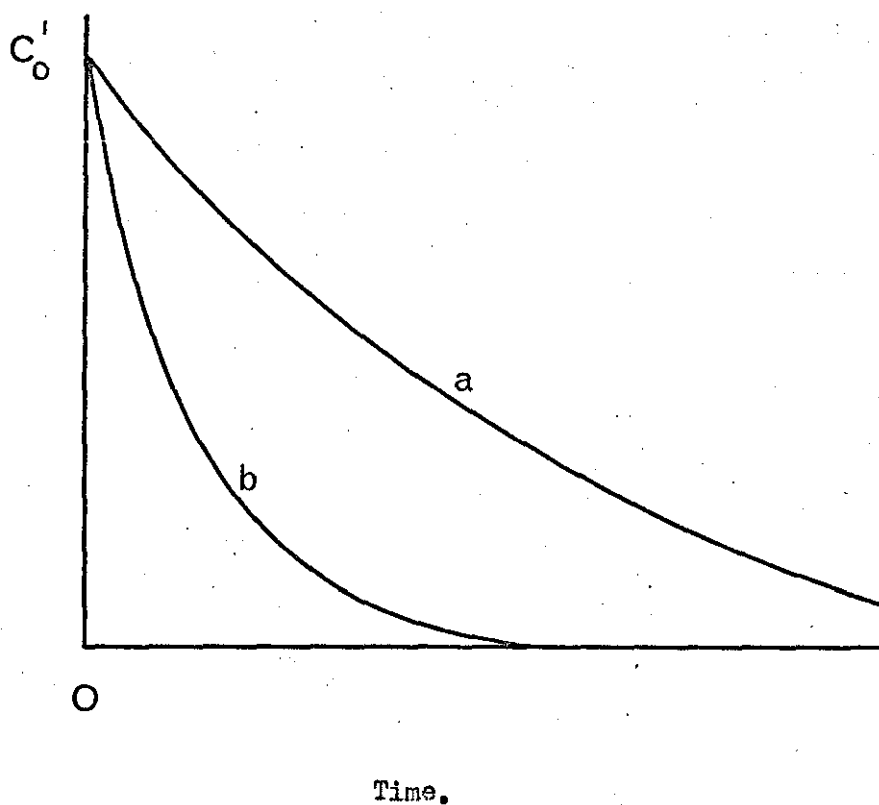
Fig. 6.2.1.1. Effectiveness of the type of stirrer for maintaining
a high oxygen concentration in the bulk of the liquid,
(a) vibromix stirrer, (b) magnetic stirrer.
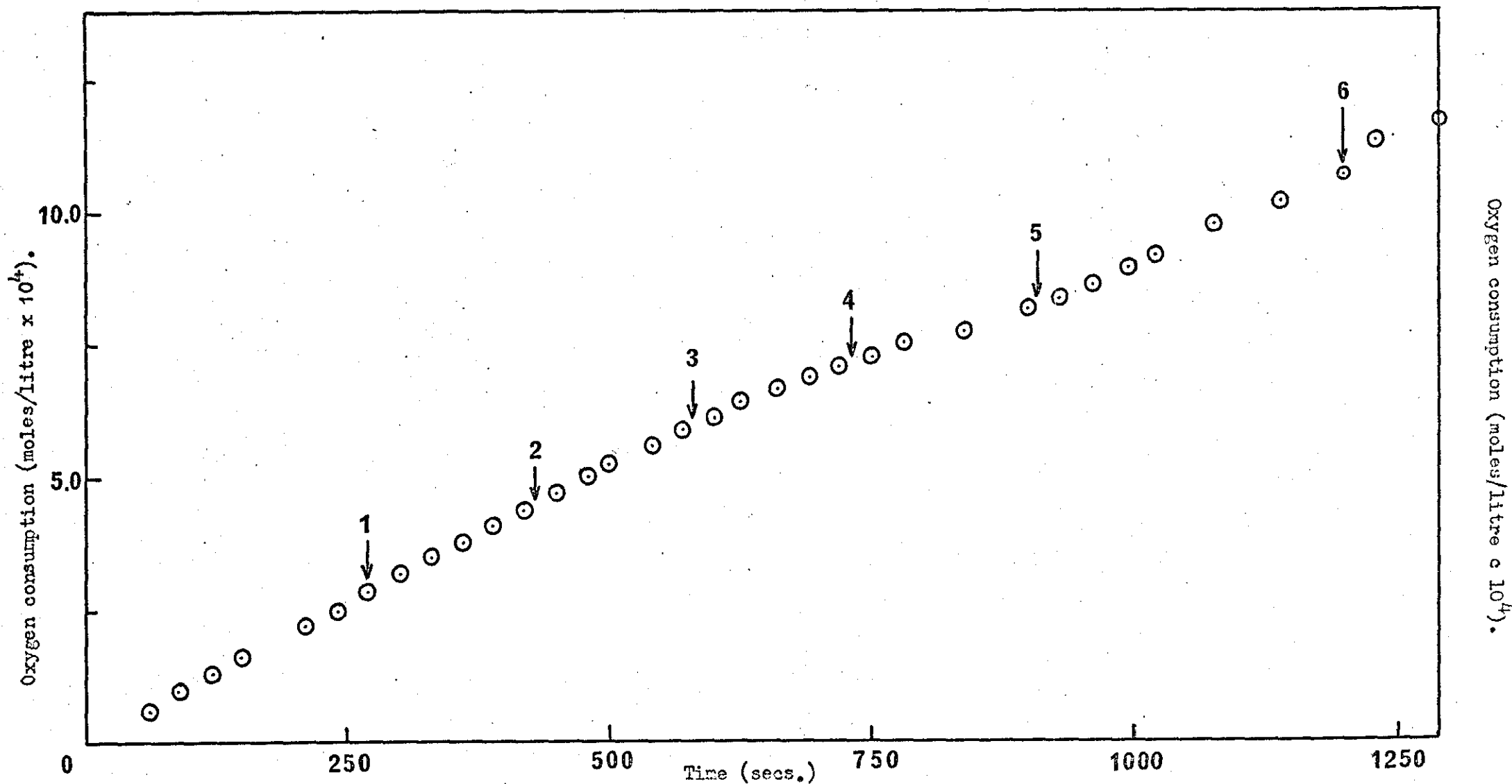
Fig. 6.2.1.2.   Effect of adding benzene sulphonic acid to the thiophenol oxidation
reaction (1,2,3,4,5 and 6 correspond to the additions (see appendix A.1.5.)).

interpreted in terms of the 4 reaction regimes of mass transfer with chemical reaction previously described in section 3.2.

(2) The General Region AB.

The region AB cannot be the kinetic regime because of the following reasons:-

(a) As stated in section 6.1.3, if the region AB was a kinetic control regime, the effect of different modes of stirring upon the rates of oxygen absorption would be similar to that shown in Fig. 6.1.3.3. This is because the rate of gas absorption in the kinetic regime is independent of the interfacial area.

(b) Van de Vusse (56) showed that, in the kinetic regime, the selectivity of competitive reactions in gas-liquid systems was not affected by changing the mass transfer rates. Although the type of gas-liquid reaction considered in this project is slightly different from that studied by van de Vusse, the selectivity of the reactions in the kinetic regime should still be independent of mass transfer rates. However, it can be seen from tables 6.1, 6.2 and 6.3 that the selectivity of the reaction in the AB region is dependent upon the mass transfer rates.

The diffusional regime describes the situation where there is neglible reaction within the liquid film and the rate controlling process is the diffusion of gas through the film; the rate of the chemical reaction is just equal to the rate of diffusion of the gas through this film. Clearly this regime only applies to a narrow range of

conditions. A small increase in the chemical reaction rate would lead to an appreciable reaction within the film (fast reaction regime). whereas a small decrease in the chemical reaction rate would tend to cause the bulk liquid to be saturated with gas (kinetic regime). Thus it is unlikely that the diffusional regime would extend over such a wide range of conditions as is found in the region AB. Also in the diffusional regime the selectivity of the reactions would be independent of the mass transfer rates, whereas, as previously stated, the selectivity in region AB is dependent upon the mass transfer rates.

Thus it would seem logical that the remaining two regimes of mass transfer with chemical reaction the fast reaction and the instantaneous reaction regime, should apply to the two general regions AB and BC respectively. The following argument strongly suggests that the region AB is in the fast reaction regime. The chemical reaction rate (the rate of oxygen absorption in the kinetic regime) is probably first order with respect to both the catalyst concentration and the oxygen partial pressure because of the following reason. In the oxidative coupling of 2,6-dimethylphenol, it has been shown fairly conclusively that the chemical reaction rate is first order with respect to both the copper catalyst concentration and the oxygen partial pressure (section 2.4). For a second order reaction where the chemical reaction rate is first order with respect to both the liquid phase reactant and the absorbing gas, van Krevelen and Hoptijzer (57) showed that in the fast reaction regime, the rate of gas absorption is first order with respect to the gas concentration at the interface and proportional to the square root of the liquid phase reactant concentration.

i.e. when $\quad r = k\, c'_o\, b_o$ $\qquad\qquad\qquad$ (6.2.1.1)

$$\bar{V} = \sqrt{k\, b_o\, D_a} \cdot c'_o \qquad\qquad\qquad (6.2.1.2)$$

where k = overall kinetic constant

$\quad D_a$ = diffusivity of the gas in the liquid.

Equation 6.2.1.2 applies only when the concentration of the liquid

phase reactant remains constant within the film; this is true when

there is a vast excess of liquid phase reactant or when the liquid

phase reactant is recycled by other very fast reactions. (The equation

6.2.1.2 was also reported by Bridgwater and Carberry (58).) Thus

if the reaction does show a first order dependence upon the catalyst

concentration, then in the fast reaction regime, the rate of removal

of thiophenol should be proportional to the square root of the catalyst

concentration. This is in agreement with the experimental evidence

as shown in Fig. 6.1.7.1 where the slope of each of the lines A'B',

A"'B"' and $A^N B^N$ is 0.5, thus suggesting that the general region AB

is a fast reaction regime. For a gaseous mixture of 88% oxygen/

12% nitrogen, in the fast reaction regime the rate of oxygen absorption

for a given catalyst concentration should be reduced to 88% of the

corresponding rate obtained with "pure" oxygen. This again is in

agreement with the experimental evidence as shown in Fig. 6.1.3.7.

where the rate of oxygen absorption for the oxygen/nitrogen gaseous

mixture was 85-90% that of the corresponding rate when "pure" oxygen

was used. Thus there is fairly conclusive evidence to show that the

general region AB is the fast reaction regime. As stated above,

the region A"B" is a special case. However, the assigning of the fast

reaction regime to the region A"B" is consistent with the explanation which is given to account for the anomalous behaviour.

(3) The General Region BC.

By deduction we can say that the general region BC is most probably the instantaneous reaction regime. As previously stated (section 3.2), Danckwerts (48) showed that in the instantaneous reaction regime when an inert gas is mixed with the soluble gas any one of the three concentration profiles shown in Fig. 3.2.3 is possible. In the experiments of this present project, when a "pure" oxygen atmosphere was used this refers to commercial grade oxygen (99.5% B.O.C).

Even with such a small percentage of insoluble gas (probably nitrogen) present, a gas-side resistance would most probably be present in the very fast or the instantaneous reaction regime. Also it has been previously stated (section 5.1) that because of the procedure used for flushing out the reaction system, there may still have been significant traces of air left in the system, This would also give a gas-side resistance in addition to that resulting from the 0.5% inerts in the commercial grade oxygen. Thus one of the concentration profiles in Fig. 3.2.3 may apply to the gas-liquid system which is being considered. The concentration profiles in Fig. 3.2.3(a), (b) and (c) correspond to situations where the liquid phase reactant diffuses through the liquid film at a rate (a) slower than (b) equal to (c) faster than the rate of diffusion of the gas through the gas film respectively. The concentration profile in Fig. 3.2.3 (a) becomes a moving boundary problem with the reaction front being at the interface at time $t = 0$ and moving away from the interface as the reaction proceeds.

The concentration profile in Fig. 3.2.3(b) is a special case

applying to only one concentration of liquid phase reactant for a given partial pressure of absorbing gas; thus this case obviously does not apply to the general region BC.

For the concentration profile in Fig. 3.2.3(a), the rate of gas absorption is given by equation 6.2.1.3 (see reference 44).

$$\bar{V} = k_L^{\,0} \left(c_o^{\,\prime} + \frac{b_o^{\,\prime}}{q} \right) \qquad\qquad (6.2.1.3)$$

where $b_o^{\,\prime}$ = concentration of liquid phase reactant at the interface

q = a stoichiometric coefficient for the reaction.

Thus for a constant partial pressure of gas, the rate of gas absorption would be dependent upon the liquid phase reactant concentration to the first power. This clearly does not apply to the region BC as shown by Figs. 6.1.3.5 and 6.1.3.7.

For the concentration profile in Fig. 3.2.3(c) the rate of gas absorption is given by equation 6.2.1.4 (see reference 44).

$$\bar{V} = k_g \, P_g \qquad\qquad (6.2.1.4)$$

where k_g = mass transfer coefficient for the gas through the gas film.

The rate of absorption is independent of the concentration of the liquid phase reactant. This is virtually in agreement with the experimental results for the regions B'C', B"C", and $B^N C^N$, but not for the region B"C". In the regime described by Fig. 3.2.3(c), a reduction in the partial pressure of a non-reacting gas such as nitrogen would produce a gas-side resistance; this would reduce the mass transfer coefficient k_g and thus would further decrease the rate of absorption. This too is in agreement with the experimental evidence

as shown by the region $A^N B^N$ in Fig. 6.1.3.7. Thus the concentration

profile in Fig. 3.2.3 (c) most probably applies to the general region

BC. The change from the fast reaction regime, AB, to the instantaneous

reaction regime, BC, is probably similar to the change occurring in

the concentration profiles from (a) to (c) in Fig. 6.2.1.3.

Fig. 6.1.3.5. shows that the break-point (the intersection of

the fast reaction and the instantaneous reaction regimes) occurs at

approximately the same catalyst concentration for all modes of stirring.

In changing from no stirring to using the magnetic stirrer, the change

in interfacial area is negligible, but the width of both the gas and

the liquid films would be greatly reduced. If the widths of the two

films were reduced by a similar proportion, the break-point for each

of the two modes of stirring would probably occur at the same catalyst

concentration. In changing from the magnetic stirrer to the vibromix

stirrer, the thickness of both the gas and the liquid films would

probably be reduced by only a very small amount, but the interfacial

area would be greatly increased. However, the increase in the inter-

facial area of the gas film would be equal to that of the liquid film

and thus it is not surprising that again the break-point for each of

the two modes of stirring occurred at approximately the same catalyst

concentration.

If, for a particular mode of stirring, the partial pressure of

the oxygen was reduced, the break-point should occur at a lower

catalyst concentration. Fig. 6.1.3.7 shows that, when the partial

pressure of oxygen was reduced by a small factor, the break-point did

occur at a slightly lower catalyst concentration. This could be used
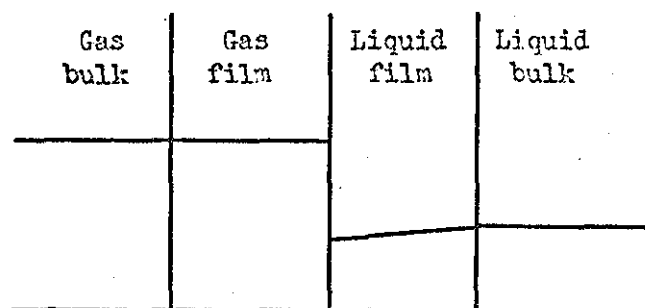
a

Lower region of the fast
reaction regime.
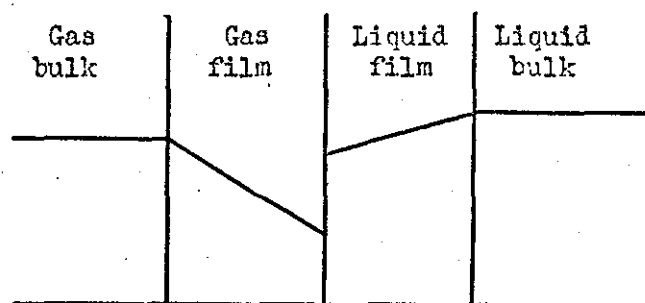
b

Upper limit of the fast
reaction regime.
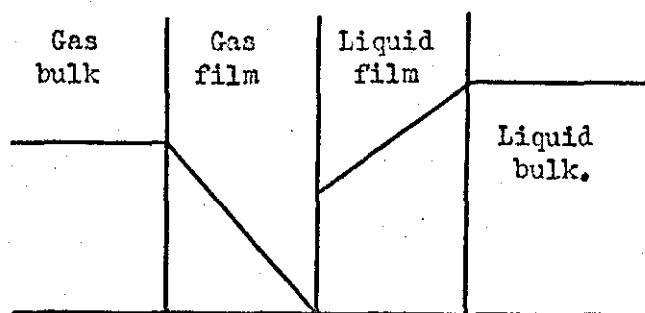
c

Lower limit of the instantaneous
reaction regime.

Fig. 6.2.1.3. Change occurring in the concentration profiles
in transferring from the fast to the instantaneous
reaction regime.

as further evidence to support the application of the concentration

profile of Fig. 3.2.3.(c) to region BC. However, the differences

both in the partial pressures of oxygen and in the catalyst concentrations

at the break-point were only small and thus it is not advisable to

attach too much significance to this evidence.

Thus the majority of experimental evidence suggests that the general

region AB is a fast reaction regime and the general region BC is an

instantaneous reaction regime. There is, however, some experimental

work which is not in full agreement with the theory. This is to be

expected since the theory is based on simplified models which, although

they give reasonably good results in most cases, are not very realistic.

(b) Selectivity of the Reaction (Figs. 6.1.3.4., 6.1.3.6., and 6.1.3.8).

It can be seen from the results in tables 6.1, 6.2, 6.3, and 6.4

that, as a general rule the extra oxygen consumed above 100% oxygen

consumption can be accounted for by the formation of the thiolsulphinate.

However, in the experiments where the vibromix stirrer was used and

the experiments at low catalyst concentrations, there was an appreciable

amount of oxygen consumed above that which was required for the

formation of the disulphide and the thiolsulphinate. Reference has

already been made in this section to the probability of higher oxidation

products of thiophenol, such as benzene sulphur acids, being formed

when there is a relatively high concentration of oxygen in the liquid

phase. In experiments using the vibromix stirrer or experiments at

low catalyst concentrations, the concentration of oxygen in the liquid

phase would be greater than that in any of the other experiments.

Thus the reaction conditions were probably favourable for the formation

of products of thiophenol, other than the disulphide and the thiolsul-

phinate. This may account for the extra oxygen consumption. The final reaction mixtures from some of the reactions in which the vibromix stirrer was used at low catalyst concentrations were tested for the presence of thiolsulphonate ($PhSO_2SPh$) by the method given by Barnard and Cole (54), but all tests proved negative. However, if the thiolsulphonate was formed, it may have been decomposed by the following reported reaction with thiophenol (38):-

$$PhSO_2SPh + PhSH \longrightarrow PhSO_2H + PhSSPh \qquad (6.2.1.5)$$
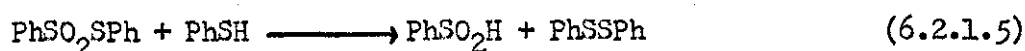
From tables 6.1, 6.2, 6.3 and 6.4, it can be seen that if higher oxidation products of thiophenol were formed, they would in most cases constitute less than 5% of the final product. Because of this, and also the fact that no relatively simple methods were available for detecting these higher oxidation products, the detection of these products was not investigated further.

Savige and Maclaren (38) reported that thiolsulphinates react with thiols according to the following equation:

$$2\ RSH\ +\ RSOSR \longrightarrow 2\ RSSR\ +\ H_2O \qquad (6.2.1.6)$$
$$\text{(where R = alkyl or aryl group)}$$
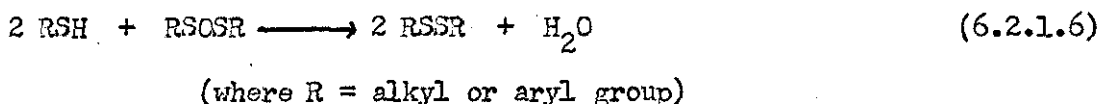
This reaction would obviously occur as a side reaction in the oxidation of thiophenol. In terms of the amount of oxygen and thiophenol which is consumed, the formation of the disulphide by this side reaction via the initial formation of the thiolsulphinate is indistinguishable from the direct oxidation of thiophenol to the disulphide. This is shown below.

$$2\ PhSH \xrightarrow{\frac{1}{2}O_2} PhSSPh\ +\ H_2O \qquad (6.2.1.7)$$
$$2\ PhSH \xrightarrow{O_2} PhSOSPh\ +\ H_2O \qquad (6.2.1.8)$$

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$$\text{PhSOSPh} + 2\text{ PhSH} \longrightarrow 2\text{ PhSSPh} + \text{H}_2\text{O} \qquad\qquad (6.2.1.9)$$

$(6.2.1.8) + (6.2.1.9)$ gives :-

$$4\text{ PhSH} \xrightarrow{\text{O}_2} 2\text{ PhSSPh} + 2\text{ H}_2\text{O} \qquad\qquad (6.2.1.10)$$
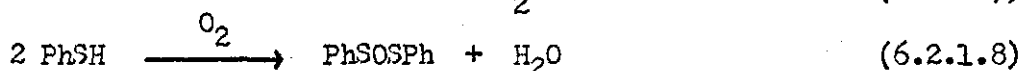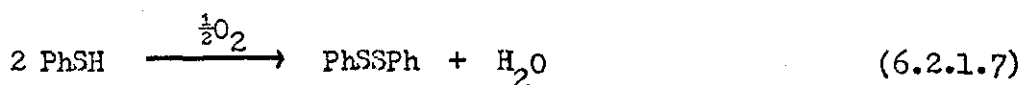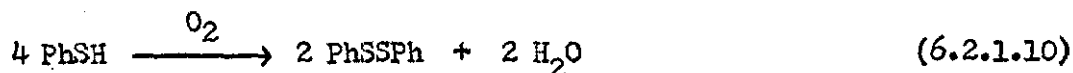
Equation 6.2.1.10 is equivalent to equation 6.2.1.7.

The fact that as much as 50% of the thiolsulphinate is present in the final reaction mixture after completion of some of the final oxidation reactions shows that this side reaction is a slow reaction. Assuming that it is not catalyzed by copper ions, this side reaction would be negligible for short reaction times, i.e. at high catalyst concentrations. As the reaction times increase, i.e. at increasingly low catalyst concentrations, this side reaction would become increasingly significant. This is probably the main reason why in Figs. 6.1.3.4, 6.1.3.6 and 6.1.3.8, as the catalyst concentration is decreased, the percentage thiolsulphinate formed appears to reach a maximum and then decrease.

It can be seen from Figs. 6.1.3.6 and 6.1.3.8 that the percentage thiolsulphinate formed decreases with either decreasing the rate of mass transfer of oxygen from the liquid phase to the gas phase or decreasing the partial pressure of oxygen. This is logical since one would expect the selectivity for the more highly oxidized product to decrease with the decreasing availability of oxygen.

6.2.1.2 Variable Thiophenol Concentrations (Figs 6.1.4.1 and 6.1.4.2).

The graph of log (initial rate of oxygen absorption) vs log (initial catalyst concentration) is similar in shape to the corresponding graph obtained by Tsuchida et al. (15) for the oxidative coupling of

2,6-dimethylphenol. Tsuchida et al. reported the similarity between their graph and the corresponding graphs for enzyme reactions. A linear relationship for the Lineweaver-Burk plot (1/rate vs 1/[substrate]) gave support to the classification of the oxidative coupling of 2,6-dimethylphenol as an enzyme type reaction. A Lineweaver-Burk plot for the oxidative coupling of thiophenol is shown in Fig. 6.2.1.4. This shows a linear relationship which suggests that the oxidative coupling of thiophenol may also be considered as an enzyme type reaction. However, it must be remembered that this set of experiments at variable thiophenol concentrations were conducted in the fast reaction regime (or possibly in the instantaneous reaction regime at very high thiophenol concentrations). In the fast reaction regime at a constant catalyst concentration, it was previously stated that:-

$$\overline{V} = \sqrt{k\, b_o\, D_a} \cdot c'_o \qquad\qquad (6.2.1.2)$$

In enzyme type reactions, the intercept of the Lineweaver-Burk plot (when 1/[substrate] = 0) is equal to $1/V_{max}$, where $V_{max} = k_2 [E]_o$. V_{max} is the maximum rate which is obtained at high substrate concentrations where the reaction is zero order with respect to the substrate. In the thiophenol oxidation, if the intercept is equal to $1/V_{max}$, then V_{max} will be given by:-

$$V_{max} = \sqrt{k\, b_o\, D_a} \cdot c'_o \qquad\qquad (6.2.1.11)$$

or

$$V_{max} = k_2 \sqrt{b_o} \qquad\qquad (6.2.1.12.)$$

where

$$k_2 = \sqrt{k\, D_a} \cdot c'_o \qquad\qquad (6.2.1.13)$$

and k_2 is the overall rate constant.
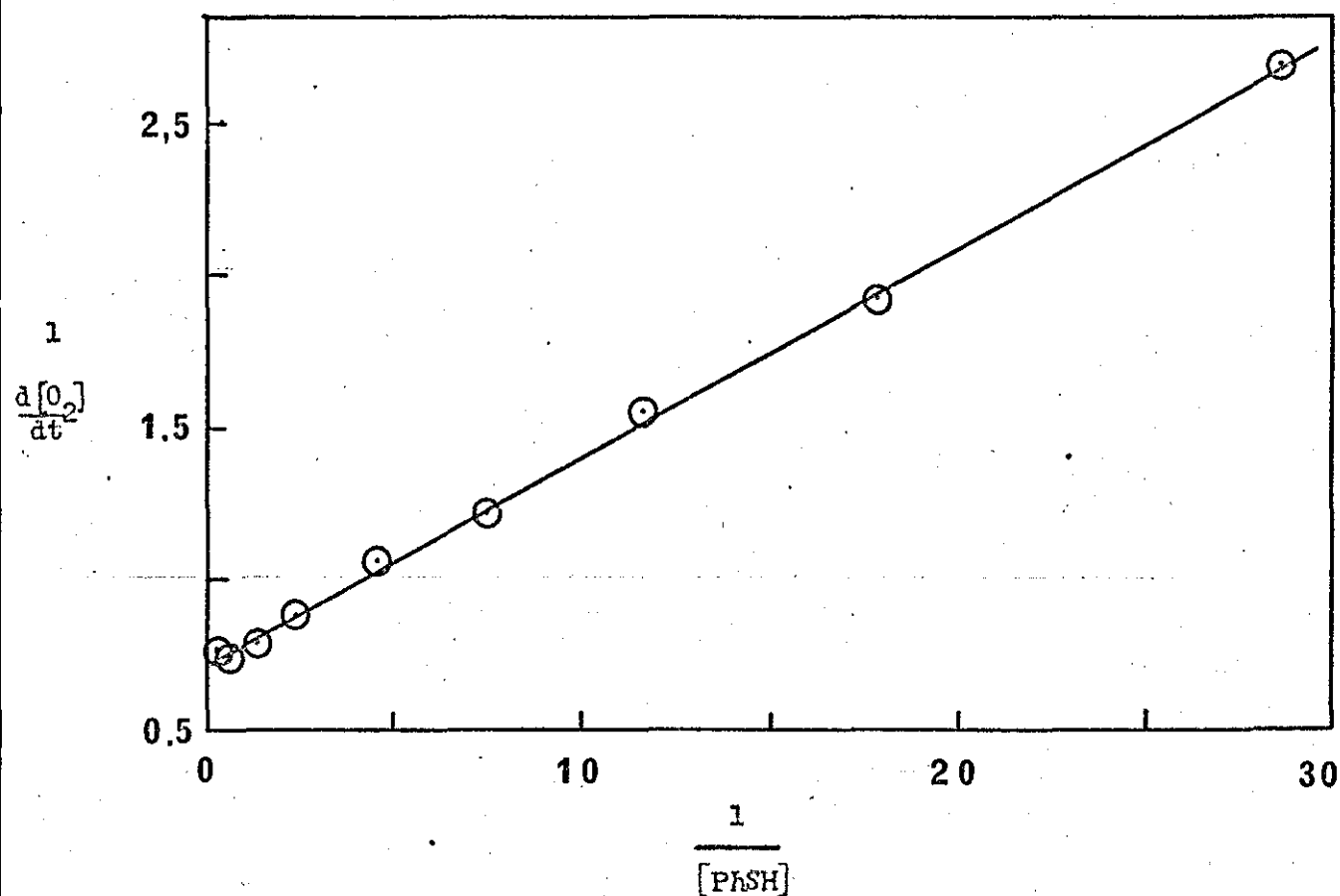
Fig. 6.2.1.4. Lineweaver-Burk plot.
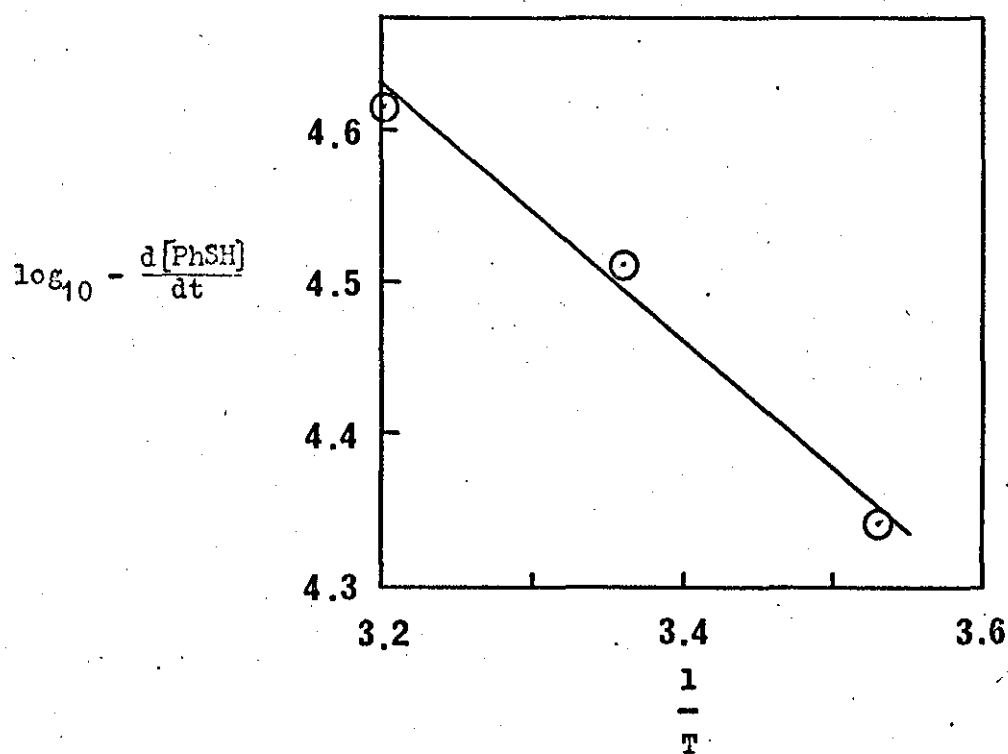
Fig. 6.2.1.5. $\log_{10} - \dfrac{d[\text{PhSH}]}{dt}$ vs $1 / T$.

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Thus if k (in this case the kinetic rate constant for thiophenol oxidation to diphenyl disulphide) and D_a were known, the value of k_2 could be found.

Similarly from the slope of the Lineweaver-Burk plot a value of K_m can be found. The significance of this value of K_m is not known because of the following reason. When the chemical reaction rate is expressed by the general enzyme rate equation (equation 2.4.8), it is virtually impossible to derive a general solution to the differential equation representing mass transfer with chemical reaction. This means that an expression for the rate of oxygen absorption (∇) in terms of K_m $[S]$ and $[O_2]$ cannot be derived.

One important conclusion arising from the above linear Lineweaver-Burk plots which have been obtained is that the linear relationships are no proof that such gas-liquid systems are occurring in the kinetic regime. Even a Lineweaver-Burk plot of 1/(rate of oxygen absorption) vs 1/(thiophenol concentration), Fig. 6.2.1.4, gives a linear relationship. In this case not only was the reaction in the fast reaction regime, but there was additional oxygen consumed in the formation of the thiolsulphinate. Thus it can be seen that much care is needed in interpreting the results of linear Lineweaver-Burk plots.

From the fact that the graphs of oxygen consumed vs time (Fig. 6.1.3.1) give straight lines for most of the reaction, one would expect that the thiophenol oxidation reaction would be zero order with respect to the thiophenol concentration, i.e. one would expect that the graph of log (initial rate of oxygen absorption) vs log (initial thiophenol concentration), Fig. 6.1.4.1, would be a straight line parallel to the

log (initial thiophenol concentration) axis. Thus Figs. 6.1.3.1. and 6.1.4.1 appear to be contradictory. Tsuchida et al. (15) obtained a similar apparent contradiction in their results for the oxidation of 2,6-dimethylphenol. However, it appears that they overlooked this matter, making no comment whatsoever upon this phenomenon. Possible explanations to account for this behaviour are now considered.

If the reaction was catalyzed by one or more of the thiophenol oxidation products, a similar effect would not be obtained for the oxidation of 2,6-dimethylphenol. One of the products of all oxidative coupling reactions is water. However, the possibility of water acting as a catalyst can be ruled out because Tsuchida et al. (15) used a drying agent to absorb the water produced in their experiments, whereas no drying agent was used in the experiments of this present project. It might be argued that the selectivity for the thiolsulphinate may be increased throughout the reaction in such a way that the expected reduction in the rate of oxygen absorption is compensated by an increase in the amount of oxygen which is consumed in the formation of the thiolsulphinate. However, not only would this be a coincidence but a similar explanation could not be given to account for the corresponding phenomenon occurring in the oxidation of 2,6-dimethylphenol.

Thus, at present, no logical explanation can be given for the apparent contradiction between Figs. 6.1.2.1 and 6.1.3.1. Further experimental work is required in order to resolve this phenomenon.

6.2.1.3 Dependence Upon Temperature.

Over the temperature range 10-40°C, the rate of oxygen absorption appears to be independent of temperature (see table 6.6). However,

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the calculated rate of thiophenol consumption increases with increasing temperature as would be expected.

The Arrhenius equation (equation 6.2.1.14) describes the dependence of the kinetic rate constant upon temperature.

$$k = Ae^{-E/\bar{R}T} \tag{6.2.1.14}$$

where $\bar{R}$ = gas constant, 1.98 cal/grm mole ^{o}K

E = activation energy

T = temperature (^{o}K)

A = constant (frequency factor).

If it is assumed that the formation of a thiophenoxy radical (PhS·) is the initial step in the formation of both the disulphide and the thiolsulphinate (see section 6.2.2), then it is possible to calculate the activation energy of the initial thiophenoxy radical formation step.

If $\bar{V}_{rad}$ is defined as the rate of absorption (moles/cm^2) of that oxygen which is consumed in producing the thiophenoxy radicals, then :-

$$\bar{V}_{rad} = \text{constant} \times \left(- \frac{d \ PhSH}{dt} \right) \tag{6.2.1.15}$$

We can say that in the fast reaction regime considered:-

$$\bar{V}_{rad} = \sqrt{k \ b_o \ D_a} \cdot c'_o \tag{6.2.1.16}$$

substituting equation 6.2.1.14 into equation 6.2.1.16 gives:-

$$\bar{V}_{rad} = \sqrt{Ae^{-E/RT} \ b_o \ D_a} \cdot c'_o \tag{6.2.1.17}$$

or

$$\text{constant} \times \left(- \frac{d[PhSH]}{dt}\right) = \sqrt{Ae^{-E/RT}b_oD_a \cdot c'_o} \qquad (6.2.1.18)$$

or

$$2 \, Log_{10}(\text{constant}) + 2 \, log_{10}\left(- \frac{d[PhSH]}{dt}\right) = log_{10}Ab_oD_a(c'_o)^2 - 2\cdot303 \frac{E}{RT}$$

$$(6.2.1.19)$$

Thus a graph of $log_{10}\left(- \frac{d[PhSH]}{dt}\right)$ vs 1/T should give a straight line of slope - (2·303/2) (E/R). This graph was plotted for the experimental results (Fig. 6.2.1.5). From the slope, the activation energy, E, was found to be 1.4 K cals/mole. This low value for the activation energy is to be expected since thiophenol is readily oxidized under the oxidative coupling reaction conditions used.

If the thiophenoxy radical was the initial species formed and the disulphide and the thiolsulphinate were formed by free radical reaction steps, then the activation energies of the subsequent free radical steps would probably be approximately zero. As the reaction temperature decreases, the rate of the initial reaction step for the formation of the thiophenoxy radical also decreases, thus consuming less oxygen. This in turn would mean that there would be more oxygen available for the formation of the higher oxidation products. If these subsequent free radical steps had activation energies of about zero, then one would expect that a higher percentage of the higher oxidation products would be formed at lower temperatures. This is in agreement with that which was found in practice as can be seen from table 6.6.

6.2.1.4 Analysis of Samples Taken During the Course
of the Thiophenol Oxidation Reaction.

The graphs of F/F_f vs percent extent of the reaction show a
similar shape to one another, Fig. 6.2.1.6 showing a typical plot
(The definitions of F, F_f and ϕ have previously been given in section
6.1.6). From Fig. 6.2.1.6, it would appear at first that the
selectivity of the reaction for the thiolsulphinate was not constant
throughout the reaction. However, the following argument shows that
the assumption of a constant selectivity (ϕ) throughout the reaction
is consistent with the experimental results.

If constant selectivity is assumed throughout the reaction, then
a graph of ϕ_i (where ϕ_i is the instantaneous value of ϕ) vs percent
extent of the thiophenol oxidation reaction would be as shown in
Fig. 6.2.1.7. The following previously reported (section 6.2.1.1)
side reaction of thiophenol with thiolsulphinates (equation 6.2.1.20)
is now considered.

$$PhSOSPh + 2\ PhSH \longrightarrow 2\ PhSSPh + H_2O \qquad\qquad (6.2.1.20)$$
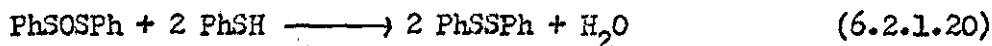
In glacial acetic acid solvent, Kice et al (59) reported that
the above reaction was first order with respect to both the thiol and
the thiolsulphinate. Although the reaction conditions differ
considerably, it is reasonable to assume that in pyridine the reaction
is dependent upon the thiolsulphinate concentration to the power m
and dependent upon the thiophenol concentration to the power n, where
n and m are both greater than zero. If this is so, then for a typical
thiophenol oxidation reaction, a plot of the percent of the thiophenol
reaction would probably be of the shape shown in Fig. 6.2.1.8. The
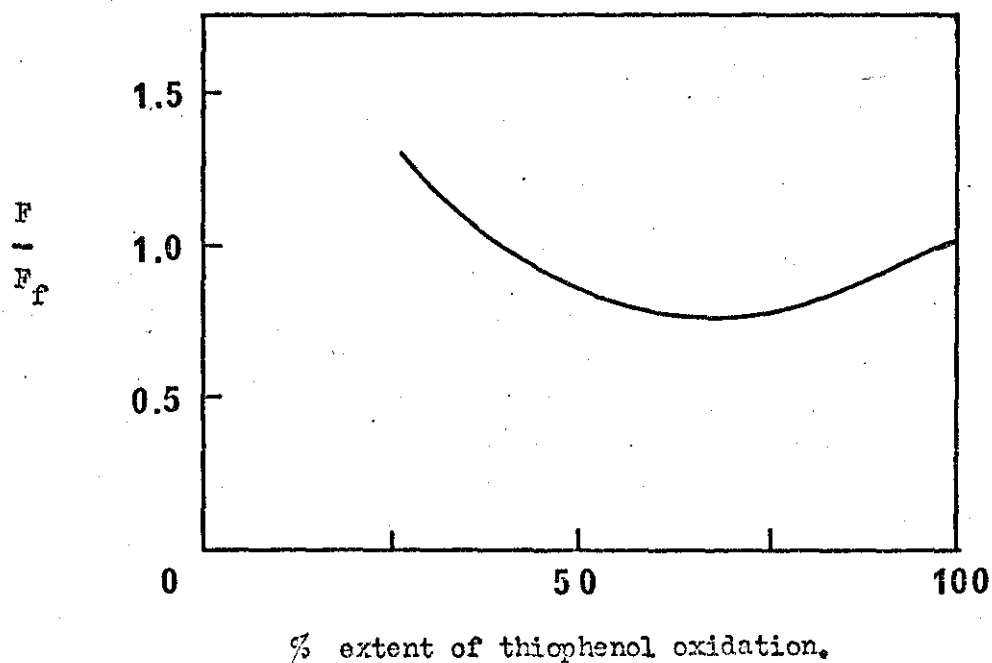
Fig. 6.2.1.6. F / F vs % extent of thiophenol oxidation reaction.

Fig. 6.2.1.7. ϕ_i vs % extent of thiophenol oxidation reaction.

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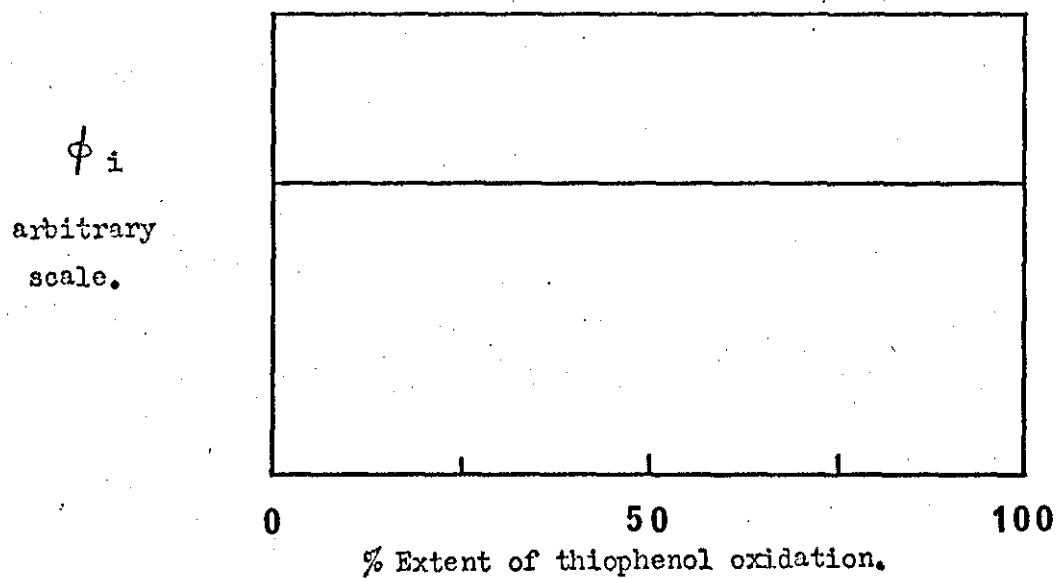
% Extent of
the side
reaction.

% Extent of thiophenol oxidation.
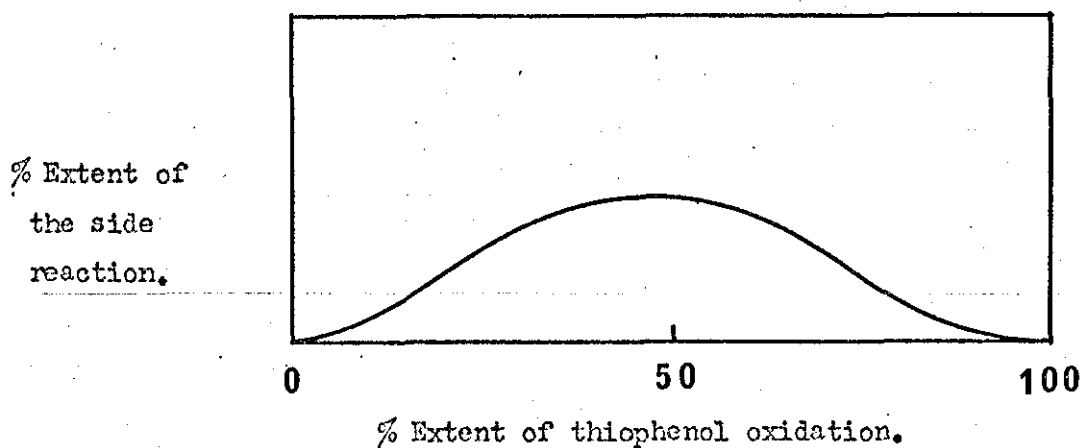
Fig. 6.2.1.8. % Extent of the side reaction vs
extent of the thiophenol oxidation.

instantaneous
net production
of PhSOSPh.

% Extent of thiophenol oxidation.
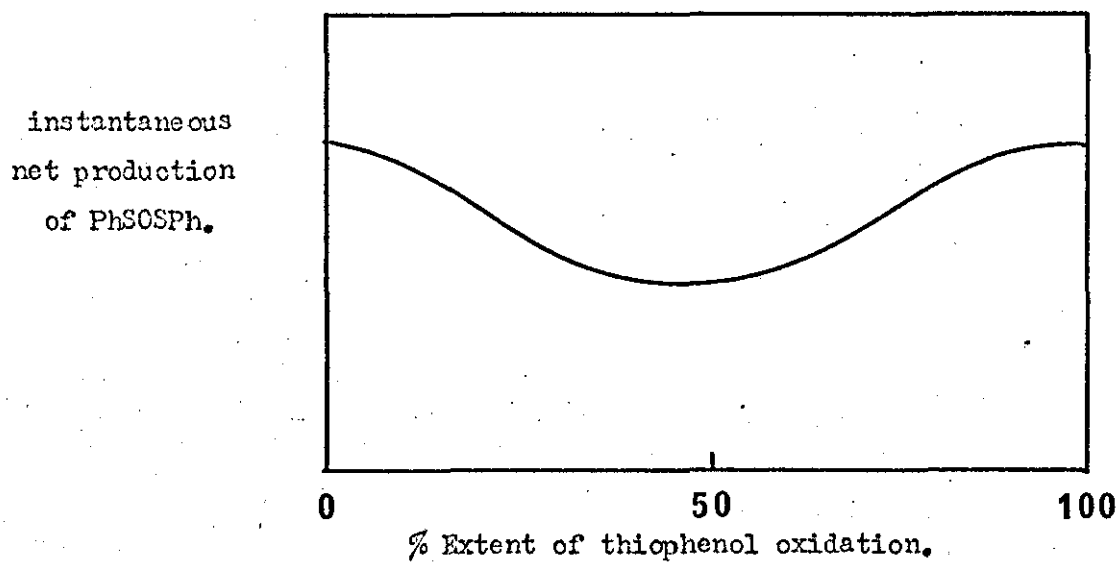
Fig. 6.2.1.9. Instantaneous net production of PhSOSPh vs
extent of the thiophenol oxidation.

shape of this graph was deduced as follows. At the start of the thiophenol oxidation, the concentration of the thiolsulphinate would be low, and thus the extent of the side reaction would be negligible. Similarly towards the end of the thiophenol oxidation, the concentration of thiophenol would be low, and again the extent of the side reaction would be negligible. Around the half-way stage of the reaction, there would be appreciable amounts of both thiophenol and the thiolsulphinate, and in this case the extent of the side reaction would be appreciable.

Thus from Figs. 6.2.1.7 and 6.2.1.8 it may be deduced that the shape of the graph of the instantaneous net production of the thiol-sulphinate vs percent extent of the thiophenol oxidation reaction would be as shown in Fig. 6.2.1.9. Furthermore from Fig. 6.2.1.9, it may be deduced that the graph of F, and thus F/F_f, vs percent extent of the thiophenol oxidation reaction would be of the shape shown in Fig. 6.2.1.6, the experimentally determined graph.

Thus although a constant selectivity for the production of the thiolsulphinate throughout the thiophenol oxidation reaction has not exactly been proved, the experimental evidence is consistent with that which would be expected for the case of constant selectivity throughout the reaction.

For reactions at higher catalyst concentrations (i.e. short reaction times) where the extent of the side reaction would be negligible, one might be able to prove a constant selectivity for the reaction. In this case F would be equal to ϕ. However, at higher catalyst concentrations there would be insufficient time available to perform

the potentiometric titration between taking samples. For future work, this problem could be solved in one of the following ways:-

(a) by developing a suitable method for the determination of thiophenol in the reaction mixture where the analysis of all the samples could be done at the end of the oxidation reaction.

(b) by developing a thiophenol determination method which takes less time (e.g. chromatographic method).

(c) by performing a number of experiments under identical conditions taking out only one sample for each experiment but for each experiment the sample would be removed at different stages of the reaction.

The disadvantage of the last method is that in order to obtain a given set of results, the amount of experimental work is greatly increased. It is feasible that a method could be developed whereby a sample may be titrated first for thiophenol and then for the thiolsulphinate in situ. The thiophenol interference in the thiolsulphinate titration would have been removed by the initial potentiometric titration for thiophenol. This method would greatly reduce the magnitude of the errors incurred in estimating the thiolsulphinate concentration. Greater accuracy would also be attained by scaling-up the experimental work. In addition it would be very useful to determine the kinetics of the side reaction (equation 6.2.1.20) by independent experiments. The extent of this side reaction in the main oxidation reaction could then be calculated.

Appreciable errors were incurred in the experimental work because of the following reason. As stated in section 6.1.6, there apparently was a product formed in the initial stages of the reaction which interfered with the thiophenol titration. This interference was

quite appreciable since the first sample in each of the 4 experiments

gave a thiophenol determination which suggested that there was more

thiophenol present in the reaction mixture at that time than at the

start of the reaction. This not only gave a meaningless result for

the first sample, but would also affect the analysis of the rest of

the samples. However, the results were sufficiently accurate to give

a qualitative picture of the composition of the reaction mixture

during the course of the reaction.

6.2.2   Reaction Mechanisms.

In the oxidative coupling of phenols, the copper catalyst

reacts with phenol to produce a phenoxy radical from which either the

diphenoquinone or the polyphenylene oxide is formed. Thus it is

probable that in the oxidative coupling of thiophenol, the copper

catalyst would react with thiophenol to produce a thiophenoxy radical

(PhS•) from which the various oxidation products of thiophenol are

formed.

(a)   Mechanism for the Formation of Thiophenoxy Radicals.

One might expect that the reaction mechanism for the formation

of thiophenoxy radicals from thiophenol would be very similar to the

mechanism for the formation of phenoxy radicals from phenol. It has

been previously shown (section 2.4) that despite the numerous

mechanisms which have been postulated for the oxidative coupling of

phenols to phenoxy radicals, no conclusive proof has been given for

any one of these mechanisms. As previously stated (section 2.4), it

was only in a recent paper by Tsuchida et al.(15) that the reaction

was shown to conform to an enzyme type mechanism. These authors

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suggested three possible mechanisms which fitted their experimental results. However, only the outline of the mechanisms were given and they were not able to indicate which of the three mechanisms was the most probable. The rate expressions they gave did not exactly correspond to the reaction mechanism which they postulated. Nevertheless the correct rate expressions for these mechanisms (given in appendix H) still fit their experimental results, i.e. the Lineweaver-Burk plots of $1/v_d$ vs $1/[S]$ and $1/k_2$ vs $1/[O_2]$ would still show linear relationships. Thus it can be seen that the obtaining of a linear relationship for a Lineweaver-Burk plot is no proof for a particular mechanism.

The last type of the three mechanisms which were proposed by Tsuchida et al.(15) is the most probable of the three for the oxidative coupling of thiophenol because of the following reason. During the experiments at high catalyst concentrations it was observed that the colour of the reaction mixture was yellow as opposed to the dark green colour of the fully oxidized catalyst solution. When copper (I) chloride is dissolved in pyridine, the colour of the solution is initially yellow but soon changes to a dark green. This suggests that the copper (I) form of the catalyst is yellow. If this is the case, then in the instantaneous reaction regime the reaction between the copper (I) catalyst and oxygen is relatively slow compared to the other reaction steps. Furthermore, this would most probably be true for the fast reaction regime also. The last of the three mechanisms proposed by Tsuchida et al. is the only one of the three in which oxygen reacts with the copper (I) species and it is for this reason that this last mechanism is preferred. However, as stated above, this mechanism was only an outline of the reaction steps. From this basic mechanism, four more detailed mechanisms have been obtained (scheme 6.1.).

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MECHANISM A

MECHANISM B

Scheme 6.1(1)

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MECHANISM C

$$HO\text{-}Cl\text{-}py_2 \quad CuII\ CuII \quad py_2\text{-}Cl\text{-}OH \xrightleftharpoons[\ k_{-1}\ ]{\substack{k_1 \\ 2PhSH \\ 2H_2O}} PhS\text{-}Cl\text{-}py_2 \quad CuII\ CuII \quad py_2\text{-}Cl\text{-}SPh \xrightarrow{k_e} PhS\cdot\text{-}Cl\text{-}py_2 \quad CuI\ CuI \quad py_2\text{-}Cl\text{-}\cdot SPh$$

$$k_r \nearrow \quad -H_2O$$

$$k_{ox} \downarrow O_2(\text{slow})$$

Ph HS—Cl—py$_2$ / CuII CuII / py$_2$—Cl—SPh H
$\xleftarrow[\substack{-2PhS\cdot}]{k_p}$ 2PhSH
PhS·—Cl—py$_2$ / CuII–O–CuII / py$_2$·Cl—·SPh
$\xleftarrow{k_{eox}}$
PhS·—Cl—py$_2$ / CuI–O–CuI / py$_2$ Cl ·SPh

MECHANISM D

HO—Cl—py$_2$ / CuII CuII / py$_2$ Cl OH
$\xrightleftharpoons[\substack{k_{-1} \\ 2H_2O}]{\substack{2PhSH \\ k_1}}$
PhS—Cl—py$_2$ / CuII CuII / py$_2$ Cl SPh
$\xrightarrow{k_e}$
PhS·—Cl—py$_2$ / CuI CuI / py$_2$ Cl ·SPh

$$k_r \nearrow \quad -H_2O$$

$$k_t \downarrow \substack{2PhSH \\ -2PhS\cdot}$$

Ph HS—Cl—py$_2$ / CuII–O–CuII / py$_2$ Cl SPh H
$\xleftarrow{k_{eox}}$
H / PhS—Cl—py$_2$ / CuI—O—CuI / py$_2$ Cl SPh H
$\xleftarrow[O_2\,(\text{slow})]{k_o}$
H / PhS—Cl—py$_2$ / CuI CuI / py$_2$ Cl SH Ph

Scheme 6.1(ii)

Reaction mechanisms for the formation of thiophenoxy radicals

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All these four mechanisms are consistent with the available experimental evidence and would also give linear Lineweaver-Burk plots. The catalyst structure proposed by Price and Nakaoka (14) has been used and the mechanisms have been modified so as to apply to thiophenol.

In mechanisms A and B, thiophenoxy radicals are produced in two different reaction steps, steps k_t and k_r. This is unusual but quite feasible. In mechanisms C and D an oxygen atom rather than an oxygen molecule is incorporated into the catalyst structure. It may appear that this would be very unlikely; however, the structure of the compound $Cu_4Cl_6O.4$ py, which is well characterized (60) consists of a tetranuclear copper structure with an oxygen in the centre and chlorine atoms on the six tetrahedral edges. It is possible that the copper chloride pyridine catalyst may consist of a tetranuclear copper framewrok.

Other possible mechanisms may also be postulated, but with the experimental evidence which is available at present it is not possible to assign a unique mechanism to the thiophenol oxidation reaction. Because of this fact, the reaction mechanism for the formation of thiophenoxy radicals will not be discussed further.

(b) Mechanism for the Formation of Products
    from the Thiophenoxy Radicals.

The disulphide molecule would most probably be formed by the combination of two thiophenoxy radicals (equation 6.2.2.1).

$$PhS \cdot \ + \ \cdot S \ Ph \ \longrightarrow \ PhSSPh \hspace{3cm} (6.2.2.1)$$

One possible mechanism for the formation of thiolsulphinate is shown in equations 6.2.2.2 to 6.2.2.6.

$$PhS\cdot \ + \ O_2 \longrightarrow PhSO_2\cdot \qquad\qquad (6.2.2.2)$$

$$PhSO_2\cdot \ + \ \cdot SPh \longrightarrow PhSOOSPh \qquad\qquad (6.2.2.3)$$

$$PhSOOSPh \ + \ \cdot SPh \longrightarrow PhSO\cdot \ + \ PhSOSPh \qquad (6.2.2.4)$$

$$PhSO\cdot \ + \ \cdot SPh \longrightarrow PhSOSPh \qquad\qquad (6.2.2.6)$$

overall $4\,PhS \ + \ O_2 \longrightarrow 2\,PhSOSPh$ .....   (6.2.2.6)
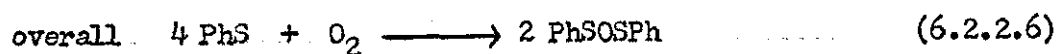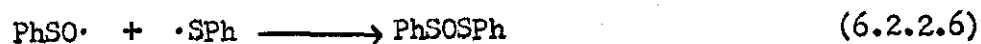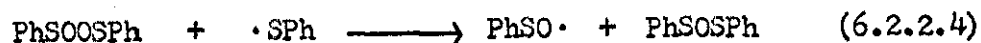
Benzene sulphur acids may be formed by the following reaction mechanisms, equations 6.2.2.7 to 6.2.2.10.

$$Ph\dot{S}OO\cdot \ \rightleftharpoons \ Ph\dot{S}OO \qquad\qquad (6.2.2.7)$$

$$Ph\dot{S}OO \ + \ H_2O \longrightarrow Ph\dot{S}\text{-}O\text{-}O \qquad\qquad (6.2.2.8)$$

with the H O H bonded below

$$Ph\dot{S}\text{-}O\text{-}O \longrightarrow Ph\dot{S}=O \ + \ \cdot OH \qquad\qquad (6.2.2.9$$

with the O, OH, and H H groups;   benzene sulphinic acid

$$PhS\cdot \ + \ \cdot OH \longrightarrow PhSOH \qquad\qquad (6.2.2.10)$$

benzene sulphenic acid
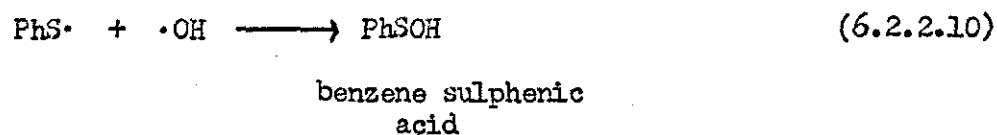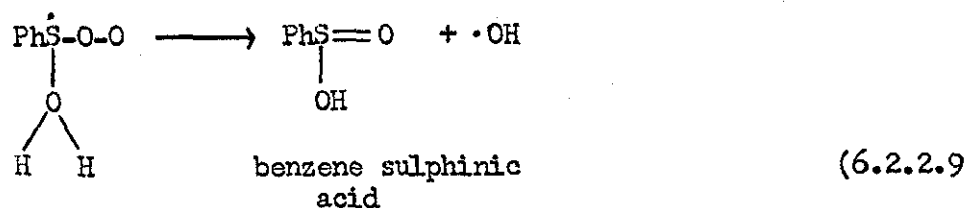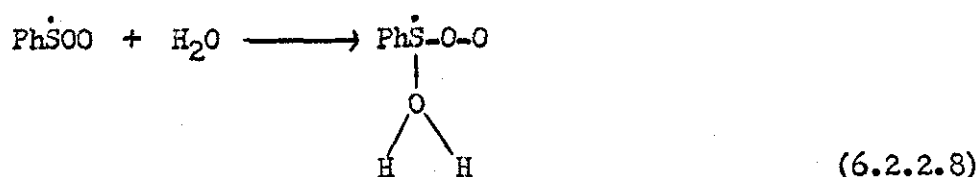
It is assumed that water is present in order that the above reaction mechanism may occur. This is probably true since pyridine is a very hygroscopic liquid and usually contains small amounts of water even when a drying agent such as molecular seives is used.

There are also other known reactions (38) which may possibly occur as side reactions in the thiophenol oxidation reaction; some of these are given in equations 6.2.2.11 to 6.2.2.15.

$$PhSH + PhSOSPh \longrightarrow PhSSPh + PhSOH \qquad (6.2.2.11)$$

$$2\ PhSOSPh \longrightarrow PhSSPh + PhSO_2Ph \qquad (6.2.2.12)$$

$$2\ PhSOH \longrightarrow PhSOSPh + H_2O \qquad (6.2.2.13)$$

$$PhSOH + PhSH \longrightarrow PhSSPh + H_2O \qquad (6.2.2.14)$$

$$3\ PhSO_2H \longrightarrow PhSO_3H + PhSO_2SPh + H_2O \qquad (6.2.2.15)$$

None of these side reactions would occur to any appreciable extent (see section 6.2.1.1). There is insufficient experimental evidence to argue for or against any of the mechanisms given in equations 6.2.2.1 to 6.2.2.15, and thus these will not be discussed further.

(c) Kinetic Scheme for the Formation of the
Disulphide and the Thiolsulphinate.

The kinetic scheme shown in scheme 6.2 is consistent with most of the experimental evidence and provides a mechanism for the formation of both the disulphide and the thiolsulphinate.

Scheme 6.2.

minor amounts of higher oxidation products of thiophenol

Reaction mechanism for the thiophenol oxidation reaction.

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If this was the kinetic scheme, the following reaction characteristics would be expected.

(1) At a given catalyst concentration, higher mass transfer rates would increase the amount of oxygen available for both the reoxidation step and the formation of the radical $PhSO_2\cdot$ and thus the selectivity for the thiolsulphinate would increase.

(2) As the catalyst concentration was increased there would be a greater demand for oxygen in the recycling step and thus the selectivity for the thiolsulphinate would decrease.

(3) As the thiophenol concentration was increased, the rate of reaction would increase thus increasing the concentration of thiophenoxy radicals and decreasing the availability of oxygen. This would favour the formation of the disulphide and decrease the selectivity for the thiolsulphinate.

The experimental evidence is in agreement with the above expected reaction characteristics and thus strongly supports the postulated kinetic scheme. It is well known that an oxygen molecule will readily attach itself to a thiol radical such as $PhS\cdot$ (61) and thus this is the most likely means whereby oxygen could be incorporated into the thiophenol oxidation product. Thus a reaction mechanism for the formation of thiophenoxy radicals would apply to the formation of the disulphide, the thiolsulphinate and any other oxidation products of thiophenol.

6.2.3 Equations Representing Mass Transfer with Chemical Reaction for Thiophenol Oxidation

As previously stated (section 3.2), solutions for models of mass

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transfer with chemical reaction can only be obtained for very simple
expressions for the chemical reaction rate. The simplest possible
expression for the chemical reaction rate of the oxidation of
thiophenol was deduced from scheme 6.2 and is shown in equations
6.2.3.1 and 6.2.3.2.

The rate of oxygen absorption for the formation of thiophenoxy
radicals is given by:-

$$\left(\frac{d[O_2]}{dt}\right)_{PhS.} = k_o [Cu] [O_2] \qquad (6.2.3.1)$$

The rate of oxygen absorption for the formation of the thiol-
sulphinate from thiophenoxy radicals is given by:-

$$\left(\frac{d[O_2]}{dt}\right)_{th} = k_{th} [PhS\cdot] [O_2] \qquad (6.2.3.2)$$

In equation 6.2.3.1 it is assumed that for a given catalyst
concentration, the reaction rate is independent of the thiophenol
concentration. This assumption is valid since for any given catalyst
concentration, the graph of oxygen absorption vs time is a straight
line for most of the reaction. Equation 6.2.3.2 has been derived from
the assumption that the rate determining step for the formation of
the thiolsulphinate from thiophenoxy radicals is the initial reaction
between an oxygen molecule and a thiophenoxy radical (equation 6.2.2.2).
It must be emphasized that equations 6.2.3.1. and 6.2.3.2. may be
simplifications of the true reaction rates and equation 6.2.3.2 has
been derived on the basis of an assumption, the validity of which at
present cannot be proved. This is necessary in order to derive equations
representing mass transfer with chemical reaction which are simple
enough to make their solution at all feasible.

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If it is assumed that the concentration of the thiophenoxy radicals is constant throughout the reaction, then the rate of generation of thiophenoxy radicals is given by equation 6.2.3.3.

$$\frac{d[PhS\cdot]}{dt} = k_o [Cu][O_2] - k_{th} [PhS\cdot][O_2] - k_{dis} [PhS\cdot]^2 = 0 \qquad (6.2.3.3)$$

giving:-

$$[PhS\cdot] = \frac{-k_{th} [O_2] + \left[(k_{th} [O_2])^2 + 4k_{dis}k_o [O_2][Cu]\right]^{\frac{1}{2}}}{2 k_{dis}} \qquad (6.2.3.4)$$

The positive root of the quadratic must be taken to give a positive value of $[PhS\cdot]$.

Thus the total rate of oxygen consumption is given by:-

$$- \frac{d[O_2]}{dt}_{total} = [O_2]k_o [Cu] + k_{th} \frac{-k_{th} [O_2] + \left[(k_{th} [O_2])^2 + 4k_{dis}k_o [O_2][Cu]\right]^{\frac{1}{2}}}{2 k_{dis}}$$

$$(6.2.3.5)$$

If equation 6.2.3.5 is substituted into the equation representing the phenomenon of mass transfer with chemical reaction (equation 3.2.1 for the penetration theory, equation 3.2.3 for the film theory), the following equations are obtained:-

(1) For the penetration theory:-

$$D_o \frac{\partial^2[O_2]}{\partial x^2} = \frac{\partial[O_2]}{\partial t} + k_o [Cu][O_2] + k_{th} [O_2][PhS\cdot] \qquad (6.2.3.6)$$

(where $[PhS\cdot]$ is defined as in equation 6.2.3.4, and D_o is the diffusivity of oxygen in pyridine.)

(2) For the film theory:-

$$D_o \frac{\partial^2[O_2]}{\partial x^2} = k_o [Cu][O_2] + k_{th} [O_2] [PhS\cdot] \qquad (6.2.3.7)$$

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The boundary conditions associated with equation 6.2.3.7 are:-

$$x = 0, \qquad c = c'_o \tag{6.2.3.8}$$

$$x = \lambda, \qquad \frac{dc}{dx} = 0 \tag{6.2.3.9}$$

Equation 6.2.3.7 can be simplified to the expression given in equation 6.2.3.10.

$$\frac{d^2c}{dx^2} = Ac^2 + Bc + Ec(Gc^2 + Hc)^{\frac{1}{2}} = f(c) \tag{6.2.3.10}$$

where: $c = [O_2]$; $A = \dfrac{-(k_{th})^2}{2\,k_{dis}}$;

$$B = k_o [Cu] \quad ; \quad E = \frac{k_{th}}{2k_{dis}} \quad ; \quad G = (k_{th})^2 \tag{6.2.3.11}$$

and $H = 4\,k_{dis}\,k_o[Cu]$

Multiplying equation 6.2.3.10 by $2(dc/dx)$ gives:-

$$2\left(\frac{d^2c}{dx^2}\right) \times \left(\frac{dc}{dx}\right) = 2\,f(c)\left(\frac{dc}{dx}\right) \tag{6.2.3.12}$$

Integrating 6.2.3.12 gives:-

$$\left(\frac{dc}{dx}\right)^2 = 2\int f(c)\frac{dc}{dx}\cdot dx + k_1 = 2\int f(c)dc + k_1 \tag{6.2.3.13}$$

where k_1 = a constant.

From 6.2.3.10 :-

$$\int f(c)dc = \frac{Ac^3}{3} + \frac{Bc^2}{2} + E\int c(Gc^2 + Hc)^{\frac{1}{2}}\,dc + k_2 \tag{6.2.3.14}$$

where k_2 = a constant

Now:-

$$E\int c(Gc^2 + Hc)^{\frac{1}{2}}dc = E\left[\frac{1}{3G}(Gc^2 + Hc)^{3/2}\frac{H}{2G}\int (Gc^2 + Hc)^{\frac{1}{2}}\,dc + k_3\right] \tag{6.2.3.15}$$

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where $\int (Gc^2 + Hc)^{\frac{1}{2}} dc = \dfrac{2Gc + H}{4G} (Gc^2 + Hc)^{\frac{1}{2}}$

$$- \dfrac{H^2}{8G \cdot \sqrt{G}} \ln(2Gc + H + 2\sqrt{G}(Gc^2 + Hc)^{\frac{1}{2}}) + k_4 \qquad (6.2.3.16)$$

and k_3 and k_4 are constants.

Thus from 6.2.3.13 :-

$$\dfrac{dc}{dx} = 2\sqrt{\dfrac{Ac^3}{3} + \dfrac{Bc^2}{2} + E \quad c(Gc^2 + Hc)^{\frac{1}{2}} dc + k_2} \qquad (6.2.3.17)$$

and $E \int c(G c^2 + Hc)^{\frac{1}{2}}$ is given by equation 6.2.3.15.

The above standard integrations were obtained from reference 62.

From equation 6.2.3.17, one can see the immensity of the task of finding an expression for either c in terms of x (the concentration profile) or dc/dx in terms of x. The chemical reaction rate equation cannot be simplified further without reducing it to a completely different expression. Thus it can be seen that even using the simplest of expressions for the reaction rate of thiophenol oxidation, a solution of the resulting equation representing the phenomenon of mass transfer with chemical reaction is virtually impossible.

If the disulphide was the only product formed, then the chemical reaction rate would be represented by equation 6.2.3.1, and, in the case of the film theory, the phenomenon of mass transfer with chemical reaction would be represented by equation 6.2.3.18.

$$\dfrac{dc}{dx} = k_o [Cu][O_2] \qquad (6.2.3.18)$$

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At constant catalyst concentrations this becomes a first order reaction. Expressions for the rate of gas absorption, the concentration gradient and the concentration profile for a first order reaction in the first reaction regime have been given by Astarita (44); from these, equations 6.2.3.19 to 6.2.3.21 are obtained.

$$\bar{V} = \sqrt{D_o\, k_o\, Cu} \cdot [O_2] \qquad\qquad (6.2.3.19)$$

$$\frac{dc}{dx} = \sqrt{\frac{k_o\,[Cu]}{D_o}} \cdot [O_2] \qquad\qquad (6.2.3.20)$$

$$\frac{[O_2]_x}{[O_2]_{x=o}} = \exp\left(-\sqrt{\frac{k_o[Cu]}{D_o}}\right) \qquad\qquad (6.2.3.21)$$

Even at the upper limit of the fast reaction regime for thiophenol oxidation reactions using the magnetic stirrer (A'B'), 30% of the product is the thiolsulphinate and thus there would be considerable errors incurred if equations 6.2.3.18 to 6.2.3.21 were used for this region. In most of the region B'C' there is only a very small percentage of the thiolsulphinate formed; however, this is the instantaneous reaction regime where the rate of absorption is independent of the chemical kinetics, and thus cannot be used to provide information about the rate constants.

For a hypothetical case where only the disulphide is formed in the fast reaction regime an equation for the rate of oxygen absorption has been derived (equation 6.2.3.19). This shows that the rate of oxygen absorption would be proportional to the square root of the copper concentration. However the graph of log $(-d[O_2]/dt)$ vs log [Cu Cl] (Fig. 6.1.3.2), which was calculated from the experimental

results, gave a straight line of slope 0.5 for the fast reaction regime. This shows that, empirically, the rate of oxygen absorption for the formation of the thiolsulphinate together with the disulphide is also proportional to the square root of the copper concentration. Thus the chemical reaction rate for the complete reaction could be expressed by equation 6.2.3.22.

$$\left(- \frac{d\,[O_2]}{dt}\right)_{total} = [Cu]\ f^n(\ [O_2]\ )$$

(6.2.3.22)

In order to determine the function, $f^n(\ |O_2|\ )$, one would need to conduct a series of experiments at various partial pressures of oxygen.

From scheme 6.2, the selectivity of the reaction for the thiolsulphinate can be expressed as:-

$$\frac{d[PhSOSPh]\ /\ dt}{-\ d[PhS\cdot]/dt} = \frac{k_{th}[PhS\cdot][O_2]}{k_o\,[Cu]\,[O_2]} = \frac{k_{th}[PhS\cdot]}{k_o\,[Cu]}$$

(6.2.3.23)

or alternatively by:-

$$\frac{d[PhSOSPh]\ /\ dt}{d[PhSSPh]\ /\ dt} = \frac{k_{th}[PhS\cdot][O_2]}{k_{dis}[PhS\cdot]^2} = \frac{k_{th}\,[O_2]}{k_{dis}[PhS\cdot]}$$

(6.2.3.24)

Substituting equation 6.2.3.4 in 6.2.3.24 gives:-

$$\frac{d[PhSOSPh]\ /\ dt}{d[PhS\cdot]\ /\ dt} = \frac{k_{th}}{k_o[Cu]}\left[\frac{-\ k_{th}[O_2]+\sqrt{(k_{th}[O_2])^2 + 4k_{dis}\ k_o[Cu][O_2]}}{2k_{dis}}\right]$$

(6.2.3.25)

Franklin (63) formulated a method whereby the rate constants of free radical reactions could be estimated. By this method the values of k_{dis} and k_{th} could be estimated. If the value of the rate constant

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k_o was known, equation 6.2.1.26 would then provide a method of predicting the selectivity of the reaction for the thiolsulphinate at given copper catalyst and oxygen concentrations. It must be remembered that this equation would only apply to the kinetic regime where the concentration of oxygen is constant throughout the liquid phase. However, this equation could be used to find the instant-aneous selectivity of the reaction at any point in the liquid where the copper and oxygen concentrations were known. It can be seen from the above discussion that, with the available experimental evidence, a classical and rigorous treatment of the thiophenol oxidation system is not possible because of the complex chemical reaction rate equation. With more experimental work it may be possible to produce a relatively simple empirical equation for the reaction rate and also derive an equation representing mass transfer with chemical reaction which can be solved.

6.3 Conclusions and Suggestions for Further Work

6.3.1 Conclusions.

(1) Under certain conditions diphenyl thiolsulphinate (PhSOSPh) was formed together with diphenyl disulphide as the major product of the thiophenol oxidation reaction.

(2) The reaction was apparently first order with respect to the catalyst concentration.

(3) The selectivity of the reaction was dependent upon both the catalyst and thiophenol concentrations.

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(4) Both the rate and the selectivity of the reaction are dependent

upon the rate of mass transfer of the oxygen from the gas phase to

the liquid phase.

(5) The reaction varies in dependency upon the thiophenol concentration

from first order to zero order.

(6) Over the range of reaction conditions used, two regimes of mass

transfer with chemical reaction have been characterized, namely the

fast and the instantaneous reaction regimes.

Although a complete quantitative kinetic treatment of the system

has not been possible with the experimental data which is available

at present, sufficient data has been obtained in this project so that

the course of the reaction under given conditions may be predicted.

As reported earlier (section 4), a relatively cheap method of producing

thiolsulphinates, such as the method considered in this project, may

regenerate interest in their use as antioxidants for synthetic

rubbers. Thus, should it be required, there is sufficient information

available in this project to design a reactor for the production of

thiolsulphinates.

This study of thiophenol oxidation can be used as a basis for

the study of the polymerization of dithiols or aminothiophenols

(see section 10). From the experimental data, one may predict the

conditions which are needed in order to form thiolsulphinate links

in the polymer chain. Alternatively, if thiolsulphinate links are

not required in the chain, one may predict the conditions which are

required in order to prevent their formation.

6.3.2 Suggestions for Further Work

To the author's knowledge, this present project is the first reported study of the kinetics of the oxidative coupling of thiols, and thus from this project it can be seen that there are a variety of paths along which the work could be developed. Some of the more important aspects of the work which call for further development are listed below:

(1) Further experiments to resolve the apparent contradiction between Figs. 6.1.3.1 and 6.1.4.1.

(2) Further experimental work to ascertain the exact cause for the phenomenon of graph A"B" in Fig. 6.1.3.5.

(3) An independent kinetic study of the reaction between thiophenol and thiolsulphinate (the side reaction in the thiophenol oxidation reaction).

(4) Further experiments at various partial pressures of oxygen.

(5) The development of the study of the effect of reaction temperature. It appears that decreasing the reaction temperature is the most effective way of increasing the selectivity for the thiolsulphinate.

(6) The development of the experimental work in which samples were removed during the course of the reaction for analysis.

(7) The use of methanol as the solvent. Throughout this project, pyridine has been used as the sole solvent. This has the major disadvantages of being both expensive and unpleasant to use.

(8)   The study of further increasing the mass transfer rates, e.g.
use of a packed column.

(9)   An investigation into the oxidation products which are formed
in addition to the disulphide and the thiolsulphinate.

(10) The sweetening of oils involves the removal of thiols, by
their oxidation to sulphur dioxide, which has little use.   Thus
it would be advantageous if a method could be developed whereby the
thiols were removed by their oxidation to a useful product such as
the thiolsulphinate.

7. ANILINE OXIDATION.

The study of the oxidative coupling of aniline may be useful as a basis for the study of the oxidative coupling of diamines and aminothiophenol, as well as being useful in its own right.

Since it was found that, under suitable conditions, diphenyl thiolsulphinate as well as diphenyl disulphide could be obtained as a product from the oxidative coupling of thiophenol it was also of interest to investigate whether or not oxidation products of aniline other than azobenzene could be formed, although azobenzene has been reported to be the only product (see section 2.7). In the oxidative coupling of aniline, the compound corresponding to the thiolsulphinate in the thiophenol oxidation, would be azoxybenzene, $C_6H_5-N=N-C_6H_5$. Azoxybenzene is a well characterized stable compound. O

7.1 Results.

An aniline oxidation reaction was conducted under conditions which might favour the formation of azoxybenzene if it was formed, i.e. high mass transfer rates (use of the vibromix stirrer) and a slow reaction rate. The reaction conditions and results are reported in Table 7.1. The graph of oxygen consumption vs time is shown in Fig. 7.1. A sample of the reaction product was tested for the presence of azoxybenzene by thin layer chromatography using a similar method to that described by Edwards et al.(64). A silica plate was used with benzene as the solvent. The authentic materials were applied directly from the reaction mixture. The positions of the spots on the plate after development were as shown in Fig. 7.2.

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Cu Cl	aniline	$-\dfrac{d\,O_2}{dt}$	% oxygen consumption
0.0404	0.428	0.22 x 10^{-4}	76

Reaction conditions: 5.0 ml pyridine; 25°C; oxygen at atmospheric pressure; vibromix stirrer; reaction time = 5 hours.

<u>Table 7.1</u>

Results: aniline oxidation.

Cu Cl	aniline
0.0067	0.116

Reaction conditions: 15.0 ml pyridine; 25°C; oxygen at atmospheric pressure; magnetic stirrer.

<u>Table 7.2</u>

Results: attempted aniline oxidation in which the reaction was not promoted.
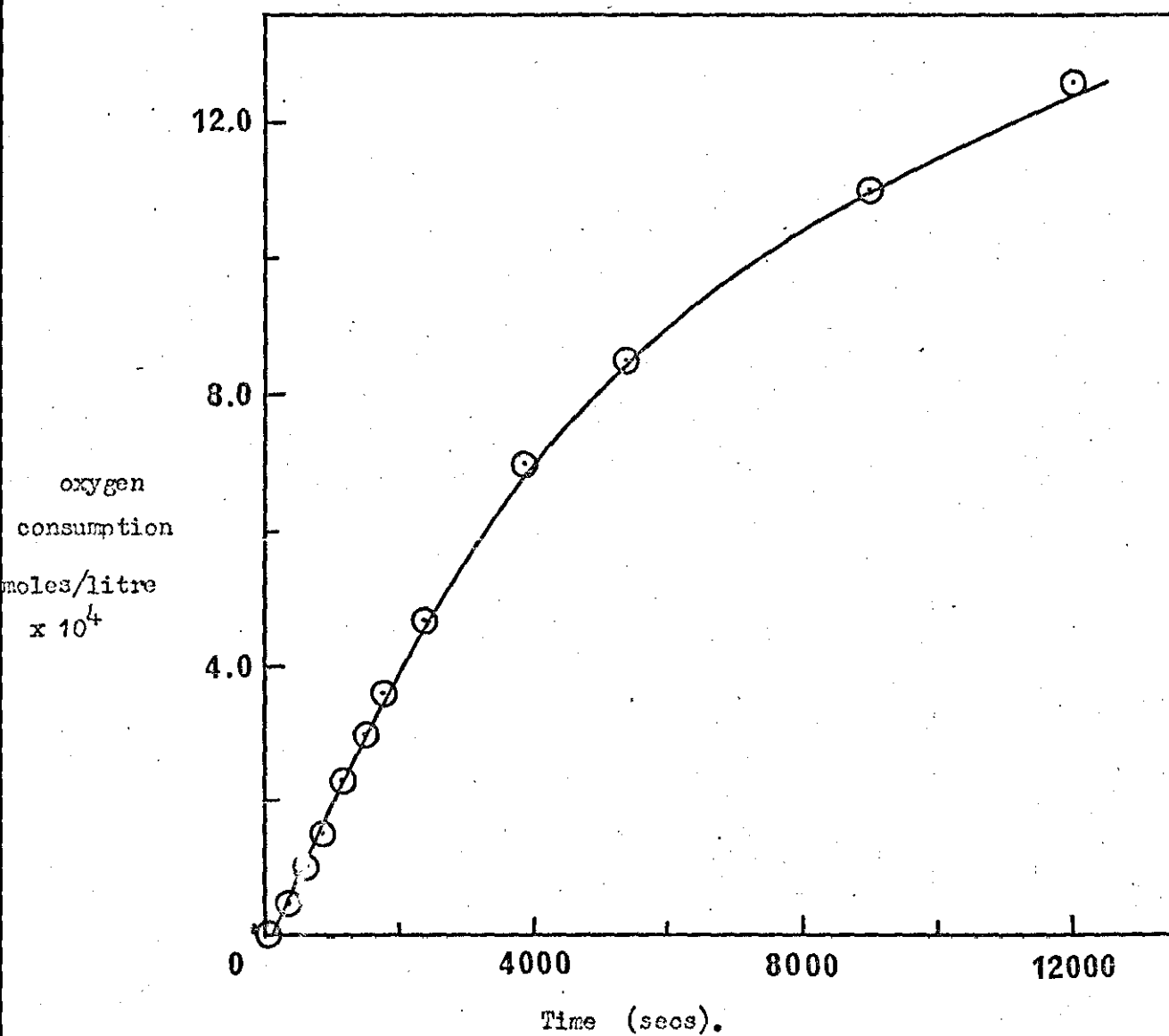
Fig. 7.1. Aniline oxidation, oxygen consumption vs time.
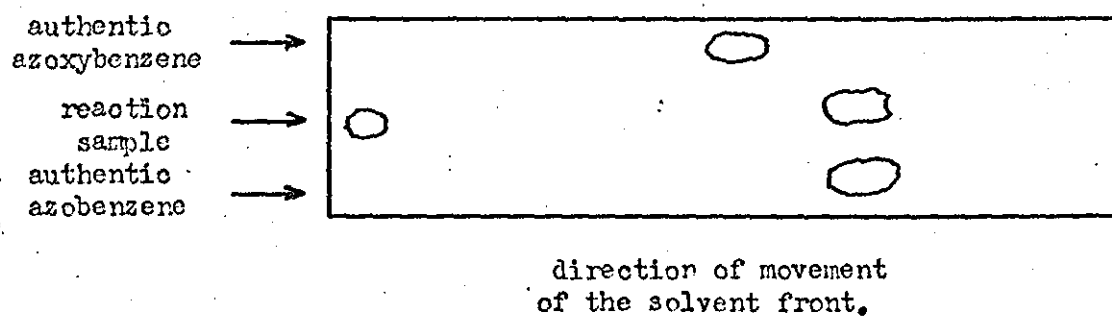
Fig. 7.2. Thin layer chromatograph of the product from aniline oxidation.

An attempted oxidation of aniline under the reaction conditions given in table 7.2 was unsucessful. The significance of this result is discussed in section 9.

7.2 Discussion.

As can be seen from Fig. 7.2, the chromatograph showed that the product was azobenzene only; no azoxybenzene was detected.

Reaction Rates.

The initial reaction rate for thiophenol oxidation corresponding to the above reaction conditions for aniline oxidation, was 3.9×10^{-4} moles/litre/sec. This is considerably faster than the initial aniline oxidation reaction rate of 0.22×10^{-4} moles/litre/sec. Thus for a substrate consisting of a mixture of thiol and amine groups, the thiol groups would most probably react before the amine groups. This probability has important consequences in the oxidation of aminothiophenols (see section 10).

Mass Transfer Effects.

Because of the very low reaction rates, it is probable that the aniline oxidation reaction occurred in the kinetic regime.

7.3 Conclusions.

(1) The oxidative coupling of aniline produced only azobenzene, no azoxybenzene being formed.

(2) When more than the equivalent amount of oxygen (100% oxygen concentration) is absorbed in the oxidative coupling of aminothiophenol,

it is unlikely that the extra oxygen will have been incorporated into the azobonds.

(3) The initial reaction rate of aniline oxidation was much lower than the corresponding rate of thiophenol oxidation.

(4) The aniline oxidation reaction may be occurring in the kinetic regime.

8 OXIDATION OF DITHIOLS.

Hay (6) reported that the oxidation of dithiols using a copper-amine catalyst yielded disulphides (equation 2.2.3). He reported that polydisulphides have useful properties, and thus a study of the kinetics of the oxidative coupling of dithiols may be useful both for the designing of reactors for the commercial manufacture of these polymers and as a basis for studying the oxidative coupling of amino-thiophenols.

From the results of the oxidative coupling of thiophenol (section 6), one would expect that the oxidative coupling of dithiols, under suitable conditions would produce polymers having thiolsulphinate bonds as well as disulphide bonds in the polymer chain. Thus a brief study of the oxidative coupling of toluene-3,4-dithiol (Fig. 8.1), a readily available dithiol, was undertaken.

$$CH_3-\langle O \rangle \begin{smallmatrix} -SH \\ -SH \end{smallmatrix}$$
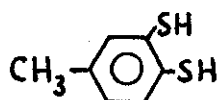
Fig. 8.1 toluene-3,4-dithiol.

8.1 Results.

A series of 4 experiments was conducted at varying catalyst concentrations using the magnetic stirrer apparatus. The concentration of dithiol was chosen to be equivalent, in terms of the concentration of thiol groups, to the concentration of thiophenol used in the corresponding thiophenol oxidation reactions at variable catalyst concentrations. The thiophenol and the dithiol oxidation reactions could then be compared. The results of these experiments are shown in table 8.1. Graphs of oxygen consumption vs time and log (initial

Cu Cl	% oxygen consumption	$-\dfrac{d\,O_2}{dt}$ ($\times 10^4$)	Initial rate of oxygen absorption for thiophenol oxidation ($\times 10^4$)
0.0808	97	3.16	4.20[a]
0.0404	100	2.72	3.90[a]
0.0202	99	0.82	3.63[a]
0.0101	65*	0.36	3.30

a   estimated from Fig. 6.1.3.2

*   after $2\frac{1}{2}$ hours reaction time

Reaction conditions: 0.23 moles/litre dithiol; 5.0 ml. pyridine; $25^{o}C$; oxygen at atmospheric pressure; magnetic stirrer.

Table 8.1.

Results: oxidation of toluene - 3,4 - dithiol .

rate of oxygen absorption) vs log (catalyst concentration) are shown

in Figs. 8.2 and 8.3 respectively.

8.2 Discussion.

The initial rates of oxygen absorption are very low in comparison

to the corresponding rates for thiophenol oxidation at the same

catalyst concentrations. The most likely cause of this effect is the

steric hindrance arising from the two thiol groups being adjacent

to one another.

The following arguments suggest that the rate controlling step

was probably the reaction between a copper species and a dithiol molecule.

(1) In contrast to the thiophenol oxidation reaction, the graphs

of oxygen consumption vs time (Fig. 8.2) were not straight lines.

This suggests that the reaction rate was not zero order with respect

to the dithiol, but that the dithiol molecule participated in the

rate controlling step.

(2) If the rate controlling step was a reaction between a copper

species and a dithiol molecule, then any steric hindrance from the

dithiol molecule in the complex formation would greatly decrease the

reaction rate. As stated above, this may be the reason for the very

low reaction rates.

(3) For the complex formation step to be the rate controlling step,

the reaction would most probably be taking place in the kinetic

regime; in any other regime the rate controlling step would involve

a reaction with oxygen. Comparison of the rates of oxygen absorption

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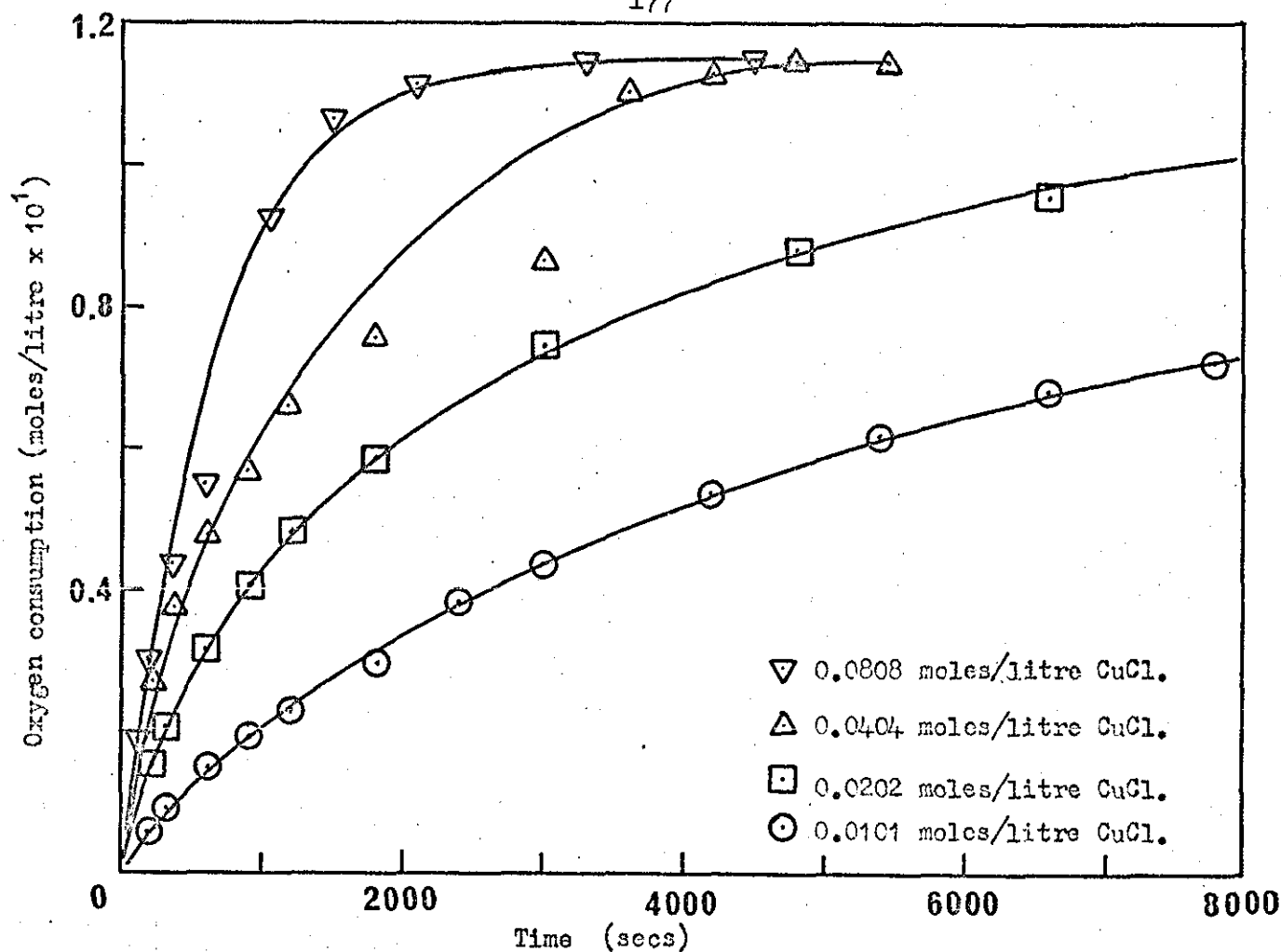
Fig. 8.2. Dithiol oxidation, oxygen consumption vs time.
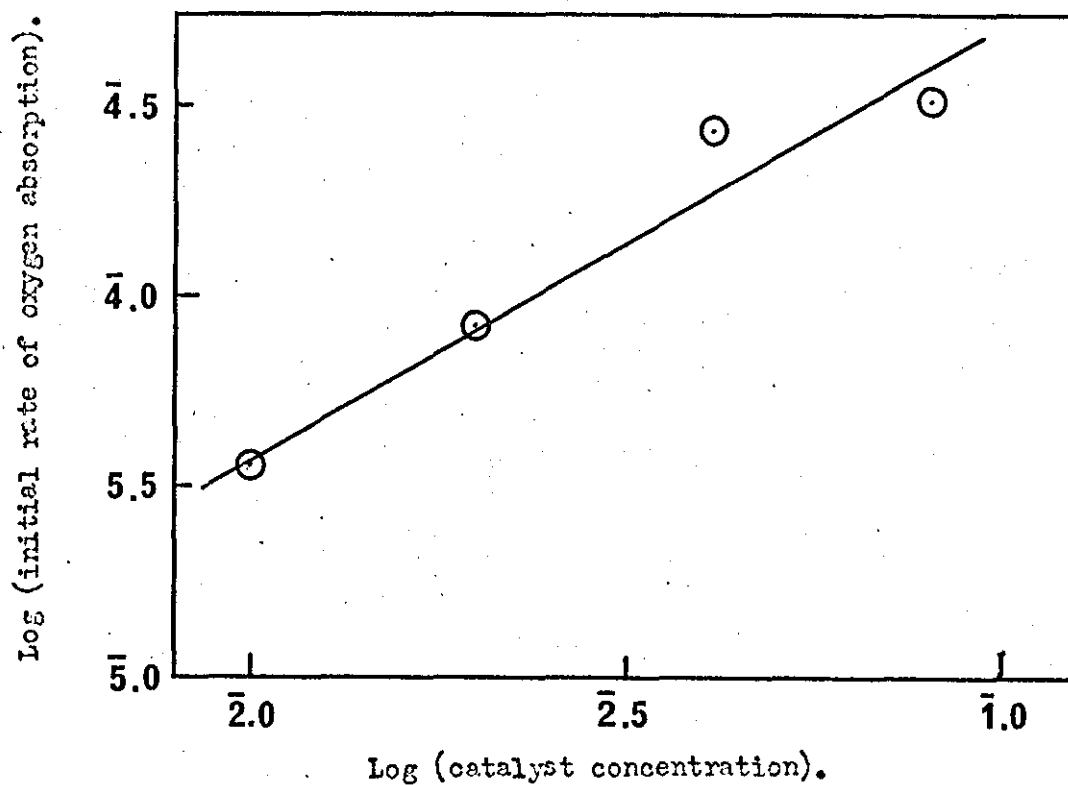
Fig. 8.3. Dithiol oxidation, log (initial rate) vs log (catalyst concentration).

for dithiol oxidation with the corresponding rates for thiophenol oxidation shows that the dithiol oxidation was probably taking place in the kinetic regime. In this case, assuming that the reaction is first order with respect to the catalyst concentration, then the rate of oxygen absorption should show a first order dependence upon catalyst concentration. Although only 4 points were plotted in Fig. 8.3, the best straight line through these points has a slope of 1.1 ; this supports the above theory.

In each of the 4 experiments, the total oxygen consumption was less than 100%, thus suggesting that no thiolsulphinate bonds were formed in the polymer chain. This is contrary to that which was expected. However, it is possible that the steric hindrance in the dithiol molecule was unfavourable for the formation of the thiolsulphinate bonds.

8.3   Conclusions and Suggestions for Further Work.

8.3.1   Conclusions.

The conclusions given below are based upon the speculative reasoning given in the above discussion (section 8.2). With so few experimental results available, the evidence for these conclusions is very scant.

(1)   In comparison with the thiophenol oxidation reactions, the reaction rates for the dithiol oxidation reactions were very low; this may have been due to steric factors in the dithiol molecule.

(2)   The reactions are most probably taking place in the kinetic regime.

(3) The rate determining step may be the reaction between the dithiol
and a copper species.

(4) There was no evidence to suggest that thiolsulphinate bonds
were incorporated into the polymer chain; their absence may be due
to steric hindrance in the dithiol molecule.

8.3.2 Suggestions for Further Work.

Only a brief investigation into the kinetics of dithiol oxidation
has been undertaken and thus there is wide scope for further work.
Probably the most important immediate work is the study of the oxidative
coupling of a dithiol which has little or no steric hindrance,
e.g. m-dithiol (Fig. 8.4).
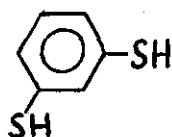
Fig. 8.4 m-dithiol.

This compound was not readily available at the time when the
above experimental work was undertaken, but it may be synthesized
from m-sulphonyl chloride (65), a readily obtainable compound.

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9. OXIDATION OF DIAMINES.

A brief study of the oxidative coupling of diamines was undertaken; it was thought that the results of this study may be useful in the investigation of the oxidative coupling of amino-thiophenols. p-Phenylenediamine (Fig. 9.1) was chosen for this study so that the steric effects in the reaction would be minimized.

$$NH_2-\langle O \rangle-NH_2$$
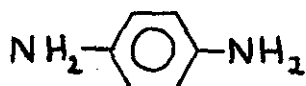
Fig. 9.1   p-Phenylenediamine .

9.1   Results .

A series of 4 experiments on the oxidative coupling of p-phenyl-enediamine was undertaken. The reaction conditions and results of these experiments are shown in table 9.1. Graphs of percentage oxygen consumption vs time are shown in Fig. 9.2. A graph of percentage oxygen consumption vs time was plotted as opposed to a graph of oxygen consumption in moles/litre vs time, for two reasons.

(1) The percentage oxygen consumption shows the percentage conversion of the reaction when the reaction has effectively stopped; this as will be seen later (in this section 9) is an important feature of these experiments.

(2) A constant initial concentration of the diamine was not used for all the experiments and thus a graph of oxygen consumption vs time may give a false impression of the percentage conversion of the reaction.

Stirring	Cu Cl	P.P.D	% Oxygen Consumption	$-\dfrac{d\,O_2}{dt}$ $(x\ 10^4)$
1. magnetic	0.101	0.21	35	2.24
2. no stirring	0.101	0.21	50	0.27
3. vibromix (1)	0.101	0.20	51	5.3
4* vibromix (2)	0.027	0.156	67	1.28

Reaction conditions: 5.0 ml. pyridine; $25^{\circ}C$; oxygen at atmospheric pressure.

P.P.D. = p-phenylenediamine

*   7.5 ml. pyridine used in this reaction.

Table 9.1

Result: oxidation of p-phenylenediamine .

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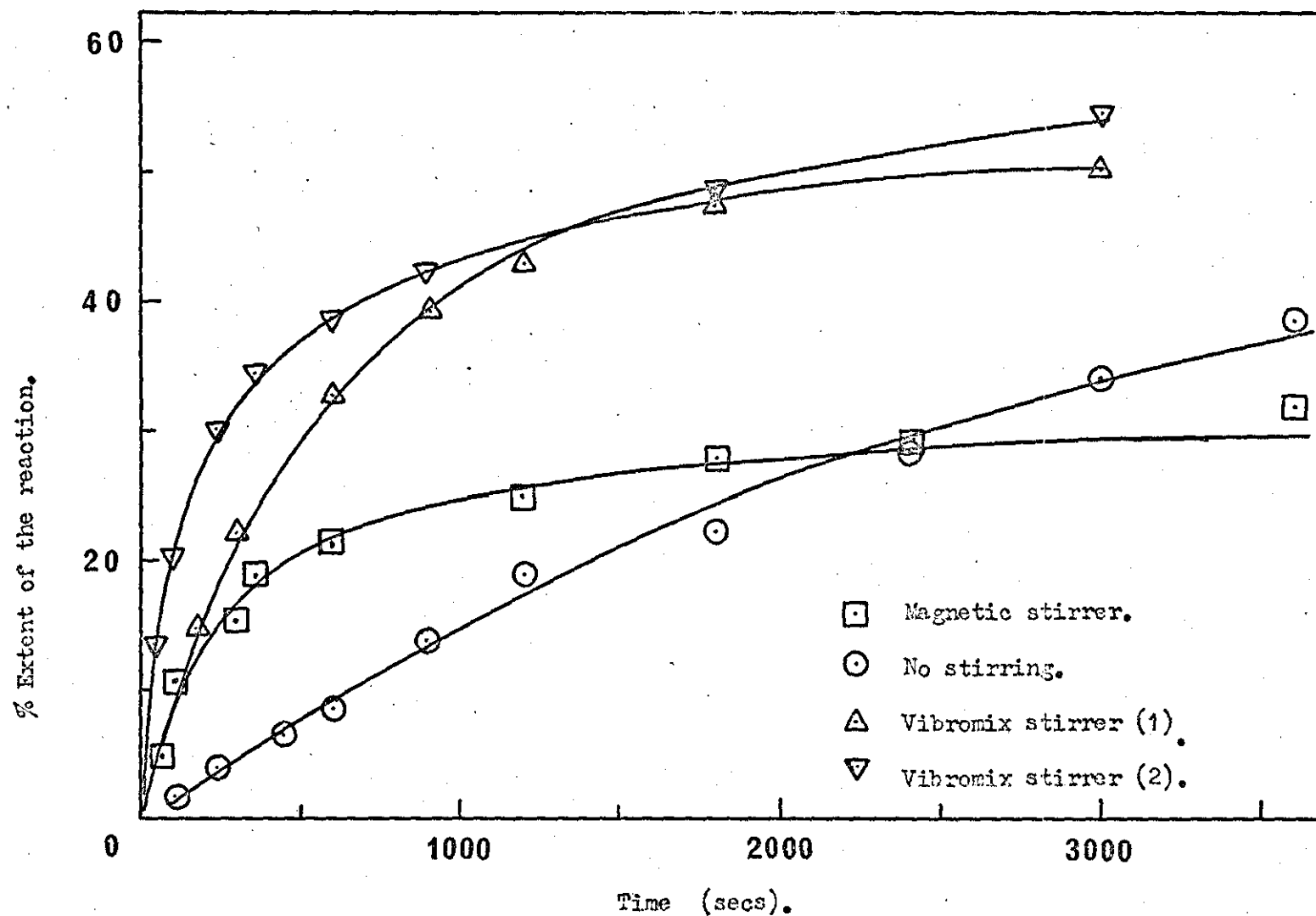
Fig. 9.2. Oxidation of p-phenylenediamine, % extent of the reaction vs time.

9.2 Discussion

The most noticeable feature of these experiments is the fact
that not one of the reactions proceeded to 100% oxygen consumption
within a reasonable reaction time. This is in direct contrast to the
work of Bach (2). Using similar conditions to those of experiments
1 - 3 (table 9.1), he reported that an equivalent amount of oxygen
was absorbed within a reasonable reaction time, e.g. 195 minutes.
The only difference between these experiments and those of Bach's
is that in the experiments of this project a different diamine was
used and the experimental work was scaled down by a factor of 10.
The possibility of the purity of the diamine having an important
effect can be ruled out since experiment 3 (table 9.1) was conducted
both with "impure" (commercial grade, Fisons supply) and recrystallized
(from benzene) p-phenylenediamine, both experiments giving the same
results. One possible explanation for the reactions not proceeding
to 100% conversion is that a copper catalyst species formed a complex
with the diamine and that this complex was less soluble in pyridine
than was either the catalyst or the diamine. This complex may have
been precipitated and deposited on the walls of the reaction flask
as a result of the stirring, thus removing the copper catalyst from
being in contact with the reaction solution. As the copper concentration
in the solution decreases, the reaction rate would similarly decrease
until it effectively stops. This explanation may at first seem very
unlikely but the following evidence shows that it is consistent with
the experimental results.

(1) In experiment 1 when the magnetic stirrer was used, a black

precipitate was deposited on the sides of the reaction flask around the edges of the reaction mixture. A black deposit also formed on the walls of the reaction flask in experiments 3 and 4, when the vibromix stirrer was used.

(2) In experiment 2, where the reaction mixture was not stirred, the reaction rate did not tail off as quickly as in the experiments where the reaction mixture was stirred. Given sufficient time, the reaction with no stirring may have proceeded to near 100% oxygen consumption. In the same experiment, some of the copper-diamine complex may have precipitated but this precipitate would still be in contact with the bulk of the liquid; thus it is possible that the copper contained in this precipitate may have been recovered by the solution and used again in the oxidation reaction.

(3) In a preliminary experiment, the attempted oxidation of aniline at a copper catalyst concentration of 0.0067 moles/litre was unsucessful (see section 7.1). Thus at a similar catalyst concentration p-phenylenediamine also would probably not be oxidized. Thus if the copper catalyst was removed from solution during the course of the reaction, the copper concentration would probably not have to drop to a very low concentration before the reaction effectively stopped.

(4) The total percentage oxygen consumption in experiment 1 was less than that in experiment 3, the same reactant concentrations being used in both experiments. This may be explained as follows. The magnetic stirrer would most probably be more efficient at depositing any precipitate from the bulk of the

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liquid onto the walls of the reaction flask. This is because any

precipitate in the bulk of the liquid would experience a centrifugal

force from the magnetic stirrer and would be thrown against the

walls of the reaction flask. On the other hand, the vibromix

stirrer vibrates on the surface of the liquid and although it causes

splashing of the liquid, it would not deposit any precipitate

contained within the bulk of the liquid onto the walls of the reaction

flask as efficiently as the magnetic stirrer. Thus if the catalyst

was removed at a faster rate by the use of the magnetic stirrer,

then the reaction would terminate at a lower total percentage oxygen

consumption. Another factor which must also be considered in

explaining the lower total percentage oxygen consumption in experiment

1 is that the initial reaction rate for experiment 3 was much greater

than that for experiment 1.

Comparison of Reaction Rates with those
of Aniline Oxidation.

The comparison of initial reaction rates for diamine oxidation

with the corresponding rates for aniline oxidation is difficult since

the reaction conditions were not standardized. In experiment 1

(table 9.1), although the concentration of diamine in terms of the

concentration of amine groups is approximately equal to the concentration

of aniline in the experiment in table 7.1, the catalyst concentration

for the diamine reaction is about $2\frac{1}{2}$ times that for the aniline

oxidation. Nevertheless, since the reaction rate for the diamine

oxidation (experiment 1) is much greater than that for the aniline

oxidation, it can be stated with a fair degree of certainty, that,

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in general, the diamine reaction would be much faster than the corresponding aniline oxidation under identical conditions. The most likely explanation for this fact is that the p-amino group has an activating effect upon the other amine group. It is well known (66) that an amine group on a benzene ring has an electron attracting inductive effect; thus according to the discussion of section 2.4, this effect should reduce rather than increase it's reactivity towards oxidative coupling. However, the amine group has an electron-donating conjugative effect which may override the inductive effect. If this is the case, as it may well be for p-phenylenediamine, one would predict a greater reactivity, for oxidative coupling for the amine group in p-phenylenediamine than that in aniline.

Mass Transfer Study.

Since, under the reaction conditions which are considered, the use of the vibromix stirrer increased the rate of oxygen absorption, it can be concluded that at least experiments 1 and 2 were not taking place in the kinetic regime (see section 3.2). From experiments 3 and 4, it can be seen that by increasing the catalyst concentration by a factor of 4 at approximately constant diamine concentrations, the initial rate was also increased by a factor of 4. If we assume that this reaction is first order with respect to the catalyst concentration (a characteristic of oxidative coupling reactions in general), then the above evidence suggests that experiments 3 and 4 were taking place in the kinetic regime.

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Thus experiments 1 and 2 were probably taking place in either the fast or the diffusional regimes; by increasing the gas-liquid mixing (use of the vibromix stirrer), the reaction probably moved into the kinetic regime.

Comparison of experiment 3 with experiment 4, where the vibromix stirrer was used, shows that a reduction in the reactant concentration led to a reduction in the initial rate but led to an increase in the total oxygen consumed. This behaviour is very similar to that of the thiophenol oxidation reactions, and it might be thought at first that oxygen was being incorporated into the polymer chain. However, the fact that no oxygen was incorporated into the product of aniline oxidation suggests that this is unlikely. It may be possible, however, that the p-amino group activates the other group in the benzene ring and allows oxygen to be incorporated into the polymer chain. Another possible explanation for this behaviour arises from the fact that in the experiment at low reactant concentrations, the surface area: volume ratio was decreased, a larger volume of liquid being used. This would decrease the rate at which the copper-diamine complex was deposited from the solution and thus may give a higher percentage oxygen consumption before the reaction terminated. In the work of Bach (2), the surface area: volume ratio was most probably much smaller than that for the experiments 1 to 4. This may be one reason why he obtained 100% conversion for his reactions whereas in the experiments of this project, the reaction terminated well before 100% conversion.

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Much of the above discussion is pure speculation; this is necessary because of the scarcity of experimental data. Further experimental work needs to be undertaken in order to test the above theories.

9.3 Conclusions and Suggestions for Further Work.

9.3.1 Conclusions.

(1) The p-phenylenediamine oxidation reactions which were considered in this project did not proceed to 100% conversion. This may have been due to a copper-diamine complex precipitating out of solution and being deposited on the walls of the reaction flask, thus reducing the concentration of the catalyst within the bulk of the liquid and essentially terminating the reaction before 100% conversion.

(2) The reactivity of the amine group in p-phenylenediamine was greater than the reactivity of the amine group in aniline; this may have been due to a p-amino group activating the other amino group of the diamine.

(3) Experiments 1 and 2 (table 9.1) were probably taking place in either the fast reaction or the diffusional regime, whereas experiments 3 and 4 were probably taking place in the kinetic regime.

9.3.2 Suggestions for Further Work.

Only a brief study of the oxidative coupling of diamines has been undertaken and thus there is a wide scope for further work. Some important features of the work which require further development are

as follows:-

(1) Investigation into whether or not the black compound which was

deposited on the sides of the reaction flask actually contained

appreciable amounts of copper.

(2) Investigation into the possibility of oxygen being incorporated

into the polymer chain.

10. OXIDATIVE COUPLING OF AMINOTHIOPHENOL.

As previously stated (section 4), the course of this present project can be attributed to a phenomenon occurring in a preliminary investigation reaction into the oxidative coupling of 2-aminothiophenol. The amount of oxygen absorbed in this reaction was 50% more than that which was expected from the prediction of the formation of a polymer containing alternate disulphide and azo bonds (equation 4.1). To the author's knowledge, the oxidative coupling of aminothiophenols has not previously been reported. In this present project the resulting "polymers" from the oxidative coupling of aminothiophenol were found to be insoluble in all the common organic solvents, concentrated sulphuric acid being the only solvent in which they would dissolve to any appreciable extent (see also section 10.4). Because of this property, the polymers may have numerous applications.

It was thought that the study of the oxidative coupling of thiophenol, aniline, dithiols and diamines may serve as a basis for studying the oxidative coupling of aminothiophenols. From knowledge of the above reactions, the course of the aminothiophenol oxidation may be predicted (section 10.1). 4-Aminothiophenol, rather than 2-aminothiophenol was chosen for the study of these reactions in order that any steric hindrance in the molecule or polymer chain may be minimized.

10.1 Prediction of the Course of the Oxidative Coupling of 4-Aminothiophenol.

As previously stated (section 4), the product that may be expected from the oxidative coupling of aminothiophenol would be a polymer

containing alternate disulphide and azo bonds (equation 10.1.1).

$$HS-\langle O\rangle-NH_2 + \tfrac{3}{4}nO_2 \longrightarrow \left[\langle O\rangle-S-S-\langle O\rangle-N=N\right] + \tfrac{3}{2}H_2O$$

<div align="right">(10.1.1)</div>
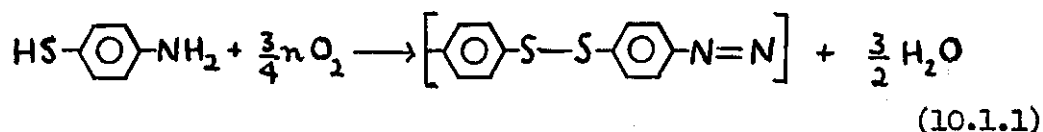
A previous comparison of the reaction rates of thiophenol oxidation with those of aniline oxidation (section 7) showed that thiol groups are much more readily oxidized than amine groups. Thus it may be predicted that the initial product from the oxidative coupling of aminothiophenol would be 4,4'-diaminodiphenyl disulphide (equation 10.1.2).

$$HS-\langle O\rangle-NH_2 + \tfrac{1}{2}O_2 \longrightarrow H_2N-\langle O\rangle-S-S-\langle O\rangle-NH_2$$

<div align="right">(10.1.2)</div>
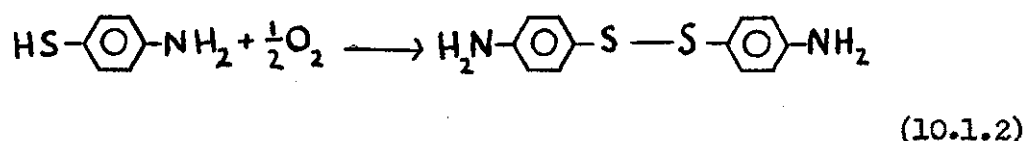
It has been shown (section 7.2) that, in the attempted oxidation of aniline at a low catalyst concentration (0.0067 moles/litre), no reaction took place. From this fact one may predict that in the oxidation of aminothiophenol at low catalyst concentrations, only the thiol groups would be oxidized giving the disulphide as the product. Furthermore, at very low catalyst concentrations, one would predict that an appreciable amount of 4,4'-diaminodiphenyl thiolsulphinate (Fig. 10.1) would also be formed.

$$H_2N-\langle O\rangle-S-\overset{\overset{\textstyle O}{\|}}{S}-\langle O\rangle-NH_2$$
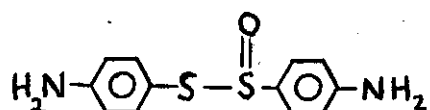
Fig. 10.1   4,4'-diaminodiphenyl thiolsulphinate.

As the catalyst concentration was further decreased, one may predict that there would be an increasing proportion of the

thiolsulphinate formed.

Thus it may be possible to selectively oxidize the thiol groups to a dimer product containing a mixture of the disulphide and the thiolsulphinate in a required ratio, and then to add excess catalyst, thereby oxidizing the amine groups and forming a long chain polymer.

10.2 Results.

A number of experiments were conducted at a constant monomer concentration and varying catalyst concentrations, using the magnetic stirrer apparatus. After a certain amount of oxygen was absorbed the reaction effectively stopped; at this point, excess catalyst solution was added in order to complete the reaction. The volume and concentration of this catalyst solution which was added was constant throughout all the experiments in this chapter. Hereafter, the first part of the reaction up to the addition of excess catalyst solution will be called the "thiol reaction" and the latter part of the reaction beginning at the addition of excess catalyst will be called the "amine reaction." The reaction conditions and results of these experiments are given in table 10.1 (experiments 1 to 7). A typical plot of oxygen consumption vs time is shown in Fig. 10.2.1.

Also shown in table 10.1 are the reaction conditions and results of two experiments in which the vibromix stirrer was used. In the first of these two experiments (No. 8 in table 10.1), the position of the stirrer disc was not changed after the thiol reaction. Thus after excess catalyst solution (10 ml.) was added, the stirrer disc was completely submerged below the surface of the liquid. This would

Cu Cl	$-\dfrac{d\,O_2}{dt}$ thiol $(\times 10^4)$	$-\dfrac{d\,O_2}{dt}$ amine $(\times 10^4)$	% Oxygen Consumption thiol	% Oxygen Consumption amine	% Oxygen Consumption total
1. 0.0404	4.06	2.31	88 - 90	216	173
2. 0.0101	2.60	2.21	93	219	176
3. 0.00101	1.98	2.40	107	224	186
4. 0.00030	1.09	2.93	110	246	201
5. 0.00010	0.92	3.50	136	270	223
6. 0.00003	0.59	2.15	141	223	193
7. 0.00001	0.52	1.70	140	165	155
8. 0.00101	3.10	1.40	126	138	126
9. 0.00101	2.59	2.51	135	74	94

Experiments 1 - 7: magnetic stirrer used; Experiments 8 and 9: vibromix stirrer used.

Reaction conditions: 0.20 moles/litre aminothiophenol; 5.0 ml. pyridine; 25°C; oxygen at atmospheric pressure.

Table 10.1

Results: oxidation of aminothiophenol.
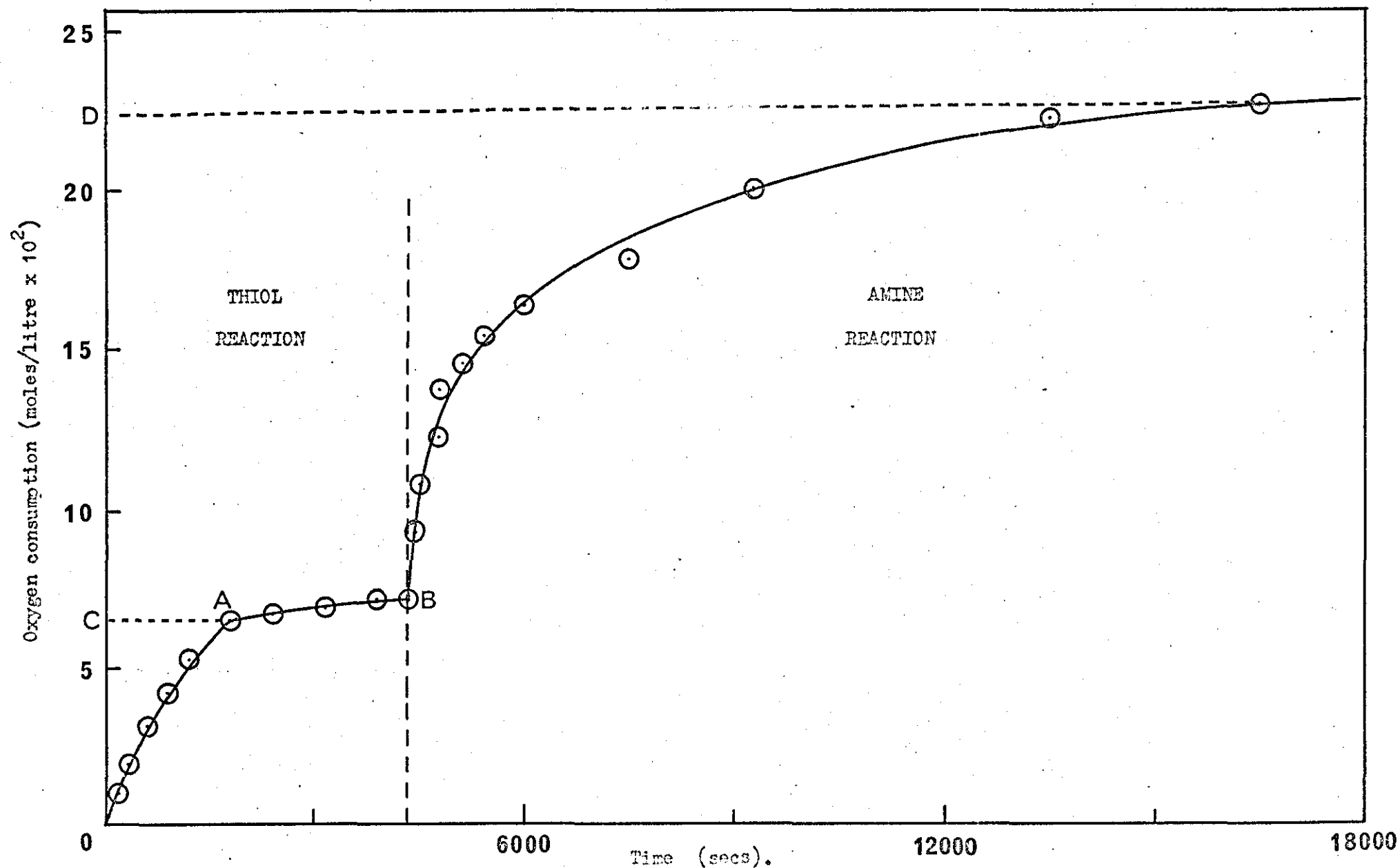
Fig. 10.2.1.   Oxidation of aminothiophenol, oxygen consumption vs time.

give good mixing within the bulk of the liquid but would greatly reduce the gas-liquid mixing. In the second experiment (No. 9 in table 10.1), the height of the stirrer disc was adjusted after the thiol reaction so that after the excess catalyst had been added, the disc was situated on the surface of the reaction liquid. The graphs of oxygen consumption vs time are shown in Fig. 10.2.2.

For experiments 1 - 7, the plot of log (initial rate of the thiol reaction) vs log (initial catalyst concentration) is given in Fig. 10.2.3. A plot of the initial rate of the amine reaction vs log (initial catalyst concentration) is given in Fig. 10.2.4. N.B. The initial catalyst concentration refers to the concentration of catalyst at the very begining of the reaction and not the concentration of the excess catalyst which was added; as stated previously, the latter concentration was constant for all the experiments.

Fig. 10.2.5 shows a plot of the percentage oxygen consumption for the thiol reaction vs log (initial catalyst concentration) and Fig. 10.2.6 shows a plot of the percentage oxygen consumption for the amine reaction vs log (initial catalyst concentration).

10.3 Preliminary Discussion.

From table 10.1 and Fig. 10.2.1 it can be seen that in general the experimental results appear to be in agreement with the predicted behaviour. The graph of Fig. 10.2.1 falls into two sections :-

(1) The thiol reaction. It appears that, in this section, the thiol groups have been oxidized to the disulphide and the thiolsulphinate, but very few or no amine groups have been oxidized.

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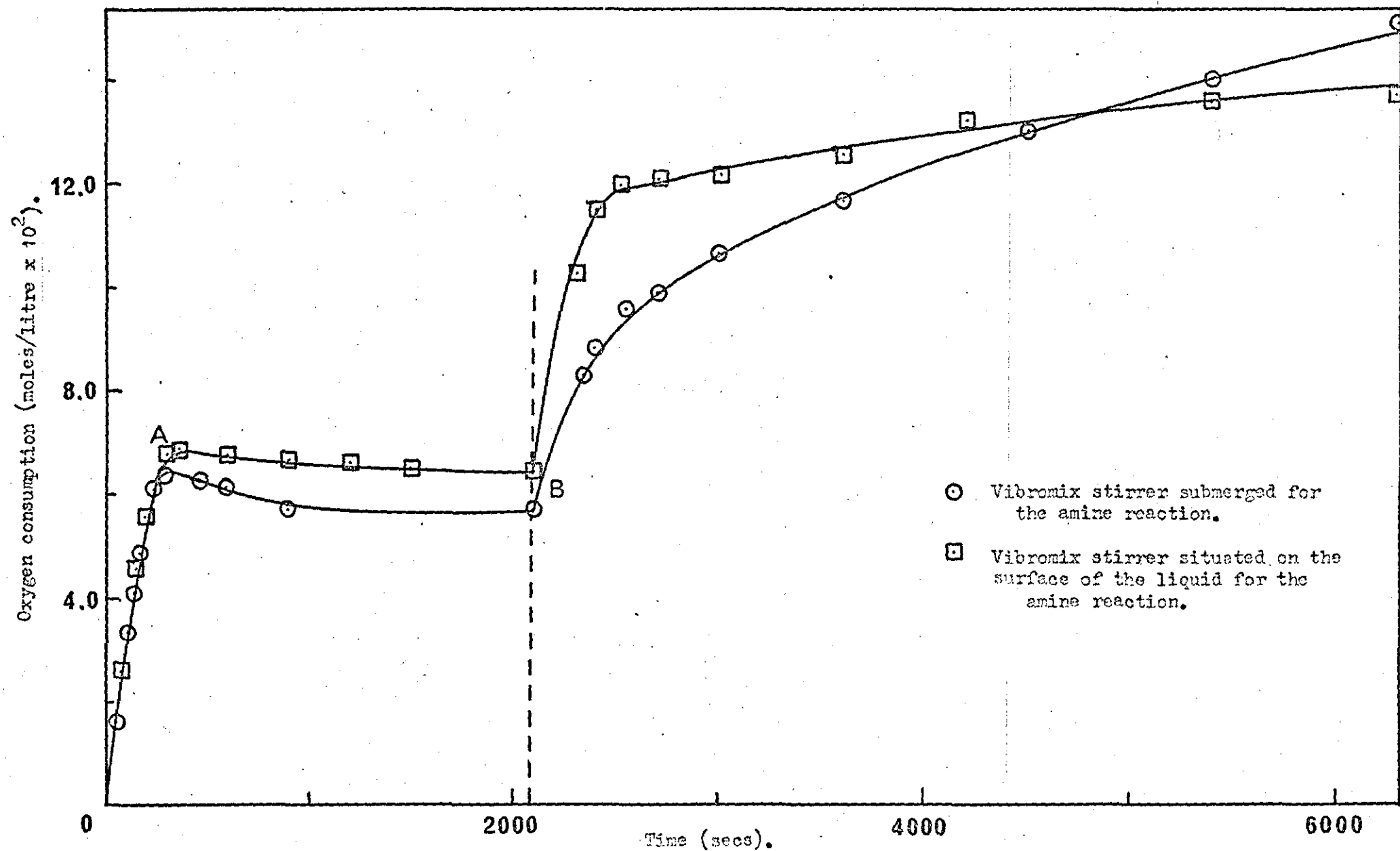
Fig. 10.2.2. Oxidation of aminothiophenol, oxygen consumption vs time for experiments using the vibromix stirrer.
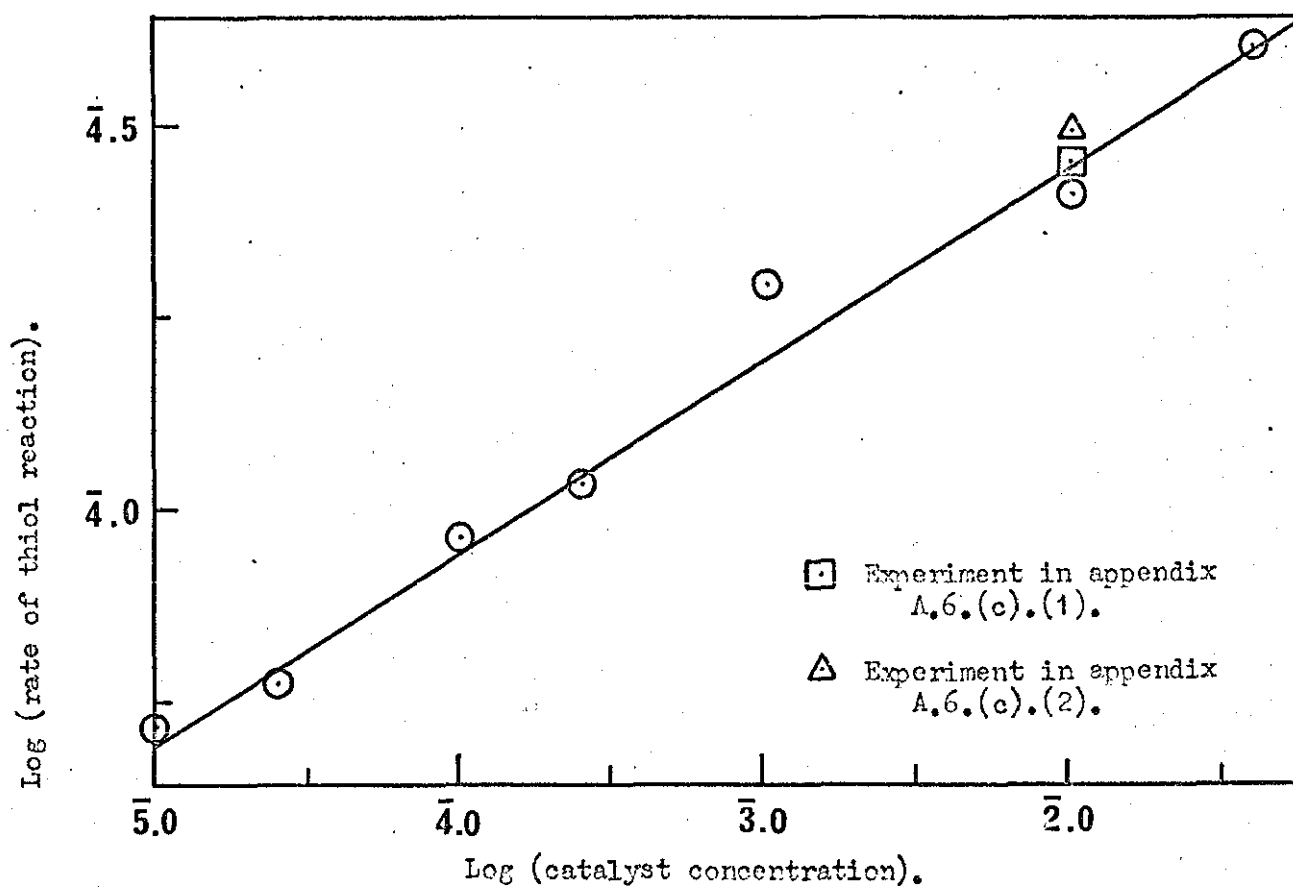
Fig. 10.2.3. Oxidation of aminothiophenol, log (initial rate of
the thiol reaction) vs log (catalyst concentration)
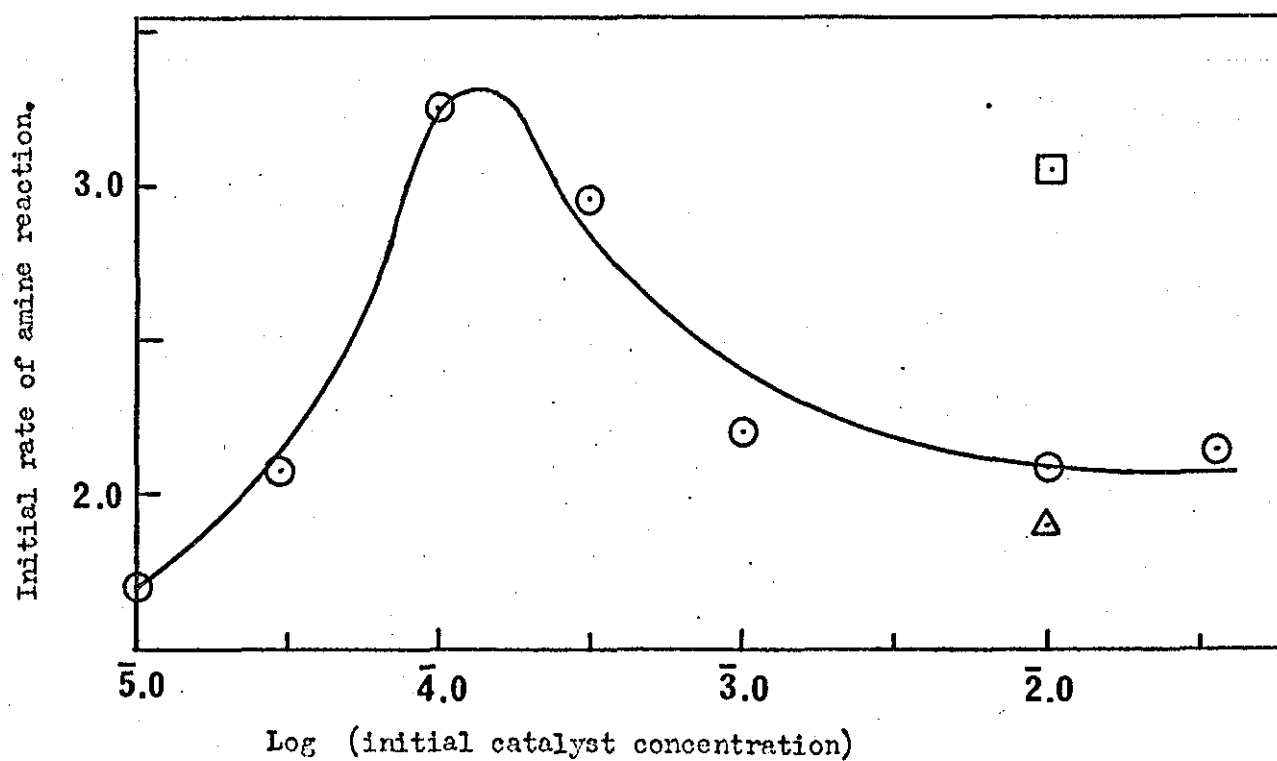
Fig. 10.2.4. Initial rate of the amine reaction vs log (initial
catalyst concentration).
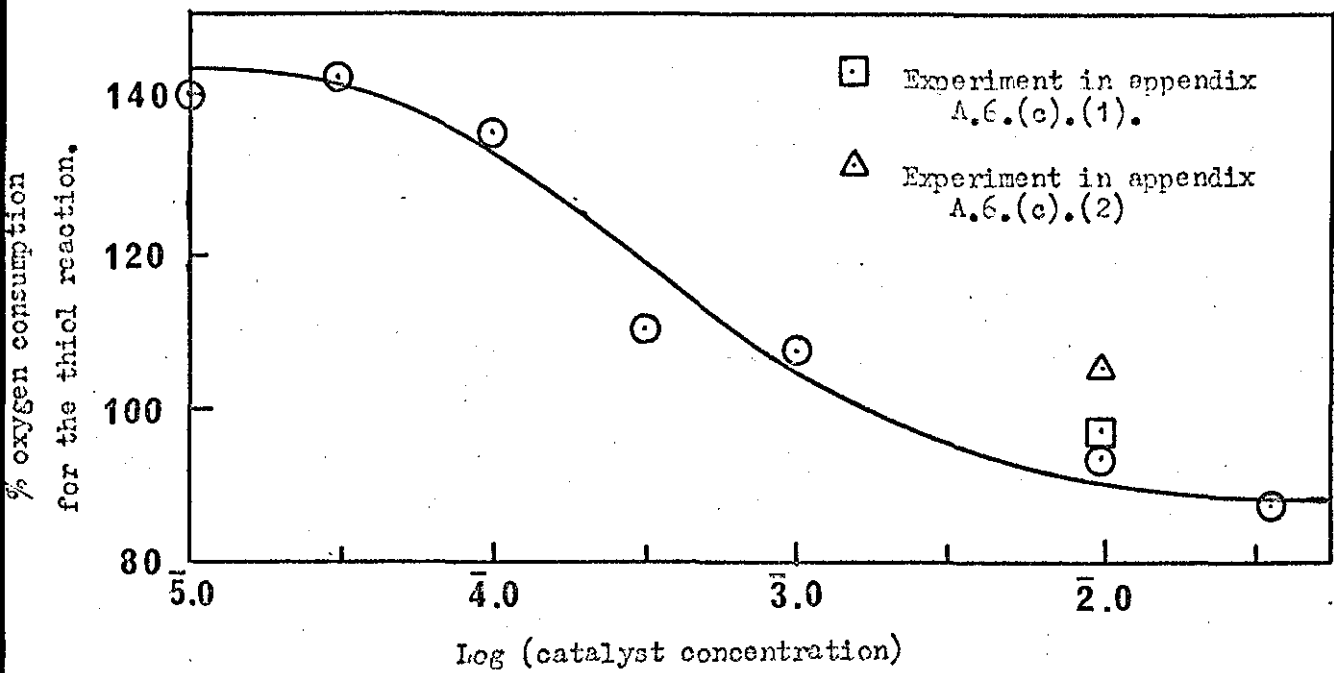
Fig. 10.2.5. Oxidation of aminothiophenol, % oxygen consumption for the thiol reaction vs log (initial catalyst concentration).
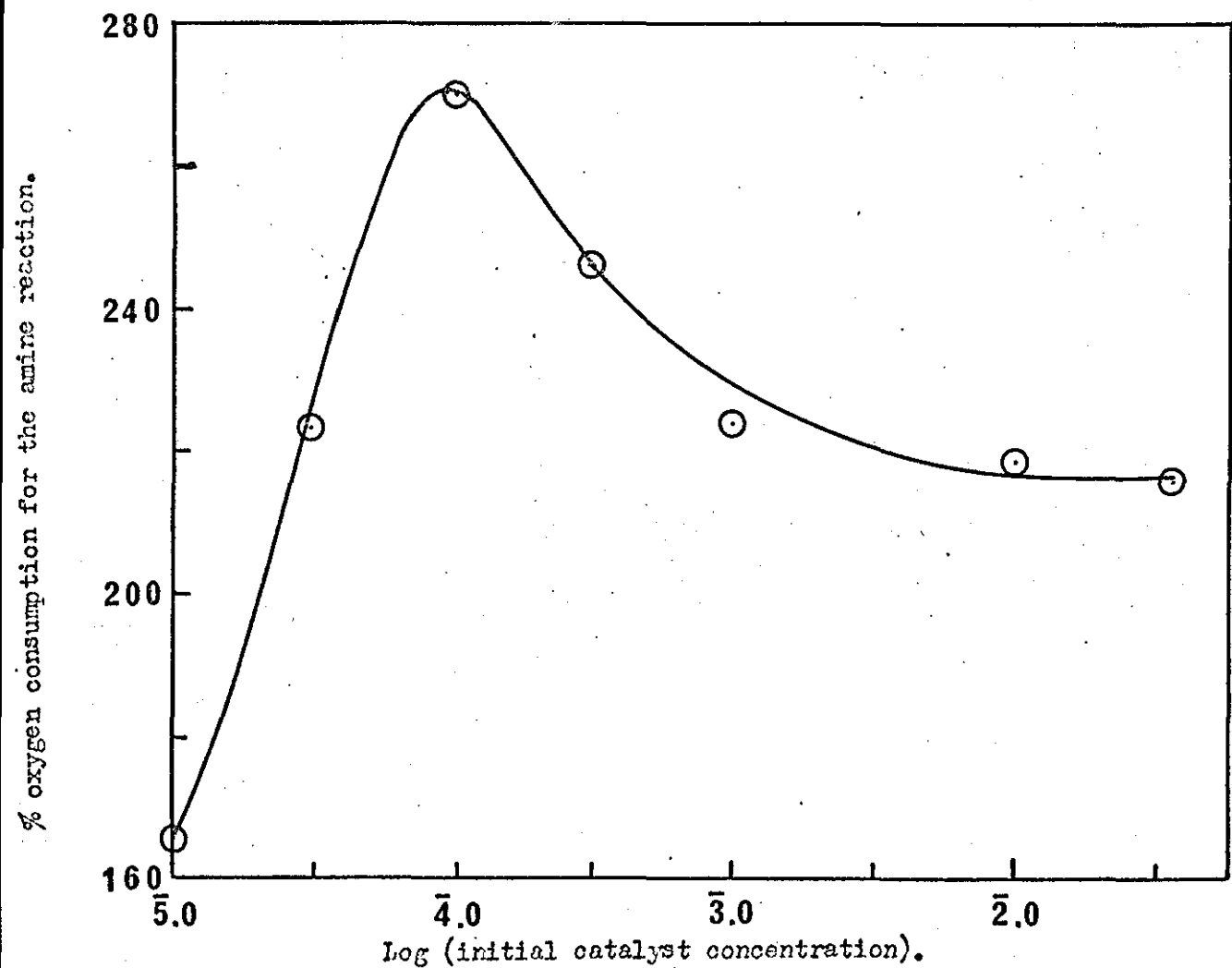
Fig. 10.2.6. Oxidation of aminothiophenol, % oxygen consumption for the amine reaction vs log (initial catalyst concentration).

(2) The amine reaction. In this section, the amine groups appear to have been oxidized.

(1) The Thiol Reaction.

In table 10.1, the percentage oxygen consumption for the thiol reaction has been based upon the complete reaction of aminothiophenol to the disulphide. The total amount of oxygen consumed in the thiol reaction is equal to C moles/litre (Fig. 10.2.1). As expected, at high catalyst concentrations, the amount of oxygen consumed corresponded approximately to the formation of the disulphide only, whereas as the catalyst concentration decreased, the amount of oxygen consumed in the thiol reaction increased.

Upon adding the monomer to the catalyst solution, the colour of the catalyst solution changed from green to yellow. This suggested that virtually all of the copper was present in the reduced form (Cu^+) and that the rate controlling step was either the transfer of oxygen from the gas phase to the liquid phase, or the reaction of oxygen with a copper (I) species.

At approximately A (Fig. 10.2.1), the colour of the reaction mixture changed from yellow through brown to black. This suggests that up to this point, very few or no azo bonds had been formed (since azo compounds are usually deeply coloured) but at A azo bonds began to be formed at an appreciable rate. The time taken for the colour change was dependent upon the catalyst concentration, ranging from about 30 minutes at the lowest catalyst concentration to an almost instantaneous colour change at the highest catalyst concentration.

Experiment 6 (table 10.1) was then repeated, a sample being taken out for thiolsulphinate determination when the colour of the reaction mixture changed from yellow to brown. The percentage oxygen consumption for the thiol reaction was 127% and the percentage thiolsulphinate in the sample was 21% (details of this experiment are given in appendix A.6.d). Thus the formation of the disulphide and the thiolsulphinate accounted for virtually all the oxygen which was consumed in the thiol reaction region. Compared with the corresponding figures for percentage oxygen consumption, this figure of 127% for the oxygen consumption was low; this may have been due to the differences in the purity of the monomer samples.

Thus there is conclusive proof that the thiol reaction represented the formation of the disulphide and the thiolsulphinate from the oxidation of the thiol groups.

(2) The Amine Reaction.

Obviously once all the thiol groups have reacted, the subsequent reaction occurring is most probably the oxidation of the amine groups to form azo bonds. This theory was supported by the occurrence of a colour change from yellow to black, at A.

In table 10.1, the percentage oxygen consumption for the amine reaction has been based upon 100% oxygen consumption representing the oxidation of all the amine groups to azo groups. The amount of oxygen consumed in the amine reaction is equal to (D - C) moles/litre (Fig. 10.2.1). There is evidently a further oxidation reaction occurring since considerably more oxygen than 100% oxygen consumption has been obtained (Fig. 10.2.6). It was thought that the experimental work

which is given in the next section, section 10.4, would be most useful
in ascertaining the nature of the reactions which were occurring in
the amine reaction region.

10.4 Further Results.

Samples of the polymers from experiments 3, 5, 6 and 7 (table 10.1)
were sent away for elemental analysis for carbon, hydrogen, nitrogen
and sulphur; the results are given in table 10.2.

It was thought that molecular weight determinations of the
polymers would provide further useful information. However, no
suitable solvent could be found for any of the polymers, concentrated
sulphuric acid being the only solvent in which they would dissolve.
Thus is was not possible to determine the molecular weights of these
polymers by the usual solution methods. Molecular weight determinations
by other methods involve tedious and lengthy procedures and were not
used for this reason. In the polymerization reaction, the polymer
was not precipitated out of solution until the later stages of the
reaction and thus the molecular weight determinations by solution
methods could be carried out on samples taken during the intermediate
stages of the reaction. This was done, but because only a very small
amount of the monomer was used and an appreciable weight of polymer
was required for a molecular weight determination, only two samples
per reaction run were taken. Thus two such samples were obtained from
each of two reactions which were conducted under identical conditions.
In each reaction, at a suitable time, half of the reaction mixture was
removed and added to a large volume of water to terminate the reaction,
The reaction of the remaininghalf of the reaction mixture was

Experiment	Elemental Analysis (% by weight)					Corresponding empirical formula based on C_{12}				
	C	H	N	S	O	C	H	N	S	O
3	55.1	3.5	11.1	23.0	7.3	C_{12}	$H_{8.75}$	$N_{1.98}$	$S_{1.79}$	$O_{1.14}$
5	56.9	3.8	10.9	22.0	6.5	C_{12}	$H_{9.46}$	$N_{1.94}$	$S_{1.71}$	$O_{1.03}$
6	56.9	3.7	11.0	22.2	6.3	C_{12}	$H_{9.24}$	$N_{1.98}$	$S_{1.74}$	$O_{.98}$
7	57.6	4.1	10.5	22.1	5.8	C_{12}	$H_{10.25}$	$N_{1.87}$	$S_{1.72}$	$O_{0.90}$

C = Carbon   H = Hydrogen   N = Nitrogen

S = Sulphur   O = Oxygen

Average empirical formula = $C_{12} H_{9.3} N_{2.0} S_{1.8} O_{1.0}$

Empirical formula for $\left[-N=N-\langle O \rangle -S-S-\langle O \rangle -\right]_n$ is $C_{12} H_8 N_2 S_2$

Table 10.2

Results: Elemental analysis of Poly(aminothiophenol)

terminated at a predetermined time by the addition of excess water. The reaction conditions and results of these two experiments including the molecular weight determinations are shown in table 10.3. Sample 1 was soluble in pyridine but insoluble in dimethylacetamide, whereas samples 2, 3 and 4 were soluble in dimethylacetamide but insoluble in pyridine. Because of this fact it was decided to conduct molecular weight determinations of samples 2, 3 and 4 only, using dimethylacet- amide as the solvent. Plots of oxygen consumption vs time for the reactions are shown in Fig. 10.4.1 ; on these graphs are shown the times at which the samples were taken and the corresponding oxygen consumption measurements.

Infrared spectra were obtained for all the polymer samples. All these spectra were virtually identical; a typical spectra is shown in Fig. 10.4.2.

10.5 Further Discussion

10.5.1 Discussion of the Elemental Analyses.

(a) Oxygen Content.

From the results of the elemental analysis for carbon, hydrogen, nitrogen and sulphur, the percentage by weight of oxygen contained in the polymer sample can be calculated assuming that only the above 5 elements were present in the polymer. The results confirm that an appreciable amount of oxygen was incorporated into the polymer chain. From these results, the empirical formulae of the polymers was calculated, working on the basis of a C_{12} unit; these empirical formulae are shown in table 10.2. It can be seen that the empirical formulae for all the 4 samples were almost identical. This is rather

Experiment	Cu Cl	$-\dfrac{d O_2}{dt}$ thiol ($\times 10^4$)	$-\dfrac{d O_2}{dt}$ amine ($\times 10^4$)	% Oxygen consumption thiol
10	0.0101	2.87	3.15	97
11	0.0101	3.15	1.91	105

Reaction conditions: 0.20 moles/litre aminothiophenol;
5.0. ml. pyridine; 25°C ; oxygen at atmospheric
pressure; magnetic stirrer

Sample	Molecular Weight
1 (10a)	not determined
2 (10b)	340
3 (11a)	380
4 (11b)	540

Samples 1 and 2 were taken from experiment 10 and samples 3 and 4
were taken from experiment 11.

Table 10.3

Results: oxidation reactions of aminothiophenol in which samples
were taken for molecular weight determination.
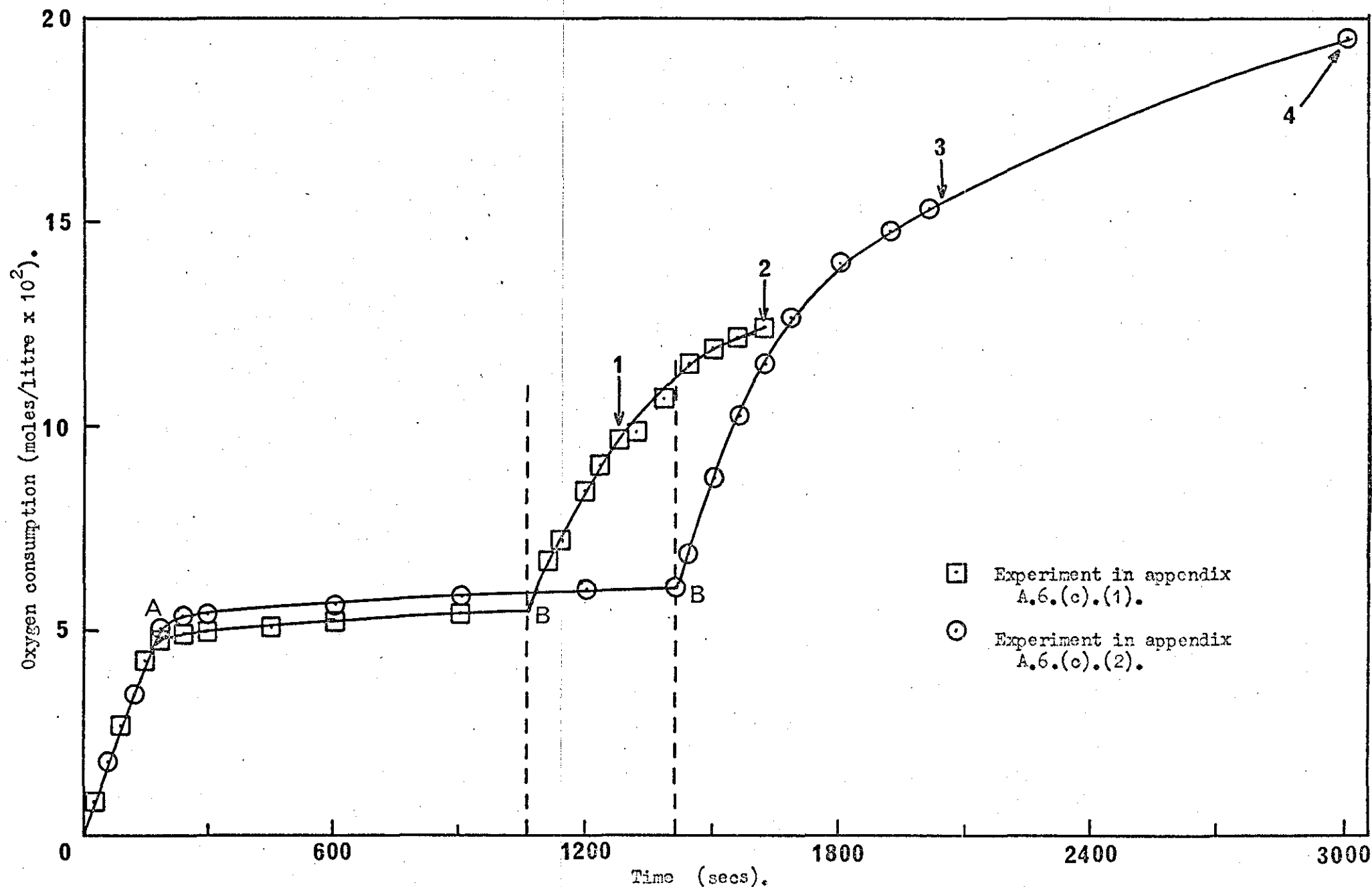
Fig. 10.4.1. Oxidation of aminothiophenol, reactions in which samples were taken out for molecular weight determinations.
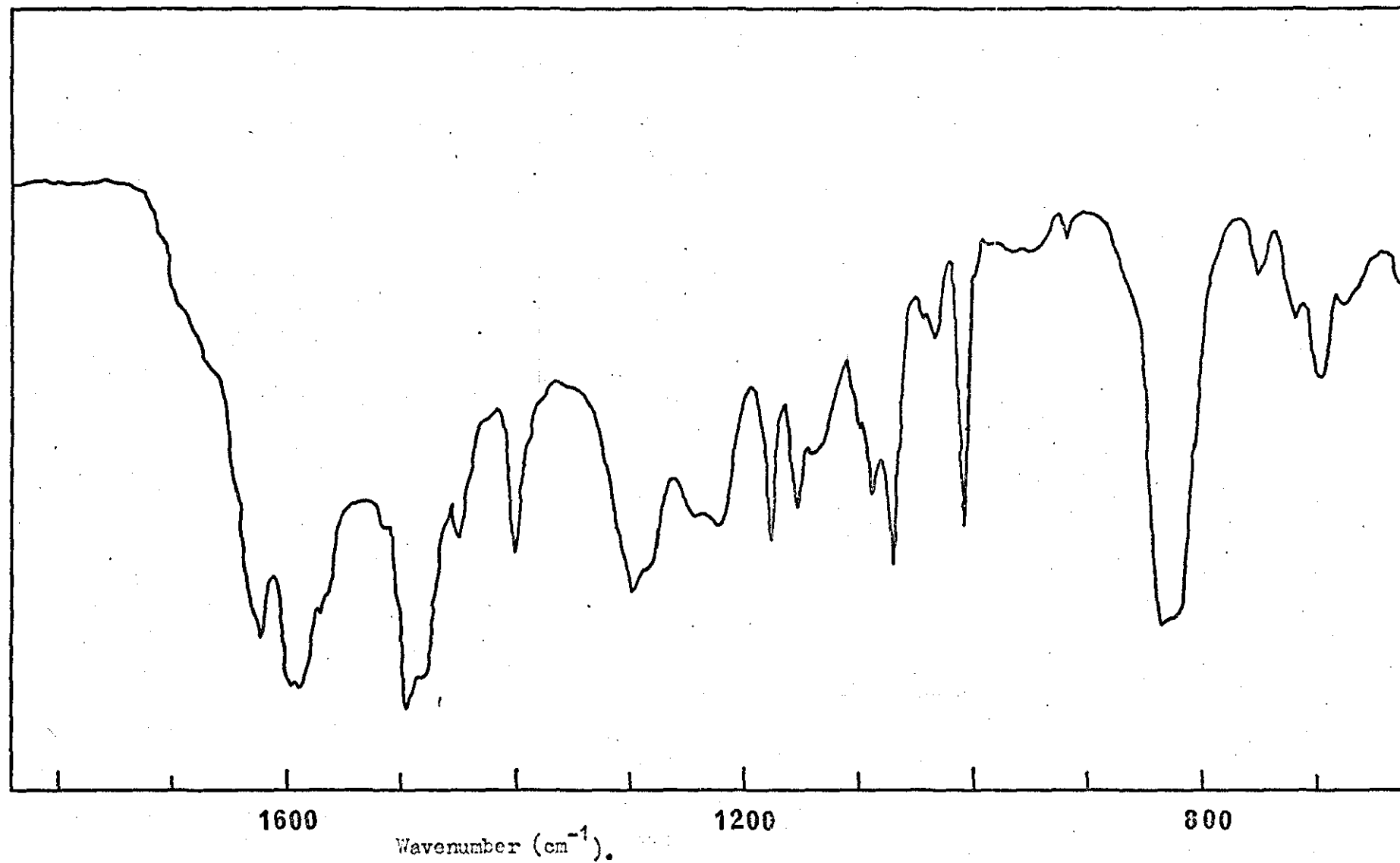
Fig. 10.4.2. Typical infrared spectra of poly(aminothiophenol).

surprising since the oxygen consumption for both the thiol and the amine reactions, and the total oxygen consumption were different for each polymer. One possible explanation for this phenomenon is as follows:-

Part of the product may have been lost in the polymer work-up procedure and thus would not be included in the sample sent for analysis. If this "lost" material contained more oxygen than the polymer, then this would explain the above phenomenon. It is feasible that oxygen-rich compounds such as sulphur acids may have been formed in the polymerization reaction. These compounds may have been soluble in water or in other solvents used in the work-up procedure and thus may not have been included in the sample which was analysed.

(b) Hydrogen Content.

In table 10.2, comparison can be made of the average empirical formula for the polymers with the corresponding empirical formula for the expected polymer product containing alternate disulphide and azo bonds (equation 10.1.1). This expected polymer product will hereafter be referred to as polymer X. Clearly the actual polymers contained more hydrogen than polymer X. Three possible explanations which could be given for this are as follows:-

(1)   The polymer contained unreacted amine groups.

(2)   Hydroxyazo bonds (-NH-NH-) were present in the polymer chain.

(3)   Sulphur acids were present as end groups.

If the average polymer chain consisted of 4 units or more of 12 carbon atoms, the maximum amount of hydrogen contained in the polymer

described by either (1) or (2) would be less than that in the empirical formula of the polymer. Evidence is given in section 10.5.4 to show that the average polymer chain does in fact consist of more than 4 units, i.e. more than a molecular weight of 500. Thus neither explanation (1) nor (2) alone can account for the total amount of hydrogen contained in the polymer, although they may make a significant contribution.

If hydroxyazo bonds were present in the polymer X instead of azo bonds, the empirical formula of the polymer would be $C_{12}H_{10}N_2S_2$. Thus we may conclude that there probably was a considerable proportion of hydroxyazo bonds in the polymer.

(c)   Nitrogen Content.

Comparison of the two empirical formulae given in table 10.2 shows that the proportion of nitrogen contained in the polymer was approximately as would be expected.

(d)   Sulphur Content.

It can be seen from the empirical formulae in table 10.2, that the proportion of sulphur contained in the polymer was slightly lower than that which was expected. The loss of sulphur from the polymer unit is rather surprising since this means that C - S bonds and possibly S - S bonds had been broken, a phenomenon which would not be expected under such mild oxidizing conditions. It may be possible that the sulphur was removed from the polymer during the work-up procedure when dilute aqueous acid or alkali was used to wash the polymer. The sulphur may have been removed from the polymer in the form of sulphur dioxide.

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It may also be possible that the difference in sulphur content
between the actual polymers formed and polymer X may have been due
to an experimental error in the elemental analyses. If this was the
case, it was a biased error rather than a random error.

From equation 10.1, it can be calculated that the incorporation
of one atom of oxygen per C_{12} unit into the polymer X (as required by
the empirical formulae) would correspond to a total oxygen consumption
of 133%. Thus there is a considerable proportion of the oxygen
consumption which is not accounted for by either the polymer formation
or the addition to the polymer chain of one oxygen atom per C_{12} unit.
This again could be explained in terms of the formation of oxygen-rich
compounds such as sulphur acids, which were lost in the polymer work-
up procedure and thus were not included in the samples sent for
analysis. Such sulphur acids may be of the type shown in Fig. 10.5.1.

$$HO_nS - \langle O \rangle - N = N - \langle O \rangle - SO_nH \qquad HO_nS - \langle O \rangle - N = N - \langle O \rangle - SO_nH$$

where   n = 1, 2 or 3

Fig. 10.5.1. Sulphur acids of the type which may have been lost in
the polymer work-up procedure.

10.5.2 Discussion of the Molecular Weight Determinations.

Table 10.3 shows that the molecular weight of the polymer was
increasing during the course of the amine reaction; this is as expected.
The percentage oxygen consumption for the amine reaction corresponding

to samples 3 and 4 was over 100% (see table 10.4). This results discounts the possibility that up to 100% oxygen consumption a polymer was being formed and thereafter oxidative degradation of the polymer was occurring. Bach (12) had previously encountered this oxidative degradation in an oxidative coupling polymerization; however, he used different reaction conditions and was synthesizing a different polymer.

In the following argument it is assumed that at the begining of the amine reaction (point B in Fig. 10.2.1) the reactant consisted of 4, 4'-diaminodiphenyl disulphide (molecular weight 248). This assumption is only approximately correct but is sufficiently accurate for the purpose of the following argument.

If we consider an hypothetical amine reaction in which all the oxygen which is consumed from point B is used to form azo bonds, then one can calculate the resulting percentage oxygen consumption for the amine reaction which would correspond to each of the molecular weights in table 10.3. The formula used for this calculation is:-

$$\text{\% oxygen consumption for the amine reaction} = 100\left(1 - \frac{1}{P}\right) \text{\%} \qquad (10.5.1)$$

where P = degree of polymerization or the average number of C_{12} units per polymer chain.

i.e. molecular weight = $P \times [248 - 4(P-1)]$ (10.5.2)

The term $4(P-1)$ accounts for the hydrogen which has been lost from the polymer chain in the formation of azo bonds from amines; this term is very small and can be neglected in this case, thus giving:-

molecular weight of polymer = $P \times 248$ (10.5.3)

This hypothetical case is equivalent to the expected oxidative coupling of aminothiophenol in which polymer X is formed (equation 10.1.1).

The calculated percentage oxygen consumption figures for the amine reaction for this hypothetical case, together with the actual percentage oxygen consumption figures are given with the corresponding molecular weights in table 10.4. Also given in table 10.4 are the fractions of the oxygen consumption (for the amine reaction) which have been used to form azo bonds (F_{azo}). This value of F_{azo} is defined by equation 10.5.4.

$$F_{azo} = \frac{\text{% oxygen consumption for the hypothetical reaction}}{\text{% oxygen consumption the actual reaction}}$$

$$= \frac{Ox_{hyp}}{Ox_{act}} \qquad (10.5.4)$$

The value of F_{azo} for the final polymer product has been calculated from the readings of experiment 2 (table 10.1) and on the basis of the assumption that in the final polymer approximately 100% oxygen consumption for the amine reaction was used in the formation of azo bonds from amine groups, i.e. virtually all the amine groups had been oxidized to azo bonds. This assumption has not been proved since the molecular weights for the final polymers could not be determined by the usual solution methods. Nevertheless, there is no evidence to suggest that amine groups can be oxidized by the copper (I) chloride pyridine catalyst system to anything but hydroxyazo[++] or Azo compounds, whereas evidence has been given to show that thiols can be oxidized

[++] the case of hydroxyazo bonds being formed in the hypothetical case is considered later in this section.

Sample	Molecular Weight of Polymer	Ox_{hyp}	Ox_{act}	F_{azo}
2	340	27	74	0.37
3	880	35	103	0.34
4	540	54	144	0.38

Ox_{hyp} = Calculated % Oxygen consumption for hypothetical reaction.

Ox_{act} = Actual % oxygen consumption.

F_{azo} = Fraction of oxygen consumption which is used to increase the molecular weight.

Value of F_{azo} for final polymer product = 0.45

Ox_{hyp}, Ox_{act} and F_{azo} all refer to the amine reaction only.

Table 10.4

Fractions of the oxygen consumption which is used to increase the molecular weight of the polymer

to products other than disulphides.

Table 10.4 clearly shows that the oxidation of amine groups to azo bonds was proceeding concurrently with the other oxidation reaction. This is in contrast to the reaction sequence which might be expected, namely the formation of polymer X and subsequent further oxidation of the polymer. Furthermore, it can be seen from table 10.2 that, of the oxygen which was consumed, the fraction which was used to form azo bonds (and thus increase the molecular weight) was small in the first part of the reaction but was much larger in the later stages of the reaction. Thus in the first part of the amine reaction the minor reaction occurring was the coupling of the amine groups to form azo bonds whereas the major reaction(s) occurring were the other oxidation reaction(s) which, at present, have not been characterized. In the later stages of the reaction, the situation may be reversed.

Evidence has previously been given to suggest that the majority of amine groups were oxidized to form hydroxyazo bonds rather than azo bonds. If we consider a similar hypothetical case, to the one described above, in which hydroxyazo bonds rather than azo bonds are formed, then the values of Ox_{act} would remain the same, but the values of Ox_{hyp} and F_{azo} would be reduced by a factor of 2. However, the above argument would still apply to this hypothetical case. The only differences being that the amine coupling to hydroxyazo bonds would feature in the oxidation reaction to an even smaller extent and in the later stages of the reaction, although comprising a greater proportion of the reaction, the hydroxyazo bond formation may not be the major reaction occurring.

10.5.3 Dependence of the Kinetics of the Thiol Reaction Upon Catalyst Concentration.

Over the range of catalyst concentrations which were studied, the graph of log (initial rate of oxygen absorption) vs log (catalyst concentration) for the thiol reaction appears to be a straight line of slope 0.25 (Fig. 10.2.3). A more correct picture of the rates of reaction would be obtained by converting the rates of oxygen absorption to the rate of removal of aminothiophenol (ATP). The rate of removal of ATP can be calculated by a similar method to that which was used to calculate the rates of removal of thiophenol from the rates of oxygen absorption for experiments in section 6.1.6. A similar equation (equation 10.5.5) to equation 6.1.6.2 can be used.

$$\text{rate of removal of ATP} \quad \left(- \frac{d[ATP]}{dt}\right) = \frac{1}{4} (1+\phi_p) \times \left(- \frac{d[O_2]}{dt}\right) \qquad (10.5.5)$$

$$\text{where:-} \quad \phi_p = \frac{\text{moles of ATP consumed to give the thiolsulphinate}}{\text{total moles of ATP consumed}}$$

$$(10.5.6)$$

The graph of log (rate of removal of ATP) vs log (catalyst concentration) is shown in Fig. 10.5.2. This graph can be interpreted in terms of two straight lines $A^p B^p$ and $B^p C^p$ which intersect at break-point B^p, having slopes of 0.5 and 0.2 respectively.

Comparison of tables 6.1 and 10.1 show that the initial rates of thiol oxidation for thiophenol oxidation and ATP oxidation are of the same order. It was previously shown in chapter 6 that for the thiophenol oxidation reaction, over a certain catalyst concentration range, the graph of log (rate of removal of thiophenol) vs log (catalyst concentration) comprised two intersecting straight lines
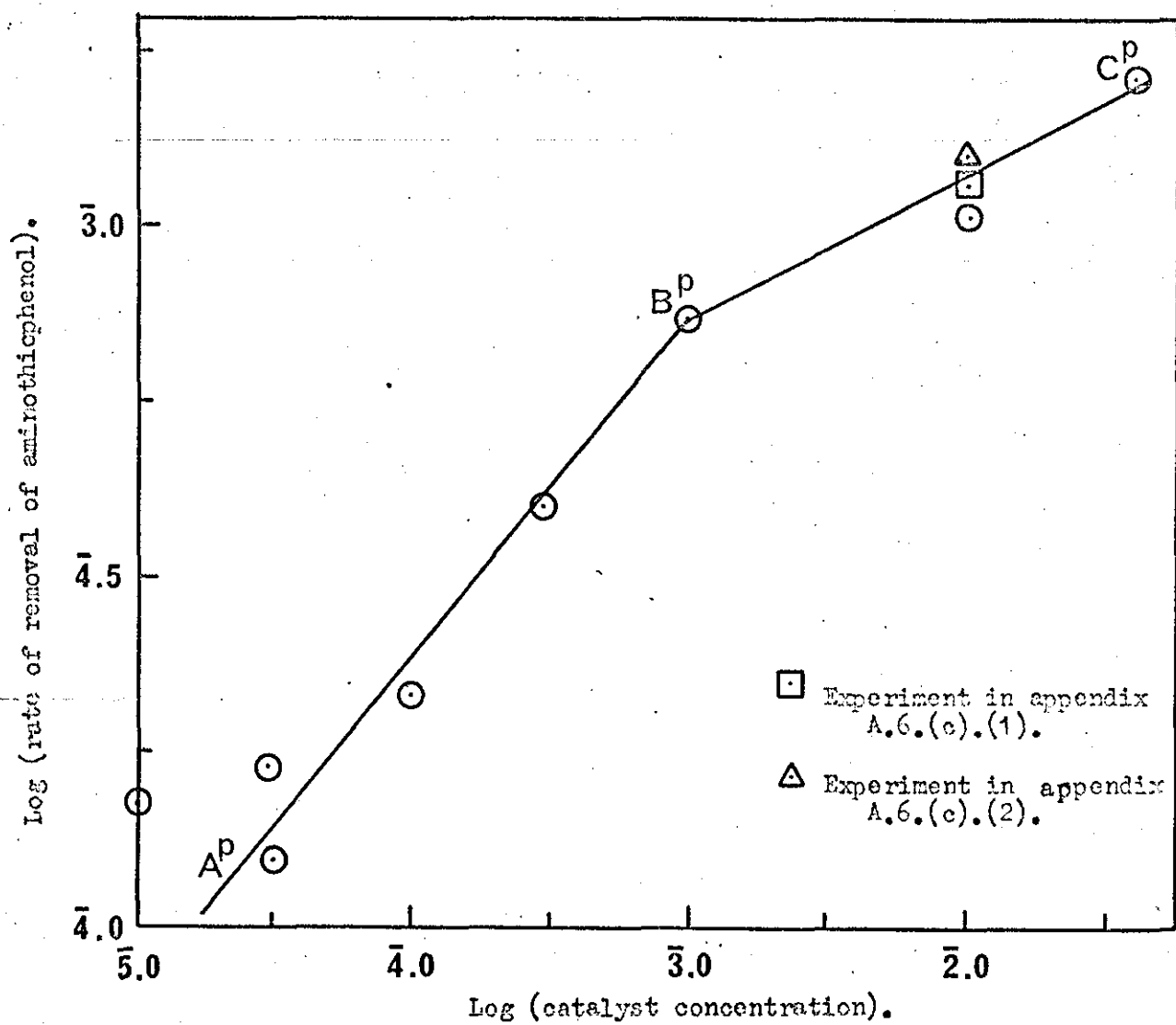
Fig. 10.5.2. Oxidation of aminothiophenol, log (rate of removal of aminothiophenol) vs log (catalyst concentration).

A'B' and B'C' of slopes - 0.5 and 0.1 respectively. These two straight lines were shown to represent the fast reaction regime (A'B') and the instantaneous reaction regime (B'C'). Thus for the ATP oxidation, similar graphs would be predicted; this is in fact the case. Furthermore, one would predict that the slopes of the two lines A^pB^p and B^pC^p would be 0.5 and approximately zero respectively. This is so for the line A^pB^p; the slope of the line B^pC^p is 0.2 but this may still be within the limits of the slope which may be obtained experimentally for an instantaneous reaction regime.

In section 6, it was suggested that in the transition from the fast reaction regime to the instantaneous reaction regime, the limiting rate became the diffusion of oxygen through the gas phase resistance to the interface. If this was true for the thiophenol oxidation reaction, then it would most probably be true also for the ATP oxidation. Since the same partial pressure of oxygen was used for both sets of experiments, then, at the break-point, one would predict that the rate of oxygen absorption should be approximately the same for both reactions. Comparison of Fig. 6.1.3.2 and Fig. 10.2.3 shows that this is indeed the case. This evidence gives added confirmation to the assigning of the specified regimes of mass transfer with chemical reaction to the general regions AB and BC in the thiophenol oxidation reaction. Also from the above evidence, it may be deduced that, in the oxidation of ATP, the fast reaction and the instantaneous reaction regime most probably apply to the regions A^pB^p and B^pC^p respectively, and that the limiting factor in the instantaneous reaction regime, B^pC^p, is most probably the diffusion of oxygen through the gas phase resistance to the interface.

For a given catalyst concentration, the rates of reaction for the ATP oxidation are lower than the corresponding rates for the thiophenol oxidation. This is consistent with the findings of Price and Nakaoka (14) who reported that in their oxidative coupling reactions using a copper chloride pyridine complex, the rate of reaction was influenced by the structure of the monomer or the substrate (see section 24). Also one may conclude that the p-amino group had a deactivating effect upon the reactivity of the thiol group. It has previously been shown (section 2.3) that electron withdrawing groups on the aromatic ring decrease the oxidative coupling rates. This is consistent with the fact that amine groups have an electron attracting inductive effect (66). The electron donating conjugative effect of the amine group in ATP may be relatively small. There may also be other important reasons why ATP is less reactive than thiophenol. One reason may be that the amine groups, although less reactive than thiol groups for oxidative coupling have an appreciable affinity for the copper complex nucleus and thus may block coordination sites on the copper which otherwise may have been taken by thiol groups.

10.5.4 Discussion of the Dependence of the Kinetics of the Amine Reaction Upon the Initial Catalyst Concentration Used for the Thiol Reaction.

In considering Fig. 10.2.4 it must again be emphasized that the initial catalyst concentration refers to the catalyst concentration at the very begining of the complete reaction and not at the start of the amine reaction.

From Fig. 10.2.4 it appears that the initial rate of oxygen consumption for the amine reaction was dependent upon the initial catalyst concentration; in other words, the initial rate of the amine

reaction was dependent upon the concentrations of the various products (the disulphide, thiolsulphinate and possibly higher oxidation products of the thiol group) which were present from the initial thiol reaction. As the initial catalyst concentration was varied, the initial rates of the amine reaction appear to pass through a maximum. However, it may be argued, with some justification, that the variation in the initial rates was small and the spread in these initial rates of the amine reaction was due to statistical flucuations which by coincidence appear in the form of a maximum. At present, it is difficult to say whether or not this maximum is significant. If the graph of Fig. 10.2.4 is compared with the graphs of Fig. 10.2.6, then it can be concluded that there is certainly a correlation between the initial rate of the amine reaction and the percentage oxygen consumption for either just the amine reaction or the total reaction. This correlation is discussed further in section 10.5.7.

10.5.5 Discussion of the Experiments in which the Vibromix Stirrer was Used (Fig. 10.2.2).

(a) The Thiol Reaction.

By using the vibromix stirrer as opposed to the magnetic stirrer, one would predict that the rate of oxygen absorption and the percentage of the thiolsulphinate formed would both increase. Comparison of the results of experiments 3, 8 and 9 in table 10.1 shows that this is indeed so.

An unusual feature of the thiol reaction is that the consumption of oxygen proceeded to point A (Fig. 10.2.2) whereupon it ceased and subsequently a small amount of gas was given off. This phenomenon was not encountered in the corresponding thiophenol oxidation experiments.

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The gas evolved may have been either oxygen or hydrogen. Further experimental work is needed in order to specify the nature of this gas evolution. It is interesting to note that Brooks (25) reported the the evolution of a gas upon mixing the reactants in the oxidative coupling of 2,6-dimethylphenol (see section 2.4). He also stated that the origin of the gas evolution was obscure.

(b)   The Amine Reaction .

One would expect that the initial rate for the amine reaction would increase as the gas-liquid mixing became more efficient. This is indeed the case as is shown in Fig. 10.2.2. When the height of the stirrer disc was adjusted to coincide with the surface of the liquid for the amine reaction (experiment 8), the efficiency of the gas-liquid mixing was increased and this had the effect of increasing the initial rate of oxygen absorption.

From Fig. 10.2.2 , it can be seen that, although the initial rate was faster for experiment 8, the reaction rate tailed off much quicker than that of experiment 9. Thus after an appreciable reaction time, the total oxygen consumption for experiment 9 was greater than that of experiment 8. This phenomenon appears to be contradictory to the findings of section 10.5.4, where it was shown that an increase in the percentage oxygen consumption coincided with an increase in the initial amine reaction rate. Clearly further experimental work using the vibromix stirrer must be done in order to ascertain the nature of the reactions occurring in this amine reaction region.

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10.5.6 Discussion of the Infrared Spectra.

The fact that all the infrared spectra of the polymers were almost identical is consistent with the findings of section 10.5.1, where the elemental analyses showed that the polymers had virtually identical empirical formulae. Smalley and Wakefield(67) reported correlation tables for infrared specta; in these are given the relative intensities and absorption frequencies for the infrared absorption peaks of functional groups, some of which may possibly be present in the polymers. If these tables are compared with the infrared spectra of the polymers, it is found that one unique functional group cannot be assigned to any one of the absorption peaks. In other words, it is not possible to say which one of a number of functional groups is present in the polymer. However, it is possible to eliminate certain functional groups when no peaks can be detected in the region of their characteristic absorption. The following functional groups were not detected in the spectra: thiols (-SH) ; sulphoxide ($\rangle S = O$) and sulphonamide (- $\overset{O}{\underset{O}{S}}$ - NH -). The absence of the sulphoxide group is significant. This suggests that fission of the thiolsulphinate bond must have occurred, thus confirming a previous suggestion of the cleavage of the C - S bond.

10.5.7 Hypothesis for the Reactions Occurring in the Amine Reaction Region.

The following hypothesis is consistent with most of the experimental results which have been discussed.

There may be two types of reaction proceeding concurrently in the amine reaction region.

(i)   Reaction A, the coupling of amine groups to form azo or hydroxyazo bonds. This reaction may proceed at a fixed rate for a fixed catalyst concentration and a fixed amine group concentration and also may be independent of the nature of the oxidized thiol groups (disulphide, thiolsulphinate or other higher oxidation products of the thiol group).

(ii)   Reaction B, the further oxidation of the oxidized thiol groups.   This reaction may be dependent upon the nature of the oxidized thiol groups.

It may be that reaction A, the polymer formation reaction, tends to stabilize the polymer and thus reduce the extent of reaction B.   At low initial rates of the amine reaction, reaction A may be proceeding at a lower rate.   Thus the polymer may be stabilized before reaction B has occurred to any great extent with the result that the percentage oxygen consumption for the amine reaction is low. Conversely, if the initial reaction rate was high, reaction B may have occurred to a considerable extent before the polymer was stabilized by reaction A, with the result that the percentage oxygen consumption for the amine reaction would be high.   As well as being quite feasible the above hypothetical reaction scheme is consistent with all the experimental results except those for the vibromix stirrer.   As stated in section 10.5.5, further experimental work using the vibromix stirrer is required in order to specify the nature of the reactions occurring in this amine reaction regime.   The above hypothesis may then be modified to be consistent with all the experimental results.

10.6 Conclusions and Suggestions for Further Work.

10.6.1 Conclusions.

The more important conclusions which can be drawn from this study

of the oxidative coupling of aminothiophenol are given below.

1. At low catalyst concentrations, the initial products of the
reaction, were 4,4'-diaminodiphenyl disulphide and 4,4'-diam-
inodiphenyl thiolsulphinate. At low catalyst concentrations when
all the thiol groups had been oxidized, the reaction effectively ceased.

2. The proportion of the thiolsulphinate in the product increased
as either the catalyst concentration decreased or the mass transfer
rate increased.

3. Two regions of mass transfer with chemical reaction were found
to be present in the range of reaction conditions studied. In the
lower catalyst concentration region, the fast reaction regime applied,
whereas in the higher catalyst concentration region, the instantaneous
reaction regime applied. The limiting factor in the instantaneous
reaction regime was the transfer of oxygen through the gas phase
resistance towards the interface.

4. The addition of excess catalyst to the reaction mixture after the
first part of the reaction promoted not only the oxidation of amine
groups to either hydroxyazo or azo bonds, but a further oxidation
reaction, the nature of which, at present, is not known. These two
oxidation reactions proceeded concurrently.

5. An appreciable amount of oxygen was incorporated into the final
polymer products, the average empirical formula being $C_{12}H_{9.3}N_{2.0}S_{1.8}O_{1.0}$.

6. There was a definite correlation between the initial rates of
oxygen absorption after the excess catalyst solution was added and
the amount of oxygen consumed in this part of the reaction.

10.6.2 Suggestions for Further Work.

Since this present project is the first reported study of the oxidative coupling of aminothiophenol, there is wide scope for further work. The more important features requiring further investigation are as follows:-

1)   The development of non-solution methods for molecular weight determination of the polymer products.

2)   Further investigation into the nature of the oxidation reactions occurring in the amine reaction region.

A.5 Oxidation of p-Phenylenediamine

   (a)   Use of the magnetic stirrer.

   (b)   No stirring.

   (c)   Use of the vibromix stirrer.

A.6 Oxidation of Aminothiophenol.

   (a)   Use of the magnetic stirrer.

   (b)   Use of the vibromix stirrer.

   (c)   Use of the magnetic stirrer, experiments in which
           samples were taken for molecular weight determinations.

A.7 Molecular Weight Determinations of Poly(aminothiophenol).

<u>Definition of Terms in the Tables of Results.</u>

[X]   concentration of X in grm. moles/litre of solvent.

Time   is recorded in seconds.

D   distance moved by the piston (cm.)

M   oxygen consumed (grm moles/litre of solvent).

V_{acid} volume of acid or alkali added to terminate the reaction (ml.)

$V_{aliq.}$ volume of aliquot taken for the thiolsulphinate titration (ml.)

V_{titre} titration reading for the thiolsulphinate titration (ml.)

$- \dfrac{d[O_2]}{dt}$ initial rate of oxygen consumption (grm. moles/litre/sec.)

V_{AgNO_3} volume of alcoholic silver nitrate solution (ml.)

E.m.f.   potential of the potentiometric cell. (mV.).

P.P.D.   p-phenylenediamine

$(X)_{Amine/Thiol/total}$ the value of X for the amine/thiol/total reaction

A.1.1.a.

[CuCl]	1.01×10^{-1}		1.01×10^{-2}		1.01×10^{-3}		2.02×10^{-4}	
[PhSH]	0.455		0.454		0.456		0.457	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0	0	0	0	0	0	0	0
15	0.35	0.15						
30	1.95	0.75	0.9	0.35	1.10	0.45	0.75	0.30
45	3.40	1.35						
60	5.10	2.00	3.75	1.55	3.25	1.35	2.75	1.15
90	8.45	3.35	6.10	2.50	5.40	2.25	4.50	1.85
120	11.60	4.65	8.60	3.55	7.40	3.05	6.30	2.60
150	15.00	5.95	10.95	4.50	9.40	3.90	7.90	3.25
180	18.80	7.45	13.30	5.50	11.35	4.70	9.60	3.95
210	22.35	8.85	15.65	6.45	13.30	5.50		
240	24.35	9.65	17.80	7.35	15.20	6.30	12.90	5.30
270	25.35	10.05	20.10	8.30	16.90	7.00		
300	25.80	10.20	21.70	8.95	18.75	7.75	16.10	6.60
360	26.25	10.40	25.75	10.65	22.15	9.15	19.25	7.90
420	26.60	10.55	26.35	10.90	25.20	10.40	22.30	9.15
480	26.75	10.60	26.45	10.95	27.70	11.45	25.20	10.35
540	26.80	10.60	26.65	11.00	29.85	12.35	27.85	11.45
600	27.05	10.70	26.75	11.05	31.35	12.95	30.25	12.40
720	27.35	10.85					33.85	13.90
750			26.75	11.05	31.85	13.20		
840	27.55	10.90					36.25	14.90
900					31.55	13.05	36.85	15.10
960	27.55	10.90					37.00	15.20
1200					31.10	12.85	37.00	15.20
1500					30.95	12.80		

V_{acid}	0.50	1.00	1.00	1.10
V_{aliq}	0.50	0.50	0.50	0.50
V_{titre}	4.40	0.40	0.80	5.80
% PhSOSPh	2	2	4	32
$-\dfrac{d[O_2]}{dt} \times 10^4$	4.50	3.30	2.58	2.36
% oxygen consumption	96	97	111	131
Normality of $Na_2S_2O_3$	0.010	0.010	0.010	0.010

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Time	[CuCl] 1.01 × 10⁻⁴ [PhSH] 0.455		[CuCl] 4.04 × 10⁻⁵ [PhSH] 0.457		[CuCl] 2.02 × 10⁻⁵ [PhSH] 0.455		[CuCl] 1.01 × 10⁻⁵ [PhSH] 0.457	
	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0.50	0.20	0.20	0.10	0.45	0.20		
30	0.80	0.30	0.95	0.40	0.50	0.20	0.55	0.20
60	2.75	1.10	1.75	0.70	0.70	0.30	1.00	0.40
120	5.70	2.25	3.40	1.40	2.35	1.00	1.80	0.70
180	8.65	3.45	5.05	2.05				
240	11.55	4.60	6.65	2.20	4.35	1.80	3.25	1.30
300	14.20	5.65	8.20	3.35				
360	17.05	6.75	9.75	3.95	6.65	2.75	4.95	1.95
420	19.75	7.85						
480	22.65	9.00	12.10	4.90	9.00	3.75	6.50	2.60
540	25.10	9.95						
600	27.75	11.00	14.95	6.10	10.90	4.55	8.00	3.20
720	32.20	12.80						
750			18.65	7.60	13.75	5.75	10.00	3.95
840	35.45	14.30						
900	37.30	14.80	22.25	9.05	16.65	6.95	12.00	4.75
960	37.90	15.05						
1200	39.50	15.70	29.10	11.85	21.80	9.10	13.75	5.45
1500	39.85	15.85	34.85	14.20	27.00	11.25		
1800	39.85	15.85	38.55	15.70	31.55	13.15	23.20	9.20
2100			39.55	16.10	35.65	14.85		
2400			39.45	16.05	38.15	15.90	30.30	12.05
3000					39.05	16.40	36.50	14.50
3300					39.05	16.40		
3600							40.00	15.90
5400							41.70	16.55
6000							41.70	16.55
V_{acid}	0.50		0.50		0.50		0.50	
V_{aliq}	0.50		0.50		0.50		1.00	
V_{titre}	6.50		8.10		9.40		12.35	
% PhSOSPh	32		41		47		31	
$-\dfrac{d[O_2]}{dt} \times 10^4$	1.76		1.14		0.80		0.52	
% oxygen consumption	138		143		143		143	
Normality of $Na_2S_2O_3$	0.010		0.0098		0.010		0.010	

b.

Time	[CuCl] 1.01×10^{-1} [PhSH] 0.449		[CuCl] 1.01×10^{-2} [PhSH] 0.449		[CuCl] 1.01×10^{-3} [PhSH] 0.449		[CuCl] 2.02×10^{-4} [PhSH] 0.449	
	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
$7\frac{1}{2}$	3.25	1.35						
10			2.30	0.95	1.10	0.45	1.35	0.55
15	7.25	3.00						
20			5.20	2.10	2.60	1.08	2.65	1.10
$22\frac{1}{2}$	11.55	4.75						
30	14.95	6.15	8.00	3.30	4.20	1.75	3.80	1.55
$37\frac{1}{2}$	19.75	8.10						
40			10.70	4.40	5.60	2.30	4.95	2.00
45	23.95	9.85						
50			13.40	5.50	7.10	2.90	6.05	2.50
$52\frac{1}{2}$	26.45	10.90						
60	27.45	11.30	15.90	6.55	8.55	3.50	7.00	2.90
75	28.35	11.65						
90	28.95	11.90	22.90	9.45	12.85	5.30	10.20	4.20
120	29.60	12.15	28.80	11.85	16.80	6.90	13.25	5.45
150	29.95	12.30	31.40	12.95	20.55	8.45	16.20	6.60
180	30.20	12.40	46.50	12.90	23.95	9.85	18.90	7.80
210	30.35	12.50	46.50	12.90	27.10	11.15		
240	30.35	12.50	46.30	12.80	29.75	12.25	24.05	9.90
270			46.30	12.80				
300					33.80	13.90	28.75	11.85
360					35.85	14.75	32.60	13.45
420					36.45	15.00		
480					36.45	15.00	38.45	15.85
600							40.80	16.85
780							41.35	17.05
840							41.35	17.05
V_{acid}	2.00		1.00		0.50		0.50	
V_{aliq}	0.50		0.50		0.50		0.50	
V_{titre}	3.20		0.70		4.95		6.95	
% PhSOSPh	2		4		25		35	
$-\dfrac{d[O_2]}{dt} \times 10^4$	22.8		11.3		6.10		4.43	
% oxygen consumption	111		114		133		152	
Normality of $Na_2S_2O_3$	0.010		0.010		0.010		0.010	

[CuCl]	1.01×10^{-4}		4.04×10^{-5}		2.02×10^{-5}		1.01×10^{-5}	
[PhSH]	0.450		0.450		0.449		0.458	
Time	D	M	T	M	T	M	T	M
0	0	0	0	0	0	0	0	0
30	2.70	1.10	1.00	0.40	1.90	0.80	1.75	0.70
60	4.85	2.00	1.70	0.70	2.55	1.05	1.95	0.80
90	6.80	2.80	3.25	1.35	3.25	1.35		
120	8.95	3.70	4.70	1.95	3.85	1.60	2.70	1.10
150	11.70	4.85	5.75	2.40	4.35	1.80		
180	13.85	5.75	6.75	2.80	4.75	1.95	3.00	1.25
240	18.10	7.50	8.70	3.65	5.60	2.30	3.25	1.35
300	22.25	9.20	10.55	4.40	6.40	2.65		
360	26.45	10.95	12.15	5.10	7.20	2.95	3.80	1.55
480	33.40	13.85	15.80	6.60	8.80	3.65	4.65	1.90
600	39.00	16.15	19.00	7.95	10.35	4.25	5.35	2.20
720	42.30	17.50						
840	43.20	17.40					6.75	2.10
900	43.20	17.90	27.25	11.40	13.90	5.75		
1200			33.40	13.95	17.00	7.00	8.85	3.65
1500			39.80	16.65	20.25	8.35	10.50	4.35
1650			40.80	17.05				
1800			40.90	17.10	23.05	9.50		
2400					28.80	11.85		
3600					39.55	16.30		
4200					44.55	18.35		
4500					45.15	18.60	25.75	10.60
4800					45.40	18.70		
4950					45.40	18.70		
7200							33.60	13.85
10800							38.10	15.70
12600							39.35	16.25
13500							39.40	16.25
V_{acid}	0.50		0.50		0.50		0.50	
V_{aliq}	0.50		0.50		0.50		0.50	
V_{titre}	9.25		10.40		10.05		2.30	
% PhSOSPh	47		53		51		12	
$-\frac{d[O_2]}{dt} \times 10^4$	3.08		1.39		0.57		0.24	
% oxygen consumption	159		151		167		142	
Normality of $Na_2S_2O_3$	0.010		0.010		0.010		0.010	

c.

	1.01×10^{-2}		1.01×10^{-3}		3.20×10^{-4}		1.01×10^{-4}	
[CuCl]								
[PhSH]	0.449		0.448		0.450		0.447	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
30			0.80	0.35	0.70	0.30	0.80	0.35
60	0·45	0.20	1.15	0.45	1.10	0.45	1.05	0.45
120	1.00	0.40	1.70	0.70	1.65	0.70	1.35	0.55
180	1.55	0.65	2.35	0.95	2.30	0.95	1.85	0.75
240	3.80	1.55	3.10	1.25	3.00	1.25	2.40	1.00
300	5.25	2.15	3.85	1.55	3.55	1.45	2.90	1.20
360	6.30	2.55	4.55	1.85	4.20	1.70	3.45	1.40
480	8.20	3.35	5.95	2.40	5.50	2.25	4.50	1.85
600	10.05	4.10	7.45	3.05	6.85	2.80	5.60	2.30
750	12.30	5.00	9.30	3.80	8.20	3.35	6.95	2.80
900	14.50	5.90	11.00	4.45	9.60	3.95	8.25	3.35
1200	17.10	6.95	14.40	5.85	12.45	5.10	10.15	4.10
1800	24.10	9.85	20.35	8.25	17.70	7.25	15.00	6.10
2400			24.50	9.95	22.35	9.15	19.85	8.05
3000	27.65	11.25	27.65	11.25	26.00	10.65	23.45	9.55
3900	28.10	11.45	28.30	11.50	28.70	11.75		
4200	28.10	11.45	28.30	11.50			28.95	11.75
4800					29.90	11.90	29.90	12.15
5100					29.00	11.90		
5700							29.70	12.05
6000							29.70	12.05

V_{acid}	1.00	0.50	0.50	0.50
V_{aliq}	1.00	1.00	1.00	1.00
V_{titre}	0.65	0.15	0.65	1.85
% PhSOSPh	2	2	2	5
$-\dfrac{d[O_2]}{dt} \times 10^4$	0.64	0.49	0.43	0.38
% oxygen consumption	101	102	105	107
Normality of $Na_2S_2O_3$	0.010	0.010	0.010	0.010

[CuCl]	6.4×10^{-5}		4.04×10^{-5}		2.02×10^{-5}	
[PhSH]	0.452		0.441		0.447	
Time	D	M	D	M	D	M
0	0	0	0	0	0	0
30	0.35	0.15	0.65	0.25	0.50	0.20
60	0.70	0.30	0.75	0.30	0.65	0.30
120	1.00	0.40	1.05	0.45	1.00	0.40
180	1.40	0.55	1.45	0.60	1.25	0.50
240	1.75	0.70	1.90	0.80	1.45	0.60
300	2.15	0.90	2.15	0.90	1.85	0.75
360	2.60	1.05	2.50	1.00	2.10	0.85
480	3.40	1.40	3.20	1.30	2.35	0.95
600	4.15	1.70	3.95	1.60	2.95	1.20
750	5.15	2.10	4.85	2.00	3.50	1.45
900	5.95	2.45	5.75	2.35	4.25	1.75
1200	7.90	3.25	7.50	3.06	5.50	2.25
1800	11.55	4.75	10.80	4.45	8.05	3.30
2400	15.60	6.40	13.95	5.70	10.50	4.30
3000	19.30	7.90	16.80	6.85	13.15	5.35
3600	21.75	8.90	20.10	8.20	15.75	6.45
5400	28.85	11.80	27.70	11.30		
6600	29.75	12.20				
6900	29.75	12.20				
7200			31.10	12.70	29.25	11.95
8700			31.55	12.90		
9000			31.55	12.90	33.10	13.50
9600					33.15	13.50

V_{acid}	0.50	0.50	0.50
V_{aliq}	1.00	1.00	1.00
V_{titre}	2.45	4.70	5.60
% PhSOSPh	6	12	14
$-\dfrac{d[O_2]}{dt} \times 10^4$	0.27	0.24	0.165
% oxygen consumption	107	116	120
Normality of $Na_2S_2O_3$	0.0101	0.0098	0.0101

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d.

	1.01×10^{-2}		1.01×10^{-3}		2.02×10^{-4}		5.05×10^{-5}	
[CuCl]								
[PhSH]	0.453		0.450		0.451		0.447	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
15	0.50	0.20	0.60	0.25	1.25	0.50	0	0
30	0.70	0.30	0.95	0.40	1.30	0.55	0.10	0.05
45	1.55	0.65	1.40	0.55	1.55	0.65		
60	2.30	0.95	2.15	0.90	2.25	0.90	0.90	0.35
90	3.90	1.60	3.50	1.45	3.75	1.55	1.85	0.75
120	5.60	2.30	4.95	2.00	5.20	2.15	2.80	1.15
150	7.00	2.85	6.20	2.55	6.60	2.70	3.65	1.50
180	8.60	3.50	7.60	3.10	7.80	3.20	4.50	1.85
210	10.60	4.35	9.10	3.70	9.10	3.75	5.45	2.20
240	12.15	4.95	10.50	4.30	10.50	4.30	6.30	2.55
270	13.75	5.60	11.75	4.80	11.90	4.90	7.20	2.95
300	15.35	6.25	12.85	5.25	13.15	5.40	7.95	3.25
360	18.35	7.50	15.85	6.45	15.90	6.55	9.55	3.95
480	24.10	9.85	20.80	8.50	21.05	8.65	12.95	5.30
600	27.70	11.30	25.45	10.40	25.30	10.40	16.40	6.70
720	29.15	11.90	28.45	11.00	29.50	12.10		
750							20.35	8.30
900	30.00	12.25	31.00	12.65			23.80	9.70
960					35.20	14.45		
1020			31.00	12.65	35.65	14.65		
1050	30.20	12.35					27.45	11.20
1080					35.70	14.65		
1200							30.50	12.45
1650							36.95	15.10
1950							37.95	15.50
2100							37.95	15.50
V_{acid}	1.00		0.50		0.50		0.50	
V_{aliq}	1.00		1.00		1.00		0.50	
V_{titre}	1.40		2.20		10.60		6.80	
% PhSOSPh	2		5		24		32	
$-\frac{d[O_2]}{dt} \times 10^4$	2.24		1.88		1.81		1.15	
% oxygen consumption	108		111		129		137	
Normality of $Na_2S_2O_3$	0.010		0.010		0.010		0.010	

[CuCl]	2.02×10^{-5}		1.01×10^{-5}		5.05×10^{-6}	
[PhSH]	0.450		0.450		0.452	
Time	D	M	D	M	D	M
0	0	0	0	0	0	0
120	1.85	0.75	1.65	0.70	0.10	0.05
180	2.40	1.00	2.60	1.05		
240	3.80	1.55	3.45	1.40	0.60	0.25
300	4.55	1.85	4.10	1.70		
360	5.45	2.25	4.25	1.75	2.45	1.00
420	6.35	2.60	4.95	2.05		
480	7.15	2.95	6.25	2.55	2.85	1.15
600	9.40	3.85	7.70	3.15	4.25	1.75
840	12.95	5.30				
900					7.00	2.85
1200	18.35	7.50	14.££	5.95	9.50	3.90
1800	26.60	10.90			14.50	5.95
2400	33.95	13.90	29.20	11.95	20.10	8.25
3000	38.75	15.85	34.00	13.90	Reaction	
3300	39.80	16.30			not taken to	
3600	39.85	16.30			completion.	
3870			40.10	16.40		

V_{acid}	0.50	n.d.	n.d.
V_{aliq}	0.50	n.d.	n.d.
V_{titre}	8.50	n.d.	n.d.
% PhSOSPh	39	n.d.	n.d.
$-\dfrac{d[O_2]}{dt} \times 10^4$	0.63	0.50	0.345
% oxygen consumption	144	144	n.d.
Normality of $Na_2S_2O_3$	0.010	0.010	---

A.1.2.

	4.04 x 10^{-5}		4.04 x 10^{-5}		4.04 x 10^{-5}		4.05 x 10^{-5}	
[CuCl]								
[PhSH]	0.0134		0.0163		0.0238		0.0349	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0	0	0.05	0	0.10	0.01	0	0
10					0.45	0.03		
15	0.05	0	0.15	0.01			0.80	0.06
20					1.15	0.08		
30	0.10	0.01	0.45	0.03			0.95	0.07
40					2.50	0.18		
45	0.20	0.015	0.80	0.055			2.45	0.17
60	0.35	0.025	1.50	0.105	3.10	0.22	3.60	0.25
75	1.10	0.075	1.95	0.135			4.00	0.28
80					3.95	0.28		
90	1.60	0.110	2.40	0.165			4.55	0.32
100					4.75	0.33		
105	2.05	0.140	2.85	0.195			5.45	0.38
120	2.35	0.160	3.30	0.230	5.50	0.39	6.35	0.44
150	3.05	0.210	4.30	0.295	6.70	0.47	7.75	0.54
180	3.40	0.235	4.90	0.340	7.85	0.55	9.05	0.63
240	4.35	0.300	6.10	0.420	9.75	0.68	11.70	0.82
360	5.40	0.375	7.45	0.515	12.25	0.86	13.55	0.95
480	5.90	0.410	7.90	0.545	13.50	0.95	16.25	1.13
600	6.20	0.430	8.25	0.570	14.30	1.00	18.55	1.30
720					15.00	1.05	19.40	1.35
750	6.30	0.435						
840							19.40	1.35
900	6.40	0.440	8.50	0.595				
1200	6.60	0.455	8.85	0.610	16.10	1.13		
1350			8.90	0.615				
1500	6.60	0.455	8.90	0.615				
V_{acid}	n.d.		n.d.		0.50		0.50	
V_{aliq}	n.d.		n.d.		1.00		1.00	
V_{titre}	n.d.		n.d.		0.95		1.40	
% PhSOSPh	n.d.		n.d.		43		42	
$-\frac{d[O_2]}{dt} \times 10^4$	0.815		0.215		0.27		0.37	
% oxygen consumption	128		129		190		155	
Normality of $Na_2S_2O_3$	—		—		0.0098		0.0095	

[CuCl]	4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}	
[PhSH]	0.0559		0.0861		0.133		0.216	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0	0	0	0	0.25	0.02	0	0
30	0.15	0.01	0.85	0.06	2.60	0.18	1.95	0.14
45	0.85	0.06						
60	1.65	0.12	2.05	0.14	5.85	0.41	4.10	0.43
75	2.95	0.21						
90	4.10	0.29	5.50	0.39	9.60	0.67	10.20	0.72
105	5.15	0.36						
120	6.30	0.44	8.40	0.59	13.20	0.91	14.10	0.99
150	8.65	0.61	11.35	0.80	16.70	1.16	18.30	1.28
180	10.75	0.75	14.20	1.00	20.10	1.40	21.55	1.51
210	12.70	0.89	16.65	1.17	23.65	1.65	25.75	1.81
240	14.15	1.06	19.50	1.37	26.60	1.86	30.00	2.11
300	17.90	1.26	24.40	1.72	32.80	2.29	38.00	2.67
360	20.55	1.45	29.55	2.08	38.65	2.70	45.15	3.17
480	24.90	1.75	37.45	2.63	49.35	3.44	60.50	4.25
600	27.05	1.90	42.85	3.01	57.55	4.01		
750							87.60	6.15
900	27.60	1.94	41.35	2.91	69.75	4.86	99.45	6.98
1020	27.85	1.96						
1200			45.00	3.17	72.90	5.08		
1440	29.45	2.07	45.35	3.19			113.20	7.94
1500					73.55	5.13		
1680			45.45	3.20	73.55	5.13		
1800			46.75	3.29			114.35	8.03
2100							114.80	8.06
2400							116.65	8.19
V_{acid}	0.50		0.50		0.50		0.50	
V_{aliq}	1.00		1.00		1.00		1.00	
V_{titre}	2.55		3.95		5.95		9.10	
% PhSOSPh	48		48		47		46	
$-\dfrac{d[O_2]}{dt} \times 10^4$	0.52		0.64		0.83		0.94	
% oxygen consumption	148		153		154		151	
Normality of $Na_2S_2O_3$	0.0095		0.0095		0.0095		0.0098	

[CuCl]	4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}	
[PhSH]	0.268		0.416		0.724		1.409	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0.30	0.10	0.65	0.25	0.90	0.35	1.35	0.55
30	0.55	0.20	1.15	0.45	1.30	0.52	1.75	0.71
60	1.55	0.65	2.00	0.80	2.20	0.90	2.75	1.10
90	2.40	0.95	2.75	1.15	3.15	1.25	3.75	1.50
120	3.20	1.30	3.65	1.50	4.10	1.65	4.75	1.90
150	4.00	1.60	4.45	1.80	5.05	2.00	5.75	2.30
180	4.80	1.95	5.30	2.15	6.00	2.40	6.75	2.75
210	5.45	2.20	6.15	2.50	6.90	2.75		
240	6.30	2.55	6.90	2.80	7.85	3.15	8.75	3.55
300	7.80	3.15	8.60	3.50	9.65	3.85	10.75	4.35
360	9.35	3.80	10.20	4.15	11.50	4.60	12.75	5.15
480	12.05	4.90	13.50	5.55	14.70	5.90	16.25	6.55
600	14.75	6.00	16.70	6.85	18.35	7.35	20.25	8.20
840	19.25	7.80						
900			23.85	9.75	26.80	10.75	29.65	12.00
1200	23.90	9.70	30.55	12.50	33.45	13.40	39.10	15.80
1500	24.55	9.95	35.45	14.50	43.10	17.25	48.80	19.70
1800	25.00	10.15	36.70	15.00	50.20	20.10	57.60	23.25
1950			36.80	15.05				
2100	25.00	10.15	36.80	15.05	56.70	22.75	62.05	25.05
2400					60.00	24.05	70.55	28.50
2700					60.95	24.45		
3000					61.00	24.45	86.40	34.90
3600							99.20	40.05
4200							101.85	41.15
4500							101.85	41.15
V_{acid}	0.50		0.50		0.50		0.50	
V_{aliq}	1.00		0.50		0.52		0.50	
V_{titre}	9.80		7.70		10.00		10.85	
% PhSOSPh	43		39		32		20	
$-\frac{d[O_2]}{dt} \times 10^4$	1.07		1.13		1.26		1.35	
% oxygen consumption	151		145		135		118	
Normality of $Na_2S_2O_3$	0.0104		0.0093		0.0103		0.0103	

	[CuCl]	4.04×10^{-5}		4.04×10^{-5}	
	[PhSH]	2.263		4.522	
Time		D	M	D	M
0		0	0	0	0
5		1.40	0.55	1.70	0.70
30		1.95	0.80	2.65	1.05
60		2.95	1.20	3.70	1.50
90		3.90	1.60	4.75	1.90
120		4.90	2.00	5.75	2.30
150		5.85	2.40	6.70	2.70
180		6.80	2.80	7.60	3.05
240		8.75	3.60	9.35	3.75
300		10.75	4.40	11.15	4.45
360		12.70	5.20	12.65	5.05
480		16.65	6.80	16.25	6.50
600		20.05	8.20	19.80	7.90
900		30.30	12.40	28.55	11.40
1200		40.00	16.35	37.75	15.10
1500		50.15	20.50	46.60	18.60
1800		59.35	24.30	55.30	22.10
2400		77.55	31.75	72.25	28.85
3000		96.35	39.40	88.85	35.50
3600		114.55	46.85	106.35	42.50
5400		157.00	64.25	158.30	63.20
6000		158.80	64.95	175.70	70.21
6300		158.80	64.95		
9000				257.50	102.90
11400				296.00	118.25
12700				296.20	118.35
V_{acid}		0.50		0.50	
V_{aliq}		0.51		1.03	
V_{titre}		11.05		12.60	
% PhSOSPh		12		4	
$-\dfrac{d[O_2]}{dt} \times 10^4$		1.33		1.32	
% oxygen consumption		115		5	
Normality of $Na_2S_2O_3$		0.0093		0.0092	

A.1.3.

Reaction temperature	10 °C		40 °C	
[CuCl]	4.04×10^{-5}		4.04×10^{-5}	
[PhSH]	0.452		0.458	
Time	D	M	D	M
0	0	0	0	0
5	0	0	0.20	0.10
30	0.05	0	1.00	0.40
60	1.00	0.45	1.90	0.75
90	1.75	0.75	3.00	1.15
120	2.35	1.00	3.75	1.45
150	3.15	1.35	4.15	1.60
180	3.95	1.70	5.30	2.05
240	5.55	2.40	7.35	2.85
300	7.00	3.00	9.00	3.50
360	8.20	3.50	10.40	4.05
480	10.90	4.65	13.25	5.75
600	13.45	5.75	17.15	6.65
750	16.80	7.20	20.40	7.90
900	19.85	8.50	23.25	9.00
1200	25.85	11.10	29.70	11.50
1500	31.55	13.50	31.70	12.30
1800	36.05	15.45	33.20	12.85
2100	40.80	17.50	33.15	12.85
2250			33.15	12.85
2400	43.55	18.65		
2700	44.55	19.10		
2850	44.55	19.10		
V_{acid}	0.50		0.50	
V_{aliq}	0.50		1.00	
V_{titre}	11.65		3.45	
% PhSOSPh	59		8	
$-\dfrac{d[O_2]}{dt} \times 10^4$	1.07		1.11	
% oxygen consumption	170		112	
Normality of $Na_2S_2O_3$	0.0098		0.0098	

A.1.4.

[CuCl]	4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}	
[PhSH]	0.457		0.448		0.460		0.452	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0.45	0.20	0.20	0.10	0.45	0.20	0.45	0.20
30	1.15	0.45	0.90	0.35	1.20	0.50	1.10	0.45
60	2.00	0.80	1.05	0.40	1.85	0.75	2.05	0.85
90	2.85	1.15	1.60	0.65	2.70	1.10	2.95	1.20
120	3.65	1.50	2.35	0.95	3.55	1.40	3.80	1.55
150	4.50	1.80	3.15	1.25	4.35	1.75	4.65	1.90
180	5.30	2.15	4.15	1.65	5.20	2.10	5.45	2.20
240	6.95	2.80	6.00	2.40	6.90	2.75	7.15	2.90
300	8.60	3.50	7.55	3.05	8.60	3.45	8.75	3.55
360	10.15	4.10	9.40	3.80	10.30	4.15	10.25	4.15
480	13.35	5.40	12.70	5.10	12.90	5.15	12.90	5.20
600	16.55	6.70	15.95	6.40	16.20	6.50	15.85	6.40
750	20.35	8.25	19.90	8.00	19.95	8.00	19.55	7.90
900	24.10	9.75	23.65	9.55	23.35	9.35	22.40	9.05
1200	29.70	12.05	29.50	11.90	30.60	12.25	28.10	11.35
1500	35.85	14.55	34.75	14.00	36.35	14.55	32.95	13.35
1800	39.80	16.15	37.90	15.25	39.45	15.50	35.50	14.35
2100	40.85	16.55	38.15	15.35	40.65	16.30	36.95	14.95
2250	40.95	16.60	38.20	15.40			36.85	14.90
2400			38.40	15.45	40.75	16.30		
2700			38.70	15.60				
2850			38.70	15.60				

V_{acid}	0.50	0.50	0.50	0.50
V_{aliq}	0.50	0.50	0.50	0.50
V_{titre}	8.35	7.00	7.80	6.35
% PhSOSPh	41	35	37	31
$-\dfrac{d[O_2]}{dt} \times 10^4$	1.13	1.18	1.13	1.16
% oxygen consumption	145	138	142	132
Normality of $Na_2S_2O_3$	0.0095	0.0105	0.0095	0.0102

	4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}		4.04×10^{-5}	
[CuCl]								
[PhSH]	0.462		0.477		0.458		0.441	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
5	0.10	0.05	0.15	0.05	0.50	0.20	0.25	0.10
30	1.25	0.50	0.85	0.35	1.25	0.50	1.20	0.50
60	1.90	0.75	1.50	0.65	1.95	0.80	2.00	0.80
90	2.30	0.95	2.25	0.90	2.70	1.10	2.90	1.15
120	3.10	1.25	3.05	1.25	3.50	1.45	3.80	1.55
150	3.95	1.60	3.90	1.60	4.30	1.75	4.70	1.90
180	4.85	1.95	4.70	1.95	5.15	2.10	5.50	2.20
240	6.50	2.65	6.35	2.60	6.75	2.75	7.25	2.90
300	8.20	3.30	7.90	3.25	8.40	3.45	9.00	3.60
360	9.85	4.00	9.40	3.85	9.95	4.05	10.70	4.30
480	12.60	5.10	12.65	5.20	12.55	5.10	.3175	5.55
600	15.80	6.40	15.70	6.45	15.60	6.35	17.00	6.85
750	19.05	7.70	19.55	8.05	19.45	7.95	21.15	8.50
900	22.90	9.25	23.35	9.60	23.00	9.40	24.70	9.95
1200	29.60	11.95	28.90	11.85	29.30	11.95	31.95	12.85
1500	35.55	14.35	35.15	14.45	35.65	14.55	37.65	15.15
1800	39.90	16.10	39.65	16.30	39.45	16.10	39.90	16.05
2100	41.10	16.60	41.15	16.90	40.70	16.60	40.20	16.15
2400	41.60	16.80	41.45	17.05	40.70	16.60	40.30	16.20
2700	40.90	16.55	41.40	17.00				
2850	40.90	16.55						
V_{acid}	0.50		0.50		0.50		0.50	
V_{aliq}	0.495		0.50		0.50		0.50	
V_{titre}	8.10		7.85		7.80		7.95	
% PhSOSPh	39		40		39		43	
$-\dfrac{d[O_2]}{dt} \times 10^4$	1.14		1.11		1.11		1.17	
% oxygen consumption	143		143		145		147	
Normality of $Na_2S_2O_3$	0.0095		0.0103		0.0101		0.0105	

Time	[CuCl] 4.04 × 10⁻⁵ [PhSH] 0.458 D	M	[CuCl] 4.04 × 10⁻⁵ [PhSH] 0.470 D	M	[CuCl] 4.04 × 10⁻⁵ [PhSH] 0.455 D	M	[CuCl] 4.04 × 10⁻⁵ [PhSH] 0.458 D	M
0	0	0	0	0	0	0	0	0
5	1.00	0.40	0.05	0	0.25	0.10	0.20	0.10
30	1.95	0.80	0.85	0.35	0.95	0.40	0.90	0.35
60	2.60	1.05	1.45	0.60	1.65	0.65	1.70	0.70
90	3.45	1.40	2.05	0.80	2.45	1.00	2.45	1.00
120	4.20	1.70	2.65	1.05	3.25	1.30	3.30	1.35
150	5.00	2.05	3.25	1.30	4.05	1.65	4.05	1.65
180	5.85	2.40	3.85	1.55	5.05	2.05	4.85	2.00
240	7.50	3.05	5.05	2.05	6.20	2.50	6.40	2.60
300	9.05	3.65	6.25	2.50	7.90	3.20	7.90	3.25
360	10.70	4.35	7.45	3.00	9.60	3.90	9.50	3.90
480	13.30	5.40	9.80	3.95	12.40	5.05	12.05	4.95
600	16.50	6.70	12.15	4.85	15.65	6.35	15.05	6.15
750	20.30	8.25	15.05	6.05	19.20	7.80	18.70	7.65
900	23.35	9.45	17.90	7.20	23.15	9.40	22.25	9.10
1200	30.00	12.20	23.30	9.35	30.25	12.25	28.35	11.60
1500	35.60	14.45	28.35	11.35	35.80	14.50	34.40	14.10
1800	39.60	16.10	32.70	13.10	40.00	16.20	37.10	15.20
2100	41.25	16.75	36.85	14.80	40.65	16.50	38.70	15.85
2250	41.25	16.75						
2400	40.05	16.05	40.05	16.05	40.85	16.55	39.05	16.00
2700			41.00	16.45	40.50	16.40		
2850							39.60	16.20
3000			41.45	16.65			39.60	16.20

V_{acid}	0.50	0.50	0.50	0.50
V_{aliq}	0.50	0.50	0.505	0.50
V_{titre}	7.55	6.55	8.30	7.20
% PhSOSPh	36	34	39	37
$-\dfrac{d[O_2]}{dt} \times 10^4$	1.11	0.81	1.12	1.07
% oxygen consumption	146	141	144	142
Normality of $Na_2S_2O_3$	0.0098	0.0097	0.0095	0.0097

[CuCl]	4.04×10^{-5}		4.04×10^{-5}	
[PhSH]	0.459		0.455	
Time	D	M	D	M
0	0	0	0	0
5	0.70	0.30	0.35	0.15
30	0.95	0.40	1.00	0.40
60	1.75	0.70	1.80	0.75
90	2.65	1.05	2.65	1.05
120	3.45	1.40	3.30	1.35
150	4.30	1.75	3.75	1.50
180	5.15	2.10	4.60	1.85
240	6.85	2.80	6.30	2.55
300	7.85	3.20	7.90	3.20
360	9.70	3.95	9.60	3.90
480	12.25	5.00	12.10	4.90
600	16.65	6.80	15.30	6.20
750	20.40	8.30	19.30	7.80
900	24.60	10.05	23.05	9.30
1200	31.80	12.95	30.10	12.15
1500	37.25	15.20	35.85	14.45
1800	39.95	16.30	39.60	16.00
2100	40.05	16.35	40.20	16.25
2400	40.25	16.40	40.20	16.25
V_{acid}	0.50		0.50	
V_{aliq}	0.50		0.51	
V_{titre}	7.60		8.40	
% PhSOSPh	38		39	
$-\frac{d[O_2]}{dt} \times 10^4$	1.14		1.14	
% oxygen consumption	142		142	
Normality of $Na_2S_2O_3$	0.0101		0.0095	

A.1.5.

$$[CuCl] = 4.04 \times 10^{-5}$$

$$[PhSH] = 0.449$$

Time	D	M	Time	D	M
0	0	0	720(4)	17.30	7.00
60	1.45	0.60	750	17.80	7.20
90	2.25	0.90	780	18.45	7.50
120	3.00	1.20	840	18.95	7.70
150	3.85	1.55	900(5)	20.00	8.10
210	5.30	2.15	930	20.50	8.30
240	6.05	2.45	960	21.15	8.60
270(1)	6.90	2.80	990	21.90	8.90
300	7.70	3.15	1020	22.50	9.10
330	8.50	3.45	1080	23.90	9.70
360	9.20	3.75	1140(6)	25.00	10.15
420(2)	10.75	4.35	1200	26.20	10.65
450	11.50	4.65	1230	27.85	11.30
480	12.20	4.95	1290	28.75	11.65
510	12.90	5.25	1320	29.20	11.85
540	13.65	5.55	1350	29.60	12.00
570(3)	14.40	5.85	1380	30.10	12.20
600	15.10	6.20	1500	31.55	12.80
630	15.75	6.40	1680	32.65	13.25
660	16.30	6.60	1800	32.65	13.25
690	16.85	6.85			

Injection	(1)	(2)	(3)
Benzene sulphonic acid added (moles)	1.3×10^{-5}	1.3×10^{-4}	2.6×10^{-3}

Injection	(4)	(5)	(6)
Benzene sulphonic acid added (moles)	2.6×10^{-3}	5.2×10^{-3}	5.0×10^{-3}

A. 2. a.

Standard (moles of PhSH)	0.1125		0.1125		0.1125		0.0117	
	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.
	0	-96	0	-102	0	-102	0	50
	2.0	-88	2.50	-106	5.00	-72	7.00	64
	4.0	-90	5.00	-98	8.10	-28	8.50	102
	6.0	-56	7.50	-66	9.10	-8	9.00	108
	8.0	-28	9.00	-28	9.60	14	9.50	116
	9.0	-12	10.00	36	10.00	44	9.90	132
	10.00	6	10.50	22	10.20	52	10.20	190
	10.55	78	10.70	312	10.30	430	10.40	234
	10.80	240	10.80	584	10.35	522	10.50	524
	11.00	550	10.90	610	10.45	596	10.60	594
	11.10	624	11.10	628	10.75	638	10.80	620
	11.30	646	11.45	640	11.25	652	11.20	660
	11.60	654	12.00	652			11.80	680

End point (ml. of $AgNO_3$)	11.00	10.75	10.30	10.50
Theoretical titration (ml. of $AgNO_3$)	11.25	11.25	11.25	11.70
of theoretical titration	98	96	92	90

Standard (moles of PhSH)	0.0117		0.0115		0.0114		0.0114	
	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.
	0	50	0	34	0	-10	0	4
	9.00	110	9.85	120	2.00	12	2.00	12
	9.80	138	10.20	150	4.00	16	4.00	22
	10.30	180	10.30	160	6.00	40	8.00	54
	10.45	200	10.40	174	8.00	56	9.00	66
	10.55	264	10.50	200	9.00	84	9.50	72
	10.60	498	10.60	410	9.50	92	10.00	90
	10.65	536	10.70	530	10.00	138	10.25	104
	10.70	574	10.80	592	10.30	326	10.40	122
	10.80	608	11.00	630	10.50	524	10.60	134
	11.00	636			10.80	570	10.82	174
					11.20	582	10.90	226
							11.00	392
							11.10	494
							11.60	568
End point (ml. of $AgNO_3$)	10.60		10.60		10.30		11.00	
Theoretical titration (ml. of $AgNO_3$)	11.70		11.50		11.40		11.40	
of theoretical titration	91		92		90		97	

Standard (moles of PhSH)	0.0057		0.0114[*]		0.0114[**]	
	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.	V_{AgNO_3}	Emf.
	0	12	0	-20	0	-40
	1.00	10	2.00	-10	9.00	26
	2.00	8	4.00	14	10.00	58
	3.00	22	6.00	12	10.35	88
	4.00	42	8.00	24	10.50	110
	4.50	52	9.00	30	10.70	416
	5.10	102	9.50	44	10.90	534
	5.20	108	10.00	66	10.90	
	5.30	132	10.25	88		
	5.40	176	10.40	124		
	5.50	518	10.50	382		
	5.60	562	10.60	492		
	5.70	582	10.80	534		
	5.80	594				
End point (ml. of AgNO_3)	5.50		10.55		10.70	
Theoretical titration (ml. of AgNO_3)	5.70		11.40		11.40	
% of theoretical titration	97		93		94	

[*]   0.50 ml. of CuCl solution (2.02×10^{-4} moles/litre) also added.

[**]   0.10 ml. of CuCl solution (2.02×10^{-4} moles/litre) also added.

b.

Volume of pyridine (ml.)	5.0		15.0	
[CuCl]	1.01×10^{-5}		6.67×10^{-6}	
[PhSH]	0.458		0.247	
Time	D*	M	D	M
0	0	0	0	0
120	2.25	0.90	2.40	0.30
240	3.20	1.30	4.40	0.60
360(5)			6.05	0.80
480	6.70	2.75		
570(1)	7.75	3.15		
870(6)			11.90	1.65
930	12.45	5.15		
1320(2)	17.25	7.15		
1530(7)			25.30	3.60
1800	22.70	9.55		
2040(3)	25.55	10.85		
2055(8)			30.20	4.35
2430			40.80	6.05
2700	31.95	13.95		
2940(4)	35.20	15.45		
3000(10)			49.30	7.50
3300	37.70	17.05		
3600	39.75	18.40		
4200	42.05	19.15		
4500	42.05	19.35	59.30	9.40

Sample removed for thiophenol titration	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
Volume of sample (ml.)	0.19	0.24	0.38	0.60	0.51	0.53	0.70	0.73	0.77	0.97
End point (ml. of 0.01 N AgNO$_3$)	8.00	6.10	5.10	1.80	11.40	10.20	10.15	n.d.	6.90	4.00

* D was corrected to allow for the volume of the sample taken out of the reaction system.

(n.d. = not determined.)

C.

Volume of pyridine (ml.)	7.50		7.50	
[CuCl]	2.02×10^{-5}		2.02×10^{-5}	
[PhSH]	0.456		0.458	
Time	D	M	D	M
0	0	0	0	0
120	4.65	1.25	3.30	0.90
240	8.10	2.20	6.90	1.85
300	10.70	2.90	8.85	2.35
350(1)	12.70	3.45		
450(4)			13.55	3.50
600	21.70	6.00		
750(2)	27.65	8.70	21.25	5.70
900	33.25	9.40	25.55	6.90
1080(5)			30.10	8.40
1200	43.85	12.65	33.20	9.30
1350(3)	48.60	13.95		
1470(6)			40.00	11.30
1500	53.00	15.40		
1620	56.05	16.40	43.45	12.40
1920			49.20	14.20
1950	59.35	17.47		
2250	60.05	17.75		
2700	60.20	17.80	55.10	16.73

Sample removed for thiophenol titration.	(1)	(2)	(3)	(4)	(5)	(6)	(7)
Volume of sample (ml.)	0.26	0.43	0.59	0.245	0.40	0.64	0.815
End point (ml. of 0.01 N $AgNO_3$)	12.80	10.20	3.45	9.85	8.10	6.10	3.90

A.3.

[CuCl]	4.04×10^{-1}	
[Aniline]	0.214	
Time	D	M

Time	D	M
0	0	0
30	0.05	0
60	0.10	0.05
120	0.15	0.05
180	0.40	0.15
240	0.60	0.25
360	1.15	0.45
480	1.65	0.65
600	2.45	1.00
720	3.00	1.20
840	3.70	1.50
960	4.35	1.75
1200	5.65	2.30
1500	7.25	2.95
1800	8.70	3.55
2400	11.50	4.70
3900	17.00	6.95
5400	34.70	8.50
9000	40.70	10.95
12000	44.60	12.55
14400	48.15	13.95
17700	53.80	16.25

A.4.

[CuCl]	8.08 × 10⁻²		4.04 × 10⁻²		2.02 × 10⁻²		1.01 × 10⁻²	
[Dithiol]								
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
10	0	0	0.30	0.10	0.15	0.05		
20	0.65	0.25	1.10	0.45	0.30	0.10		
30	1.40	0.55	1.80	0.75	0.80	0.35	0.20	0.10
40			2.35	0.95	0.95	0.40		
45	2.65	1.10						
50			2.80	1.15	1.20	0.50		
60	3.60	1.45	3.15	1.30	1.35	0.55	0.55	0.20
75	4.20	1.70	3.65	1.50	1.70	0.70		
90	4.80	1.95	4.15	1.70	1.85	0.75	0.80	0.35
120	5.80	2.35	5.10	2.10	2.45	1.00	1.00	0.40
150	6.65	2.70	5.70	2.35	3.00	1.20		
180	7.35	3.00	6.45	2.65	3.40	1.40	1.50	0.60
240	8.55	3.50	7.60	3.10	4.35	1.75	2.05	0.85
360	10.60	4.35	9.15	3.75	5.85	2.40		
450							2.85	1.15
480	12.30	5.00	10.20	4.15	6.95	2.85		
600	13.45	5.50	11.70	4.80	7.75	3.15	3.70	1.50
900	14.65	6.00	13.85	5.65	9.90	4.05	4.75	1.95
1200	25.20	10.30	16.00	6.55	11.90	4.85	5.65	2.30
1800	26.60	10.85	18.60	7.60	14.30	5.80	7.35	3.00
2400	27.50	11.25	20.10	8.20			9.40	3.85
3000			21.15	8.65	18.40	7.50	10.70	4.35
3300	28.05	11.45						
4200			27.60	11.25			13.20	5.35
4500	28.15	11.50						
4800			27.95	11.40	21.55	8.75	14.20	5.80
5400			27.95	11.40			15.10	6.15
6600					23.40	9.50	16.60	6.75
7800							17.70	7.20
8400							18.70	7.60
9000					27.50	11.20	18.70	7.60
9300							18.95	7.70
9750					28.70	11.70		

$-\dfrac{d[O_2]}{dt} \times 10^4$	3.16	2.72	0.82	0.36
% oxygen consumption	97	100	99	65*

* Reaction time = $2\frac{1}{2}$ hours, i.e. not taken to completion.

A.5.

Type of stirring	Magnetic		No stirring		Vibromix		Vibromix	
[CuCl]	1.01×10^{-1}		1.01×10^{-1}		1.01×10^{-1}		2.7×10^{-2}	
[P.P.D.]	0.21		0.21		0.20		0.156	
Time	D	M	D	M	D	M	D	M
0	0	0	0	0	0	0	0	0
20					1.30	0.55		
30	0.75	0.30						
40					4.40	1.80		
45	1.50	0.60						
60	2.45	1.00	0.80	0.35	6.80	2.75	1.15	0.25
75	3.30	1.35						
80					8.45	3.45		
90	4.10	1.70						
100					9.80	4.00		
120	5.25	2.15	0.80	0.35	10.80	4.40	1.45	0.30
150	6.10	2.50			12.20	4.95	1.95	0.40
180	6.85	2.80	1.40	0.55	13.25	5.40	2.40	0.50
240	8.05	3.30	2.05	0.85	14.80	6.05	3.50	0.70
360	9.55	3.95			16.70	6.80	5.90	1.20
450			3.25	1.35				
480	10.55	4.35			18.10	7.40	8.35	1.70
600	10.75	4.40	4.25	1.75	19.10	7.80	10.70	2.20
900	11.10	4.55	7.00	2.85	20.70	8.45	15.65	3.20
1200	12.35	5.05	9.55	3.90	21.50	8.75	18.90	3.85
1800	13.95	5.75	11.20	4.60	23.20	9.45	23.15	4.75
3600	16.05	6.60	18.25	7.50			29.60	6.00
4500					25.10	10.25		
4800			20.80	8.55				
6330	17.40	7.15						
6600			23.40	9.60	25.30	10.30		
7200			24.20	9.95				
7800			25.10	10.30				
9600					25.30	10.30		
$-\dfrac{d[O_2]}{dt} \times 10^4$	2.24		0.27		5.3		1.28	
% oxygen consumption	35		50		51		67	

A.6.a.

[CuCl]	4.04×10^{-2}
[A.T.P.]	0.100

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	1950	extra catalyst	
10	0.70	0.30		injected.	
20	1.65	0.70	1995	17.55	7.20
30	2.70	1.10	2010	18.35	7.50
40	3.75	1.55	2025	19.25	7.90
50	4.65	1.90	2040	20.05	8.20
60	5.35	2.20	2055	20.90	8.55
80	6.70	2.75	2070	21.65	8.85
90	7.15	2.95	2100	22.80	9.75
120	8.35	3.40	2160	24.60	10.05
180	9.40	3.85	2220	26.85	10.60
240	9.95	4.05	2400	27.65	11.30
360	10.70	4.40	2700	29.55	12.10
600	11.65	4.75	2925	31.25	12.80
900	12.45	5.10	3900	33.95	13.90
1200	13.65	5.60	4800	37.20	15.20
1800	14.55	5.95	6000	40.60	16.60
			7200	43.20	17.70
			10500	47.70	19.50
			13200	49.35	20.20
			16500	52.50	21.50
			Final reading	63.50	26.00

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 4.06 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 2.31 \times 10^{-4}$$

$$\left(\begin{array}{c}\text{oxygen}\\ \text{consumption}\end{array}\right)_{Thiol} = 88\text{-}90\ \% \qquad \left(\begin{array}{c}\text{oxygen}\\ \text{consumption}\end{array}\right)_{Amine} = 216\ \%$$

$$\left(\begin{array}{c}\text{oxygen}\\ \text{consumption}\end{array}\right)_{Total} = 173\ \%$$

Time of colour change = 75 secs.

[CuCl] 1.01×10^{-2}

[A.T.P.]   0.100

THIOL REACTION				AMINE REACTION		
Time	D	M		Time	D	M
0	0	0		4620	extra catalyst	
15	0.35	0.15			injected.	
30	1.60	0.65		4680	16.00	6.35
45	2.55	1.00		4695	16.90	7.05
60	3.50	1.40		4710	17.75	7.05
75	4.45	1.75		4725	18.50	7.35
90	5.45	2.15		4740	20.70	8.25
120	7.40	2.95		4770	20.70	8.25
150	9.30	3.70		4800	21.85	8.70
195	10.85	4.30		4830	23.05	9.20
240	11.25	4.50		4860	24.05	9.60
300	11.40	4.55		4920	24.65	9.80
360	11.50	4.60		4980	25.15	10.00
480	11.75	4.70		5250	27.30	10.90
600	11.90	4.75		5400	28.10	11.20
900	12.30	4.90		5700	29.20	11.65
1200	12.45	4.95		6300	30.55	12.15
1500	12.55	5.00		9600	36.25	14.45
2700	13.00	5.20		Final reading	66.45	26.45
3600	13.10	5.25				

$$\left(-\frac{d[O_2]}{dt^2}\right)_{Thiol} = 2.60 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt^2}\right)_{Thiol} = 2.21 \times 10^{-4}$$

$$\left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Thiol} = 93\% \qquad \left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Amine} = 219\%$$

$$\left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Total} = 176\%$$

Time of colour change = 210 secs.

[CuCl] 1.01×10^{-3}

[A.T.P.]   0.100

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	2200	extra catalyst	
15	0.10	0.05		injected.	
30	0.90	0.35	2235	16.85	6.75
45	1.45	0.60	2265	18.80	7.55
60	2.05	0.80	2280	19.70	7.90
80	2.90	1.15	2300	20.85	8.35
120	4.45	1.80	2320	21.90	8.75
150	5.70	2.30	2340	22.85	9.15
180	6.90	2.75	2370	24.20	9.70
240	9.10	3.65	2400	25.55	10.25
300	11.10	4.45	2460	28.45	11.40
360	12.80	5.15	2520	30.15	12.10
390	13.25	5.30	2700	32.30	12.95
420	13.45	5.40	3150	35.15	14.10
480	13.70	5.50	3600	36.80	14.75
600	13.95	5.60	4500	38.60	15.45
900	14.25	5.70	7080	43.40	17.40
1200	14.30	5.75	16800	48.30	19.35
1800	14.40	5.80	Final reading	69.25	27.75

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 1.98 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 2.40 \times 10^{-4}$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Thiol} = 107\,\% \qquad \left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Amine} = 224\,\%$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Total} = 186\,\%$$

Time of colour change = 370 - 405 secs.

| | [CuCl] | 3.03×10^{-4} | | |
| | [A.T.P.] | 0.100 | | |

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	5760	extra catalyst	
15	0.40	0.15		injected.	
30	0.80	0.30	5790	15.60	6.20
45	1.20	0.50	5805	16.80	6.70
60	1.65	0.65	5820	17.90	7.10
75	2.05	0.80	5835	18.95	7.55
90	2.45	0.95	5850	19.90	7.90
120	3.25	1.30	5880	21.55	8.55
150	3.95	1.55	5940	25.55	10.15
180	4.80	1.90	6000	28.05	11.15
240	6.30	2.50	6180	31.80	12.65
300	7.60	3.00	6360	32.45	12.90
480	11.45	4.55	6600	34.45	13.70
600	13.20	5.25	7800	36.25	14.40
660	13.65	5.45	13500	42.20	16.80
750	13.85	5.50	21600	49.10	19.55
900	14.05	5.60	Final reading	75.60	30.05
1200	14.25	5.65			
3600	14.80	5.90			

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 1.09 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 2.93 \times 10^{-4}$$

$$\left(\begin{matrix} oxygen \\ consumption \end{matrix}\right)_{Thiol} = 110\% \qquad \left(\begin{matrix} oxygen \\ consumption \end{matrix}\right)_{Amine} = 224\%$$

$$\left(\begin{matrix} oxygen \\ consumption \end{matrix}\right)_{Total} = 201\%$$

Time of colour change = 645 - 700 secs.

[CuCl]	1.01×10^{-4}
[A.T.P.]	0.101

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	2800	extra catalyst	
30	0	0		injected.	
60	1.00	0.40	2835	21.00	8.55
90	1.70	0.70	2850	22.60	9.20
120	2.30	0.95	2880	25.20	10.25
150	2.85	1.15	2895	26.30	10.70
180	3.30	1.35	2910	27.40	11.15
240	5.30	2.15	2925	28.90	11.75
360	7.75	3.15	2940	30.10	12.25
480	10.45	4.25	2970	32.25	13.10
600	12.80	5.20	3000	34.10	13.88
750	13.60	5.55	3150	38.50	15.65
900	15.45	6.20	3600	41.55	16.90
1200	17.00	6.90	5400	45.65	18.55
1350	17.00	6.90	9000	50.75	20.65
1500	17.30	7.05	18900	59.75	24.30
1800	17.50	7.10	Final*	83.45	33.95
2520	17.50	7.10	reading		

* Piston was at the bottom of the gas burette when the final reading was taken.

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 0.92 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 3.50 \times 10^{-4}$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Thiol} = 136\% \qquad \left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Amine} = 270\%$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Total} = 223\%$$

Time of colour change = 1230 - 1320 secs.

[CuCl]　　　　3.03×10^{-5}

[A.T.P.]　　　　0.102

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	4320	extra catalyst	
20	0.40	0.15		injected.	
40	0.95	0.40	4350	19.25	7.55
60	1.25	0.50	4365	20.40	8.10
80	1.55	0.60	4380	21.15	8.40
100	1.85	0.75	4395	21.95	8.75
120	2.15	0.85	4410	22.85	9.10
150	2.55	1.00	4425	23.60	9.40
180	3.00	1.20	4440	24.40	9.70
240	3.85	1.55	4470	25.80	10.25
300	4.75	1.90	4500	27.10	10.80
480	7.00	2.80	4560	29.55	11.75
600	8.00	3.20	4680	33.10	13.15
900	10.65	4.25	4800	34.60	13.75
1200	13.30	5.30	5100	37.00	14.70
1800	16.30	6.50	6000	41.05	16.35
2700	17.25	6.85	9300	30.30	20.00
3150	17.45	6.95	16500	57.55	22.90
3600	18.00	7.15	22500	59.60	23.70
3900	18.00	7.15	Final reading	73.95	29.40

$$\left(-\frac{d[O_2]}{dt^2} \right)_{Thiol} = 0.59 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt^2} \right)_{Amine} = 2.15 \times 10^{-4}$$

$$\left(\begin{array}{c} \text{oxygen} \\ \text{consumption} \end{array} \right)_{Thiol} = 141\% \qquad \left(\begin{array}{c} \text{oxygen} \\ \text{consumption} \end{array} \right)_{Amine} = 223\%$$

$$\left(\begin{array}{c} \text{oxygen} \\ \text{consumption} \end{array} \right)_{Total} = 193\%$$

Time of colour change　=　3600 - 4200 secs.

[CuCl]	1.01 x 10^{-5}			
[A.T.P.]	0.102			

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	6985	extra catalyst injected.	
20	0.45	0.40			
40	1.00	0.40	7245	21.25	8.60
60	1.25	0.50	7260	21.75	8.80
90	1.75	0.70	7275	22.30	9.00
120	2.15	0.85	7290	22.85	9.25
150	2.50	1.00	7320	23.70	9.60
180	2.90	1.15	7350	24.30	9.80
240	3.70	1.50	7380	24.75	10.00
360	5.10	2.05	7440	25.80	10.45
480	6.50	2.65	7560	26.80	10.85
600	7.75	3.15	7800	28.05	11.35
780	9.10	3.70	8400	29.60	11.95
900	10.05	4.05	10200	31.95	12.90
1200	11.75	4.75	13500	37.35	15.10
1800	14.40	5.80	20100	43.05	17.40
2400	16.10	6.50	24900	46.10	18.65
3000	16.60	6.70	Final reading	58.30	23.55
3600	16.80	6.80			
6600	17.85	7.20			

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 0.52 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 1.70 \times 10^{-4}$$

$$\left(\begin{array}{c}oxygen \\ consumption\end{array}\right)_{Thiol} = 140\% \qquad \left(\begin{array}{c}oxygen \\ consumption\end{array}\right)_{Amine} = 165\%$$

$$\left(\begin{array}{c}oxygen \\ consumption\end{array}\right)_{Total} = 155\%$$

Time of colour change = 3600 - 5400 secs.

b.

$$[CuCl] \qquad 1.01 \times 10^{-3}$$

$$[A.T.P.] \qquad 0.100$$

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	2160	extra catalyst	
15	0.55	0.20		injected.	
30	1.50	0.60	2340	20.20	8.25
45	2.75	1.10	2400	21.60	8.80
60	3.90	1.60	2490	22.15	9.05
75	4.95	2.00	2580	23.40	9.55
90	6.15	2.50	2700	24.20	10.00
120	8.15	3.35	2850	25.20	10.30
150	10.10	4.10	3000	26.10	10.65
180	11.90	4.85	3600	28.60	11.65
240	14.90	6.10	4500	31.80	13.00
270	15.50	6.30	5400	34.40	14.05
300	15.60	6.35	7200	39.35	16.05
360	15.55	6.35	10800	46.70	19.05
480	15.30	6.25			
600	15.00	6.10			
900	14.40	5.70			
1800	14.40	5.70			

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 3.10 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 1.40 \times 10^{-4}$$

$$\left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Thiol} = 126\% \qquad \left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Amine} = 138\%$$

$$\left(\begin{array}{c}oxygen\\consumption\end{array}\right)_{Total} = 126\%$$

Time of colour change = 260 - 265 secs.

[CuCl] $\qquad$ 1.01×10^{-3}

[A.T.P.] $\qquad$ 0.100

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	2160	extra catalyst	
15	0	0		injected.	
30	2.50	1.00	2340	26.85	10.20
45	3.30	1.30	2370	27.70	11.15
60	4.20	1.70	2400	28.75	11.50
75	5.50	2.20	2430	29.15	11.65
90	6.45	2.60	2460	29.50	11.80
135	9.70	3.85	2520	29.95	11.96
150	10.60	4.25	2700	30.20	12.05
180	12.30	4.90	300	30.35	12.10
210	13.95	5.50	3600	31.25	12.50
240	15.25	6.10	4200	33.05	13.20
270	16.45	6.55	6300	34.20	13.65
300	16.90	6.75	7500	35.35	14.10
360	17.05	6.80			
480	17.00	6.80			
600	16.90	6.75			
900	16.70	6.65			
1200	16.50	6.60			
1500	16.10	6.45			

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 2.59 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 2.51 \times 10^{-4}$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Thiol} = 135\% \qquad \left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Amine} = 74\%$$

$$\left(\begin{array}{c}\text{oxygen}\\\text{consumption}\end{array}\right)_{Total} = 94\%$$

Time of colour change = 285 - 295 secs.

c.

[CuCl] 1.01×10^{-2}

[A.T.P.] 0.101

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	1080	extra catalyst injected.	
10	0.50	0.20			
20	1.10	0.45	1125	17.50	7.00
30	1.95	0.80	1140	18.00	7.20
40	2.70	1.10	1155	18.95	7.60
50	3.50	1.40	1170	19.60	7.85
60	4.30	1.75	1185	20.40	8.20
75	5.45	2.20	1200	21.05	8.45
90	6.65	2.65	1230	22.45	9.00
120	8.70	3.50	1280(a)	24.05	9.65
150	10.75	4.30	1320	24.55	9.85
180	11.95	4.80	1350	25.00	10.05
240	12.20	4.90	1380	25.80	10.70
300	12.40	5.00	1440	26.65	11.55
450	12.65	5.10	1500	27.10	11.90
600	13.10	5.25	1620(b)	27.75	12.40
900	13.50	5.40			
1500	14.40	5.80			
2100	14.75	5.90			
2700	14.95	6.00			

At (a), half of the reaction mixture was taken from the flask
and added to a large excess of water (sample 1).

At (b), a large excess of water was added to the remaining
reaction mixture (sample 2).

$$\left(-\frac{d[O_2]}{dt}\right)_{Thiol} = 2.87 \times 10^{-4} \qquad \left(-\frac{d[O_2]}{dt}\right)_{Amine} = 3.15 \times 10^{-4}$$

$$\left(\begin{array}{c}\text{oxygen} \\ \text{consumption}\end{array}\right)_{Thiol} = 97\%$$

Time of colour change = 160 secs.

[CuCl] 1.01×10^{-2}

[A.T.P.]   0.101

THIOL REACTION			AMINE REACTION		
Time	D	M	Time	D	M
0	0	0	1410	extra catalyst	
10	0.95	0.40		injected.	
20	1.70	0.70	1470	19.70	7.85
30	2.40	0.95	1485	20.80	8.30
40	3.15	1.25	1500	21.90	8.75
50	3.85	1.55	1515	22.95	9.15
60	4.50	1.80	1530	23.85	9.50
80	5.95	2.35	1545	24.90	9.95
100	7.35	2.95	1560	25.90	10.35
120	8.65	3.45	1590	27.60	10.95
150	10.75	4.29	1620	29.00	11.55
180	12.75	5.10	1680	31.85	12.70
210	13.15	5.25	1800	35.15	14.05
240	13.40	5.35	1920	37.20	14.85
300	13.65	5.45	2010	38.45	15.35
450	14.10	5.65	2040(a)	38.85	15.50
600	14.10	5.65	2880(b)	44.05	19.65
750	14.35	5.75			
900	14.50	5.80			
1200	15.10	6.05			

Sample 3 was taken at (a) and sample 4 was taken at (b).

$$\left(- \frac{d[O_2]}{dt} \right)_{Thiol} = 3.15 \times 10^{-4} \qquad \left(- \frac{d[O_2]}{dt} \right)_{Amine} = 1.91 \times 10^{-4}$$

$$\left(\begin{array}{c} \text{oxygen} \\ \text{consumption} \end{array} \right)_{Thiol} = 105 \%$$

Time of colour change = 175 secs.

d.

[CuCl]		3.03×10^{-5}
[A.T.P.]		0.099

Time	D	M
0	0	0
15	0.80	0.30
30	1.20	0.50
60	1.65	0.65
90	2.05	0.81
120	2.40	0.95
150	2.65	1.05
180	3.10	1.25
240	3.80	1.50
300	4.50	1.80
360	5.25	2.10
480	6.75	2.70
600	7.70	3.05
750	9.20	3.65
1050	11.85	4.70
1200	12.70	5.05
1500	14.65	5.80
1800	15.55	6.15
2400	16.20	6.45
2640	16.25	6.45

V_{acid}	0.50
V_{aliq}	2.00
V_{titre}	7.00
Normality of $Na_2S_2O_3$.	0.010
% PhSOSPh	21
$\left(-\dfrac{d[O_2]}{dt}\right)_{Thiol} \times 10^4$	0.50
$\left(\begin{array}{c}\text{oxygen}\\ \text{consumption}\end{array}\right)_{Thiol}$	127 %

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A. 7.

Calibration using benzil.

Concentration of solution (C) (grms/litre)	Voltage (mV.)				
	V_1	V_2	V_3	$V_{ave.}$	$\dfrac{V_{ave}}{C}$
20.04	648.9	672.8	645.8	655.8	32.8
10.02	371.2	369.1	362.8	367.7	36.8
5.01	184.8	184.9	-	184.9	37.0
2.50	97.7	106.5	102.6	102.3	40.9

$$(V/C)_{C\ 0} = 40.5$$

$$K = 8510 = \text{Calibration constant.}$$

C	V_1	V_2	V_3	V_{ave}	$\dfrac{V_{ave}}{C}$
11.70	176.0	161.4	167.2	168.2	14.4
7.00	125.4	112.4	112.8	116.9	16.7
4.20	94.5	90.9	-	92.7	22.1
2.50	53.4	55.5	-	54.5	21.8

$$(V/C)_{C\ 0} = 25.0$$

$$\text{Molecular weight} = 340$$

c	V_1	V_2	V_3	V_{ave}	$\dfrac{V_{ave}}{c}$
9.90	259.2	243.5	243.5	247.8	25.1
7.40	178.3	183.6	-	181.0	24.5
5.60	140.1	130.4	127.8	134.0	24.0

$$(V/C)_{C \quad 0} = 22.5$$

$$\text{Molecular weight} = 380$$

c	V_1	V_2	V_3	V_{ave}	$\dfrac{V_{ave}}{c}$
10.4	127.9	127.6	116.0	113.8	10.9
7.3	100.0	92.8	97.2	96.7	13.3
5.1	71.3	69.1	68.2	69.5	13.7
3.57	51.2	49.9	49.9	50.3	14.1

$$(V/C)_{C \quad 0} = 15.9$$

$$\text{Molecular weight} = 540$$

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Calculation of the Rate of Oxygen Absorption and the Percentage Oxygen Consumption.

(a) Rate of Oxygen Absorption.

The partial pressure of oxygen (P_o) in the closed system is given by:-

$$P_o = P_{atmos} - P_{py} + P_{piston} \qquad (A.B.1)$$

where P_{atmos} = atmospheric pressure (mm.Hg).

P_{py} = vapour pressure of pyridine (mm.Hg).

P_{piston} = pressure exerted by the piston and the mercury seal (mm.Hg).

P_{py} at 25°C = 20 mm.Hg (see reference 68).

The frictional forces between the piston and the walls of the gas burette have been neglected. These forces were assumed to be negligible as compared to the other terms in equation A.B.1.

P_{piston} is given by:-

$$P_{piston} = \frac{\text{Total weight of the piston and the mercury seal } (=9.9 \text{ grms})}{\text{C.S.A of gas burette } (= 0.4^2 \text{ x } \pi) \text{ x } \rho_{Hg}}$$
$$(A.B.2)$$

where C.S.A = cross sectional area

ρ_{Hg} = density of mercury.

Thus the moles of oxygen consumed/litre at S.T.P. (M) can be given by:-

$$M = D \text{ x C.S.A. x } \frac{1000}{V_{py}} \text{ x } \frac{273}{273 + T} \text{ x } \frac{P_o}{760} \text{ x } \frac{1}{22,390} \qquad (A.B.3)$$
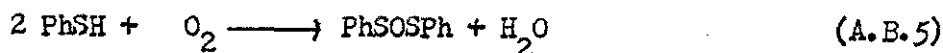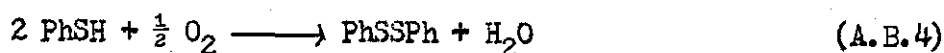
where V_{py} = volume of pyridine (solvent) in the reaction mixture.

T = reaction temperature (°C).

22,390 cc = gram molar volume of oxygen.

(b) Percentage Oxygen Consumption.

Reactions occurring in the thiophenol oxidation are:-

$$2 \text{ PhSH} + \tfrac{1}{2} O_2 \longrightarrow \text{PhSSPh} + H_2O \qquad\qquad (A.B.4)$$

$$2 \text{ PhSH} + \phantom{\tfrac{1}{2}} O_2 \longrightarrow \text{PhSOSPh} + H_2O \qquad\qquad (A.B.5)$$

The percentage oxygen consumption is given by:-

$$\% \text{ oxygen consumption} = \frac{\text{actual moles of oxygen consumed/litre}}{\text{moles of oxygen consumed for the complete oxidation of PhSH to PhSSPh}} \times 100\% \qquad (A.B.6)$$
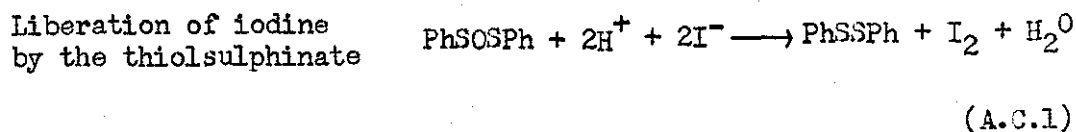
and thus can be expressed by:-

$$\% \text{ oxygen consumption} = \frac{\text{actual moles of oxygen consumed/litre} \times 4 \times 100\%}{\text{initial concentration of thiophenol (moles/litre)}}$$

$$(A.B.7)$$

Calculation of the Percentage
Thiolsulphinate (see section 5.2).

The reactions occurring in the titration are:-

Liberation of iodine
by the thiolsulphinate

$$PhSOSPh + 2H^+ + 2I^- \longrightarrow PhSSPh + I_2 + H_2O$$

(A.C.1)

Titration of Liberated
iodine by $Na_2S_2O_3$

$$I_2 + Na_2S_2O_3 \longrightarrow 2I^- + 2Na^+ + Na_2S_4O_6$$

(A.C.2)
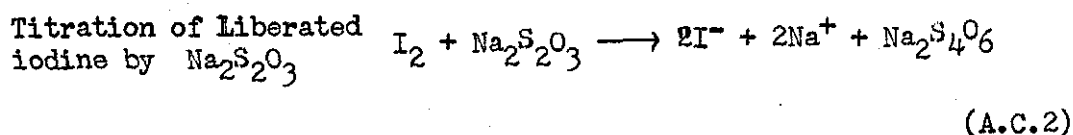
Thus the weight of thiolsulphinate in the reaction mixture

$(W_{thiol.})$ is given by:-

$$W_{thiol} = \frac{\text{Titre of } Na_2S_2O_3 \times \text{Normality of } Na_2S_2O_3 \times \text{molecular weight of PhSOSPh}}{2000} \times \frac{V_r + V_{acid}}{V_{aliq.}}$$
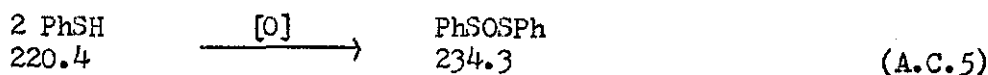
(A.C.3)

where V_r = volume of the reaction mixture (ml.).

V_{acid} and $V_{aliq.}$ were defined in appendix A.

The percentage thiolsulphinate can be expressed as:-

$$\% \, PhSOSPh = \frac{\text{Weight of thiophenol oxidized to PhSOSPh}}{\text{Total weight of thiophenol oxidized}}$$

(A.C.4)

By considering the following mass balance:-

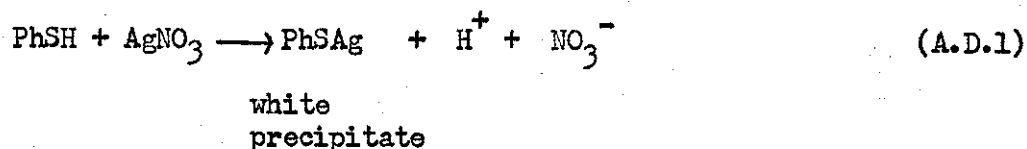$$\underset{220.4}{2 \, PhSH} \xrightarrow{[O]} \underset{234.3}{PhSOSPh}$$

(A.C.5)

it can be seen that equation A.C.4 can be written as:-

$$\% \, PhSOSPh = \frac{W_{thiol.} \times \frac{220.4}{234.3}}{\text{Initial weight of thiophenol}}$$

(A.C.6)

Calculation of the Thiophenol
Concentration (see section 5.3).

The reaction occurring in the thiophenol titration is:-

$$PhSH + AgNO_3 \longrightarrow PhSAg + H^+ + NO_3^- \qquad (A.D.1)$$

<div align="center">white
precipitate</div>

$$\begin{array}{l} \text{moles/litre of} \\ \text{thiophenol in the} \\ \text{sample} \end{array} = \begin{array}{l} \text{titre of} \\ \text{AgNO}_3 \end{array} \times \begin{array}{l} \text{normality} \\ \text{of AgNO}_3 \end{array} \times \frac{1}{0.94} \times \frac{V_r}{V_{py}} \qquad (A.D.2)$$

$\dfrac{1}{0.94}$ is the correction factor (see section 5.3).

V_{py} and V_r were defined in appendix B and appendix C, respectively.

V_r/V_{py} is a correction factor which compensates for the volume
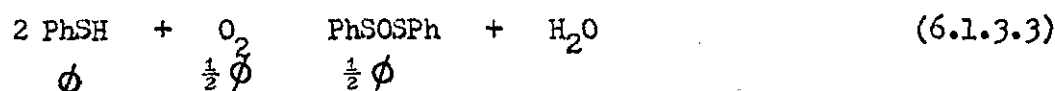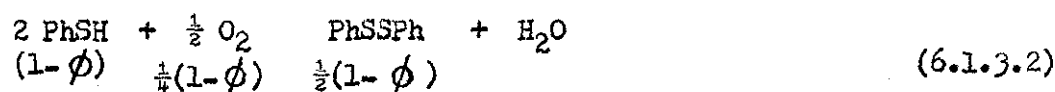fraction of the thiophenol in the reaction mixture.

Calculation of the Factor 'f' (see section 6.1.6).

i.e. to prove that:-

$$f = \tfrac{1}{4} (1 + \phi)$$

where: $\phi = \dfrac{\text{moles of PhSH consumed to give PhSOSPh}}{\text{moles of PhSH consumed to give PhSSPh and PhSOSPh}}$

From the previously reported equations 6.1.3.2 and 6.1.3.3 :-

$$\begin{array}{llll}
2\text{ PhSH} & + \ \tfrac{1}{2}\,O_2 & \text{PhSSPh} & + \ H_2O \\
(1-\phi) & \tfrac{1}{4}(1-\phi) & \tfrac{1}{2}(1-\phi)
\end{array}$$ (6.1.3.2)

$$\begin{array}{llll}
2\text{ PhSH} & + \ O_2 & \text{PhSOSPh} & + \ H_2O \\
\phi & \tfrac{1}{2}\phi & \tfrac{1}{2}\phi
\end{array}$$ (6.1.3.3)

we obtain:- $\dfrac{-\dfrac{d[O_2]}{dt}}{-\dfrac{d[\text{PhSH}]}{dt}} = \dfrac{\tfrac{1}{4}(1-\phi)+\tfrac{1}{2}\phi}{1-\phi+\phi}$ (A.E.1)

but since : $-\dfrac{d[O_2]}{dt} = -\dfrac{d[\text{PhSH}]}{dt} \times f$ (equation 6.1.6.3)

therefore $\dfrac{-\dfrac{d[O_2]}{dt}}{-\dfrac{d[\text{PhSH}]}{dt}} = f = \tfrac{1}{4}(1+\phi)$
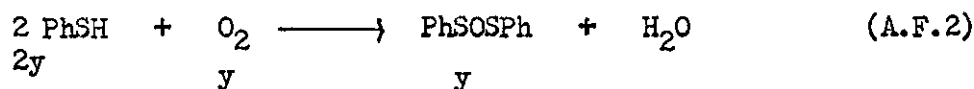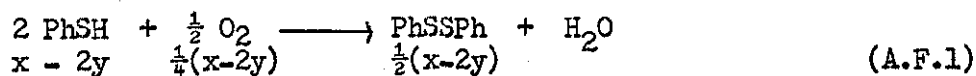
Calculations Showing the Inadequacy of the Iodometric
Titration for Thiolsulphinate Determination of Samples
Taken During the Course of the Thiophenol Oxidation
Reaction   (see section 6.1.6).

The three major chemical species present at time, t, are
thiophenol, diphenyl disulphide and diphenyl thiolsulphinate.
The normal determination of thiolsulphinate is by liberating iodine
from acidic iodide solution (equation A.F.4), the liberated iodine
being titrated against standard sodium thiosulphate solution. However,
the liberated iodine reacts with any thiophenol which is present
(equation A.F.5). We now consider the case where a known excess
of iodine in potassium iodide solution is added to the titration mixture
before titrating against standard sodium thiosulphate. The net iodine
liberated by the sample, even when it is a negative quantity, can
then be calculated.

Let (i)   moles of thiophenol in the
          initial reaction mixture   =   S

    (ii) moles of thiophenol consumed at time, t =   x

    (iii) moles of diphenyl thiolsulphinate
          produced at time, t   =   y

$\therefore$ moles of thiophenol remaining at time, t = S - x

The following mass balance is then obtained :-

$$2 \text{ PhSH} + \tfrac{1}{2} O_2 \longrightarrow \text{PhSSPh} + H_2O$$
$$x - 2y \quad \tfrac{1}{4}(x-2y) \quad \tfrac{1}{2}(x-2y) \qquad\qquad (A.F.1)$$

$$2 \text{ PhSH} + O_2 \longrightarrow \text{PhSOSPh} + H_2O \qquad (A.F.2)$$
$$2y \qquad y \qquad\qquad y$$
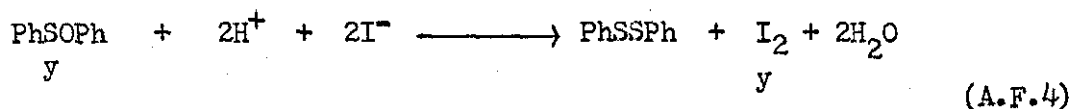
Thus the total moles of oxygen consumed at time, t (C) is given by:-

$$C = y + \tfrac{1}{4} (x - 2y)$$ (A.F.3)

Iodine Titration

Iodine is liberated by the reaction :-

$$\text{PhSOPh} + 2\text{H}^+ + 2\text{I}^- \longrightarrow \text{PhSSPh} + \text{I}_2 + 2\text{H}_2\text{O}$$
$$y y$$ (A.F.4)

and iodine is consumed by the reaction :-

$$2\ \text{PhSH} + \text{I}_2 \longrightarrow \text{PhSSPh} + 2\text{H}^+ + 2\text{I}^-$$
$$\text{S} - x \quad \tfrac{1}{2}(\text{S}-x)$$ (A.F.5)
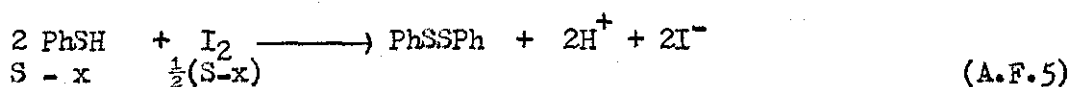
Thus: iodine liberated by y moles of PhSOSPh $= y$ moles

iodine consumed by $(S - x)$ moles of PhSH $= \tfrac{1}{2} (S - x)$ moles.

The net iodine liberated (L) is thus given by :-

$$L = y - \tfrac{1}{2} (S - x)$$ (A.F.6)

multiplying A.F.3 by 2 and rearranging gives :-

$$2\,C = y + \frac{x}{2}$$ (A.F.7)

equation A.F.6 rearranges to

$$L = y + \frac{x}{2} - \frac{S}{2}$$ (A.F.8)

(A.F.7) - (A.F.8) gives :-

$$\underline{2\,C - L = \frac{S}{2}} \quad \text{or} \quad \underline{L = 2C - \frac{S}{2}}$$ (A.F.9)

Thus equations A.F.3 and A.F.6 cannot be solved for x and y i.e. they are not independent equations but there exists a relationship between C, L and S as shown by equation A.F.9. This means that, at any time, t, during the course of the reaction, the net amount of iodine liberated in the iodometric titration is dependent only upon the initial thiophenol concentration and the oxygen consumed up to time, t, and is independent of the relative amounts of the 3 species present.

Upon careful consideration, it can be deduced that the iodometric titration will fail to determine the relative amounts of the 3 species present at any time, t. The starting material was thiophenol and as a result of the oxidation reaction up to time, t, and the iodometric titration of a sample at time, t, the end product of this sample was diphenyl disulphide only. This is always true regardless of the relative amounts of the 3 species present in the reaction mixture at that time, t.

Calculation of the Relative Amounts of the
Three Species (PhSH, PhSSPh and PhSOSPh)
Present During the Course of the Thiophenol
Oxidation Reaction (see Section 6.1.6).

---

(1) Thiophenol Titrations.

The calculation for the thiophenol concentration in a given

sample has been described in appendix D (equation A.D.2).

moles of thiophenol consumed/litre of solvent at time, t	=	initial concentration of thiophenol in the reaction mixture (moles/litre)	−	Concentration of thiophenol in the sample at time, t (moles/litre).

$$(A.G.1)$$

(2) Thiolsulphinate Titration at the End of the Reaction.

The thiolsulphinate concentration cannot be determined exactly

as in appendix C since an appreciable volume of the reaction mixture

was removed during the course of the reaction. The weight of thio-

lsulphinate in the sample taken for the titration is given by:-

$$\text{Weight of PhSOSPh in the titration sample} = \frac{\text{Titre of } Na_2S_2O_3 \times \text{Normality of } Na_2S_2O_3 \times \text{molecular weight of PhSOSPh}}{2000} \qquad (A.G.2)$$

$$\begin{pmatrix} \text{Volume of reaction mixture left at the end of the reaction} \\ (V_{final}) \end{pmatrix} = \begin{pmatrix} \text{initial volume of the reaction mixture} \\ (V_{initial}) \end{pmatrix} - \sum \begin{pmatrix} \text{volume of samples removed for PhSH titrations} \\ (V_{sample}) \end{pmatrix}$$

$$(A.G.3)$$

$$\therefore \quad \begin{matrix} \text{Volume of solution from which} \\ \text{the aliquot was taken for} \\ \text{PhSOSPh titration } (V_x) \end{matrix} \quad = \quad V_{final} + V_{acid} \qquad (A.G.4)$$

V_{acid} was previously defined in appendix A.

$\therefore$
$$\begin{array}{l}\text{weight of PhSOSPh} \\ \text{in the final reaction} \\ \text{mixture if no samples} \\ \text{had been removed} \\ (W_{thiol})\end{array} = \begin{array}{l}\text{weight of PhSOSPh} \\ \text{in the titration} \\ \text{sample}\end{array} \times \frac{V_x}{V_{aliq}} \times \frac{V_{initial}}{V_{final}}$$

(A.G.5)

$\therefore$ % PhSOSPh $= \dfrac{W_{thiol} \times \frac{220.4}{234.3}}{\begin{array}{l}\text{Initial weight of} \\ \text{thiophenol}\end{array}}$ as in equation A.C.6.

(3) Moles of Oxygen Consumed/litre (M).

In order to obtain the total moles of oxygen consumed/litre (M) at any time, t, the method of calculation given in appendix B has to be modified. This is because the total volume of the reaction mixture changes when a sample is removed for the thiophenol titration. A value of $M(M_n)$ has to be calculated for each section of the reaction, one section being the interval between successive sampling. The total value of M up to any time, t, is the cumulative total of the calculated M_n's up to time t. The individual values of M_n are calculated as follows:-

$$M_n = D \times \begin{array}{l}\text{C.S.A of the} \\ \text{gas burette}\end{array} \times \frac{273}{273+T} \times \frac{P_o}{760} \times \frac{1}{22,390} \times \frac{1000}{V_{py(t)}}$$ (A.G.6)

where

$$V_{py(t)} = \begin{array}{l}\text{volume of pyridine} \\ \text{in reaction mixture} \\ \text{at time, t.}\end{array} = \begin{array}{l}\text{initial volume} \\ \text{of pyridine in} \\ \text{reaction mixture} \\ (V_{py})\end{array} - \begin{array}{l}\text{volume of sample} \\ \text{taken for the} \\ \text{thiophenol} \\ \text{titration}\end{array}$$

(A.G.7)

N.B. The value of D is corrected to compensate for the volume of the sample which was removed from the closed system for the thiophenol titration.

Therefore:- M, at time t = $\sum\limits_{o}^{t} M_n$ (A.G.8)

and:-

$\%$ oxygen consumption $(X) = \dfrac{M, \text{ at time } t \times 4 \times 100}{\text{initial concentration of PhSH}}$ (A.G.9)

If the thiolsulphinate and the disulphide were the only products of the thiophenol oxidation reaction then:-

$\%$ oxygen consumption $(X) = 100 + \% \text{ PhSOSPh}$ (A.G.10)

For the thiophenol oxidation reactions considered in section 6.1.6, this is not exactly true but X was greater than $(100 + \% \text{ PhSOSPh})$ by about 10%. As stated in section 6.2.1.1.(b), oxidation products of thiophenol other than the disulphide and the thiolsulphinate were probably formed. Thus these products must be taken into account in the present calculations. As stated in section 6.2.1.1. (b), the thiolsulphonate $(PhSO_2SPh)$ was not detected in the final reaction mixture of the oxidation reaction and thus the compounds $PhSO_2SOPh$ and $PhSO_2SO_2Ph$ would probably not have been formed either. Other possible products are PhSOH, $PhSO_2H$ and $PhSO_3H$. If the extra 10% oxygen consumption was used to form:-

(1) PhSOH, then 5% of the initial thiophenol concentration would be used to form PHSOH.

(2) $PhSO_2H$, then 2.5% of the initial thiophenol concentration would be used to form $PhSO_2H$.

(3) $PhSO_3H$, then 1.7% of the initial thiophenol concentration would

be used to form $PhSO_3H$.

If we assume that 3.4% of the initial thiophenol concentration was used in consuming the extra 10% oxygen consumption, then the maximum error would be $\pm 1.7\%$ of the initial thiophenol concentration (i.e. well within the limits of experimental error).
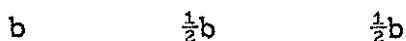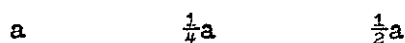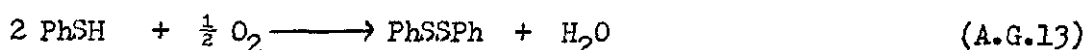
Thus it is assumed that 96.6% of the initial thiophenol present was used to give the disulphide and the thiolsulphinate. Then:-

$$\bullet\bullet\ \begin{array}{l}\text{Concentration of PhSH} \\ \text{consumed in producing }(G_o) = \\ \text{PhSSPh and PhSOSPh}\end{array}\ \begin{array}{l}\text{thiophenol} \\ \text{consumed} \\ \text{(moles/litre)}\end{array}\ \times\ 0.966 \qquad (A.G.11)$$

Similarly, the value for the moles per litre of oxygen consumed has to be corrected.

$$\bullet\bullet\ \begin{array}{l}\text{moles/litre of oxygen} \\ \text{consumed in producing }(M_c) = \\ \text{PhSSPh and PhSOSPh}\end{array}\ \begin{array}{l}\text{actual moles/} \\ \text{litre of oxygen} \\ \text{consumed}\end{array}\ \times\ \dfrac{100 + \%PhSOSPh}{X}$$

$$(A.G.12)$$

We now consider the following two reactions occurring in the thiophenol oxidation.

$$2\ PhSH\ +\ \tfrac{1}{2}\ O_2\ \longrightarrow\ PhSSPh\ +\ H_2O \qquad\qquad (A.G.13)$$

$$a \qquad\quad \tfrac{1}{4}a \qquad\qquad \tfrac{1}{2}a$$

$$2\ PhSH\ +\ O_2\ \longrightarrow\ PhSOSPh\ +\ H_2O \qquad\qquad (A.G.14)$$

$$b \qquad\quad \tfrac{1}{2}b \qquad\qquad \tfrac{1}{2}b$$

From the above mass balances we obtain :-

$$a\ +\ b\ =\ G_c \qquad\qquad\qquad\qquad (A.G.15)$$

$$\tfrac{1}{4}b\ +\ \tfrac{1}{2}b\ =\ M_c \qquad\qquad\qquad\qquad (A.G.16)$$

These two equations can be solved for a and b thus giving the relative amounts of the disulphide and the thiolsulphinate present in the reaction mixture at time, t; from this the values of F(see section 6.1.6) can be found.

Derivation of the Kinetic Rate Expressions
From the Kinetic Schemes Given by Tsuchida et al(15)

The three kinetic schemes considered were:-

1. $E + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} E.O_2$; $E\,O_2 + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES\,O_2 \overset{K_e}{\longrightarrow} ES\,O_2{}' \overset{K_d}{\longrightarrow}$

$\qquad\qquad E\,O_2{}' + S' \longrightarrow$ coupling $\qquad\qquad$ (A.H.1)

$\qquad\qquad\quad\downarrow$

$\qquad\qquad\quad E$

2. $E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES$; $ES + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} ES\,O_2 \overset{K_e}{\longrightarrow} ESO_2{}' \overset{K_d}{\longrightarrow}$

$\qquad\qquad E\,O_2{}' + S' \longrightarrow$ coupling $\qquad\qquad$ (A.H.2)

$\qquad\qquad\quad\downarrow$

$\qquad\qquad\quad E$

3. $E + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \overset{K_e}{\longrightarrow} ES'$; $ES' + O_2 \underset{K_{-ox}}{\overset{K_{ox}}{\rightleftharpoons}} ESO_2{}' \overset{K_d}{\longrightarrow}$

$\qquad\qquad E\,O_2{}' + S' \longrightarrow$ coupling $\qquad\qquad$ (A.H.3)

$\qquad\qquad\quad\downarrow$

$\qquad\qquad\quad E$
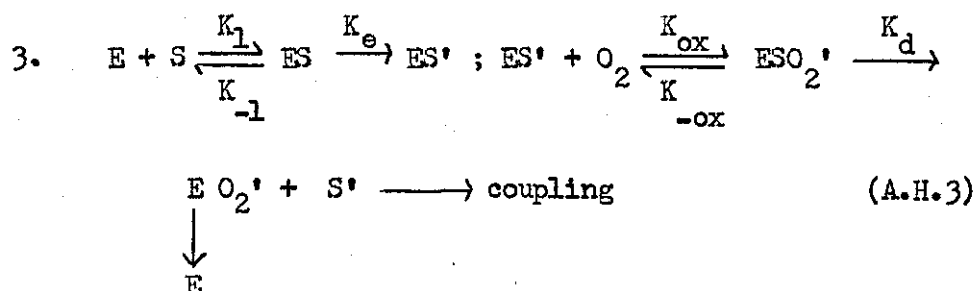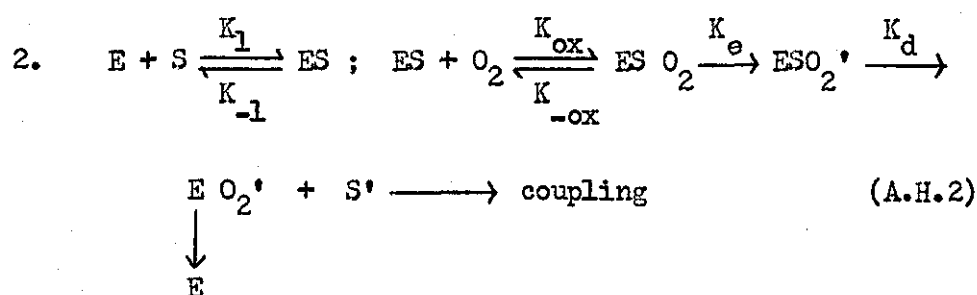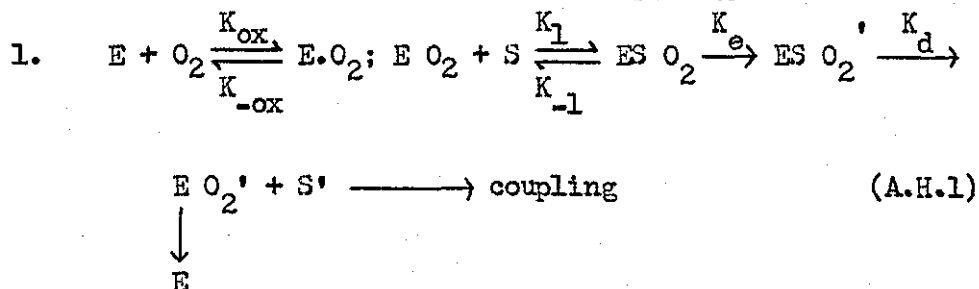
Where E = copper catalyst species

S = substrate (phenol monomer)

$E\,O_2$ = copper-amine-oxygen complex

$ES\,O_2$ = copper-amine-phenol-oxygen complex

$ES\,O_2{}'$= activated copper-amine-phenol-oxygen complex

ES = copper-amine-phenol complex

and ES' = activated copper-amine-phenol complex

The reaction rate, v_d was given by $k_d[ESO_2']$ and was expressed by :-

$$v_d = \frac{V_{max} [S]}{[S] + k_m} \qquad (A.H.4)$$

where $V_{max} = \frac{A [O_2]}{C[O_2] + B} [E]_o \qquad (A.H.5)$

and $K_m = \left(\frac{K_{-1} + K_e}{K_1} \right) \cdot \left(\frac{K_d}{K_e + K_d} \right) \qquad (A.H.6)$

$A = K_{ox} K_e K_d$ for equations A.H.1, A.H.2 and A.H.3.

$B = K_d (K_{-1} + K_e)$ for equation A.H.1

$B = K_d (K_{-ox} + K_e)$ for equation A.H.2.

$B = K_e (K_{-ox} + K_d)$ for equation A.H.3.

$C = K_{ox} (K_e + K_d)$ for equations A.H.1, A.H.2., and A.H.3.

substituting equation A.H.5 in equation A.H.4 and simplifying gives:-

$$v_d = \frac{A[O_2][E]_o [S]}{C[O_2] [S] + B [S] + k_m C [O_2] + B k_m} \qquad (A.H.7)$$

Derivation of the Kinetic Rate
Equation From the Kinetic Scheme.

It is assumed that (1) the concentrations of the complexes EO_2, ESO_2, ESO_2', ES and ES' are constant during the reaction and (2) there is a negligible concentration of the complex $E O_2'$

Equation A.H.1

$$\frac{d|EO_2|}{dt} = K_{ox}[E][O_2] - K_{-ox}[E \cdot O_2] - K_1[E \cdot O_2][S] + K_{-1}[ESO_2] = 0 \quad (A.H.1.1)$$

$$\frac{d|ESO_2|}{dt} = K_1[E \cdot O_2][S] - K_{-1}[ESO_2] - K_e[ESO_2] = 0 \quad (A.H.1.2)$$

$$\frac{d|ESO_2'|}{dt} = K_e[ESO_2] - K_d[ESO_2'] = 0 \quad (A.H.1.3)$$

$$[E_o] = [E] + [E \cdot O_2] + [ESO_2] + [ESO_2'] \quad (A.H.1.4)$$

Thus we have 4 independent equations (A.H.1. 1-4) and 4 variables (the four expressions on the right hand side of equation A.H.14) and thus the values of the 4 variables can be found.

The rate is given by :-

$$v_d = K_d[ESO_2'] \quad (A.H.1.5)$$

By manipulation of equations A.H.1. 1-4, an expression for ESO_2' in terms of known quantities can be found. Substituting this expression in equation A.H.1.5 and rearranging gives the following expression :-

$$v_d = \frac{K_{ox} K_e K_d [E_o][S][O_2]}{\frac{K_{-ox}K_d}{K_1}(K_{-1}+K_e) + K_e K_d[S] + \frac{K_d K_{ox}}{K_1}(K_{-1}+K_e)[O_2] + K_{ox}(K_e+K_d)[S][O_2]} \quad (A.H.1.6)$$

This equation is not the same as that given by Tsuchida et al. However, it is now shown that an expression of this form would still give linear Lineweaver-Burk plots.

Equation A.H.1.6. is of the form :-

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$$v_d = \frac{F\,[O_2]\,[S]\,[E]_o}{G\,[O_2] + H\,[S]\,[O_2] + J\,[S] + L} \tag{A.H.1.7}$$

where   F, G, H, J and L are constants

Then $\dfrac{1}{v_d} = \dfrac{G}{F[S][E]_o} + \dfrac{H}{F[E]_o} + \dfrac{J}{F\,[O_2]\,[E]_o} + \dfrac{L}{F\,[O_2][S][E]_o}$ (A.H.1.8)

$\therefore \quad \dfrac{1}{v_d} = \dfrac{1}{[S]}\left(\dfrac{G}{F[E]_o} + \dfrac{L}{F[O_2][E]_o}\right) + \dfrac{H}{F[E]_o} + \dfrac{J}{F[O_2][E]_o}$ (A.H.1.9)

It can be clearly seen that a plot of $1/v_d$ vs $1/[S]$, the Lineweaver-Burk plot, would be linear (provided the partial pressure of oxygen was constant).

Thus, the kinetic scheme given by equation A.H.1 would give a linear Lineweaver-Burk plot.

Equation A.H.2

8   Using a similar procedure to that for equation A.H.1., it can be shown that the rate expression corresponding to the kinetic scheme of equation A.H.2 is given by:

$$v_d = \frac{K_{ox}\,K_e\,K_d\,[E]_o[S][O_2]}{\dfrac{K_d K_{-1}}{K_1}(K_{-ox}+K_e) + \dfrac{K_e K_{ox} K_d}{K_1}[O_2] + K_d(K_{-ox}+K_e)[S] + K_{ox}(K_e+K_d)[S][O_2]} \tag{A.H.2.1}$$

This is again different to the equation obtained by Tsuchida et al., but is still of the general form given in equation A.H.1.7 and thus would still give linear Lineweaver-Burk plots.

Equation A.H.3

Using a similar procedure to that for equation A.H.1, it can be shown that the rate expression corresponding to the kinetic scheme of equation A.H.3 is given by:-

$$v_d = \frac{A[E]_o[S][O_2]}{C K_m [O_2] + C[O_2][S] + B [S]}$$

(A.H.3.1)

where the values of A, B, C and K_m are those previously defined. Again this equation is different to the one given by Tsuchida et al. However, again it can be seen that the Lineweaver-Burk plot would still give a linear relationship.

Thus although the kinetic rate expressions derived from the given kinetic schemes, differ slightly from those given by Tsuchida et al., all the corresponding Lineweaver-Burk plots would give linear relationships.

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