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REACTIONS OF METAL COMPLEXES WITH LEWIS BASES AND THEIR UTILISATION IN THE SELECTIVE FILTRATION OF SMOKE.

A thesis submitted to the Council for National
Academic Awards in partial fulfilment of the
requirements for the Degree of Doctor of Philosophy.

by

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North London
in collaboration with
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Declaration

Whilst registered as a candidate for this degree the author has not been registered as a candidate for any other award.

J.S.MORGAN

J.S. Morgan Reactions of metal complexes with Lewis bases and their utilisation in the selective filtration of smoke.

Abstract

This thesis is concerned with internal redox reactions of metal complexes and the application of such reactions in the selective filtration of tobacco smoke.

The reactions of Fe(II), Fe(III) and Cu(II) quinoneoximic complexes and of some other complexes of these metals with Lewis bases (e.g. Ph_3P and py) have been investigated. From the results obtained and from a critical consideration of analogous reactions reported in the literature the behaviour of metal chelates towards Lewis bases has been assessed. It has been established that the reaction between a metal chelate and a Lewis base may lead to: (i) Adduct formation, (ii) condensation and (iii) to an internal redox reaction,

$$M(chel)_n \xrightarrow{LB} M(chel)_{n-1}(LB)_x + chel^{\bullet}$$

The latter is favoured when the metal in $M(chel)_n$ has a stable lower oxidation state, by Lewis bases capable of π-bonding and by chelating ligands exerting a strong ligand field. The type of behaviour shown by $chel^{\bullet}$ has been considered. The dissociated radical may: (i) Abstract a hydrogen atom to give the protonated ligand, (ii) dimerise, (iii) undergo coupling or degradation.

A detailed investigation of the reactions of Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ with Ph_3P (including kinetic studies) showed that these complexes undergo internal redox reactions to give iron(II) complexes and products arising from the deoxygenation of the nqo$^{\bullet}$ radical. Mechanisms for these resctions have been proposed.

The behaviour of quinoneoximic complexes of iron towards the Lewis base CO has been examined both directly and indirectly by studying the behaviour of nqoH towards $Fe(CO)_5$ or $Fe(CO)_5/PhNH_2$. $Fe(CO)_5$ and 1-nqoH or 2-nqoH afforded complexes of the type Fe(nqo)$_2$, without formation of CO adducts or deoxygenation products. In the presence of $PhNH_2$ complexes of type Fe(nqo)$_2$ and Fe(nqo-A)$_2$ resulted, where nqo-A is a species arising from the coupling of the nqo ligand with $PhNH_2$. Both systems also afforded various organic products. On the basis of Mössbauer and other techniques oligomeric structures have been suggested for the complexes Fe(nqo)$_2$ and Fe(nqo-A)$_2$. Whereas CO did not react with Fe(nqo)$_2$ or Fe(nqo)$_2$.2py, it reacted with Fe(nqo)$_3$, possibly via an internal redox process. For Fe(2-nqo)$_3$, products arising from a deoxygenated ligand and a complex tentatively formulated as the nitrene species, Fe(2-nq)$_2$, were isolated.

The reactivity of the Fe(nqo)$_3$ complexes towards CO has been successfully utilised in the selective filtration of tobacco smoke. Both Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ were shown to be capable of significantly reducing the level of CO in tobacco smoke under smoking conditions when supported on suitable filters. Reduction of the levels of other Lewis bases in tobacco smoke, e.g. nicotine and furfural, was observed.

The complexes Fe(nqo)$_2$, Fe(nqo)$_2$.2py and Fe(nqo)$_3$ reacted readily with NO to give complicated mixtures, but their effectiveness in removing NO from tobacco smoke has not been unambiguously established.

Acknowledgements

Special thanks to my supervisor, Dr J.Charalambous and also to Dr H.D.Mathewson and Dr L.I.B.Haines for their help, encouragement and perseverance.

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Chapter 3 The reaction of selected quinone monooximes with iron pentacarbonyl and the interaction of quinone monooximic and related complexes with carbon monoxide and/or nitric oxide.

Chapter 4 The interaction of selected metal complexes with Lewis bases present in tobacco smoke.

Chapter 5 Experimental

Introduction

This thesis examines the reactions of metal complexes with Lewis bases and their utilisation in the selective filtration of smoke.

A number of the complexes examined are derived from quinone monooximes. Compounds of this type exhibit tautomeric behaviour and thus the nomenclature of these compounds varies and may appear confusing. Throughout this thesis the term 'quinoneoxime' is generally used. However, occasionally the term 'nitrosophenol' is used. This does not necessarily imply that the particular compound possesses one structure or the other, or exists in that form.

For the convenience of the reader the list below summarises the common abbreviations used for the compounds in this thesis.

qoH	quinone monooxime
nqoH	naphthoquinone monooxime
1-nqoH	1,2-naphthoquinone-1-oxime
2-nqoH	1,2-naphthoquinone-2-oxime
5-MeoqoH	5-methoxy-1,2-quinone-2-oxime
nqH	naphthoquinone monoimine
$M(L)_n$	Metal complex derived from one of the above ligands.
$1\text{-}nH_2$	1-amino-2-naphthol

CHAPTER 1

1 Internal redox reactions of metal compounds.

1.1 Introduction

The term internal redox reaction is a description of the homolytic bond cleavage that can occur in metal compounds to give rise to a reduced metal species and a radical (Reaction 1.1).

$$L_xM^{n}\overset{\sim}{-}L \longrightarrow L_xM^{n-1} + L^{\bullet}$$

Reaction 1.1

It was first used by McCleverty et al to describe the manner in which nickel and iron dithiocarbamate complexes undergo reduction in the presence of Lewis bases to give rise to stable metal complexes in lower oxidation states.[1] The term has been used little since then. However, a number of reactions have been reported which indicate clearly the involvement of an internal redox reaction, but are not described as such. Instead, a variety of terms have been used which include redox reactions, charge transfer reactions or electron transfer reactions. In the majority of these studies little attention has been paid to the fate of the displaced ligand radical.

In general, internal redox reactions are induced by Lewis bases and/or photochemical or thermal means. They are of considerable significance in catalysis and synthesis and also play an important role in a number of biological systems.

Whether or not a metal will undergo reduction in the presence of a Lewis base depends on the base used, the metal and the nature of the ligand. When the metal is in a low oxidation state, or is not easily reduced, reaction with a Lewis base usually leads to adduct formation (Reactions 1.2[2-5] and 1.3[6,7]) with the oxidation state of the metal remaining unchanged.

$$Cu(Et_2NCSS) + 2Ph_3P \longrightarrow Cu(Et_2NCSS)(Ph_3P)_2$$

Reaction 1.2

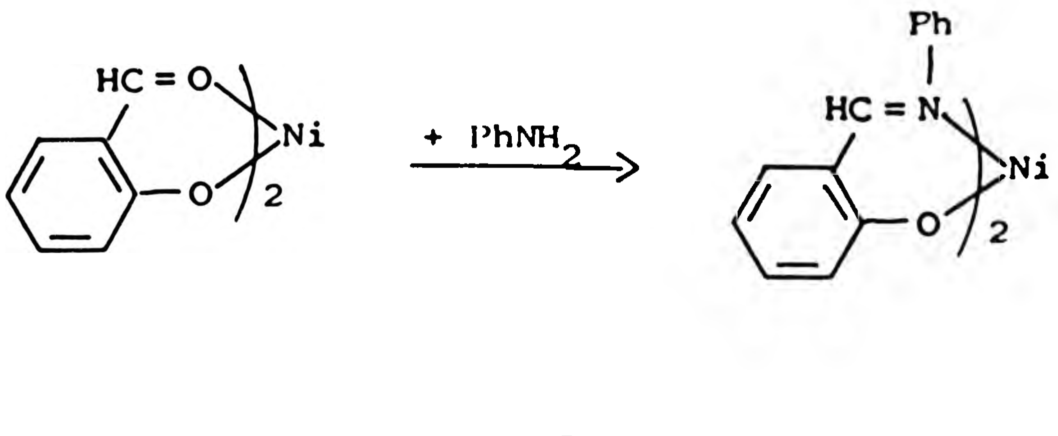
$$Ni(Sacac)_2 + 2py \longrightarrow Ni(Sacac)_2{\cdot}2py$$

Reaction 1.3

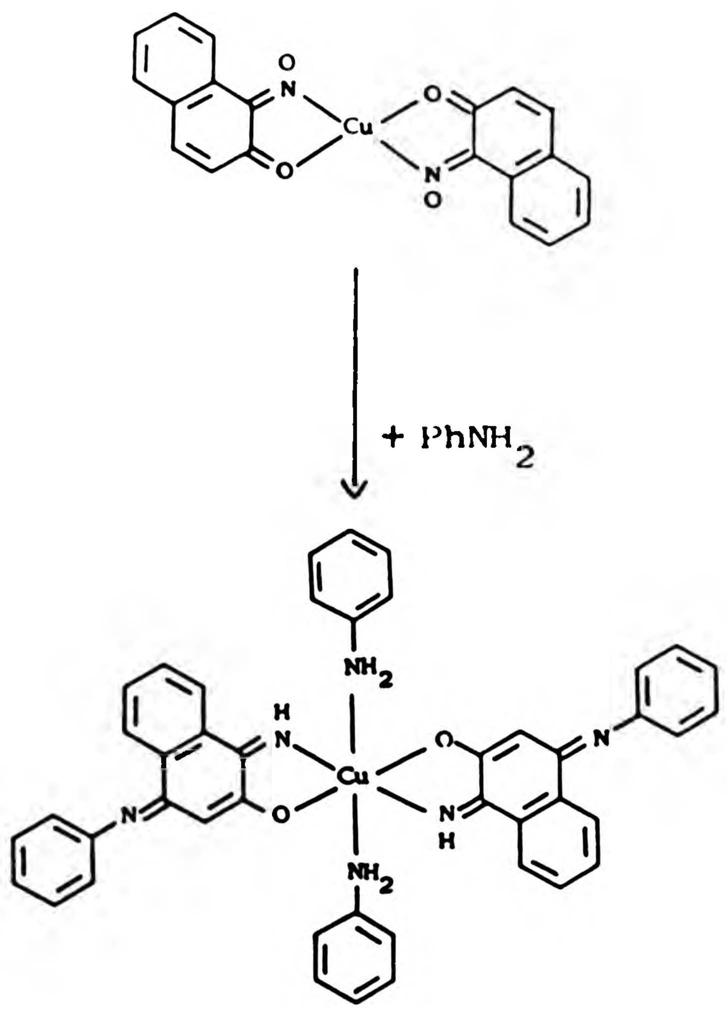
In some cases the reaction with the Lewis base involves more complex behaviour, such as ligand displacement, condensation, coupling, or a combination of these. In such reactions (e.g. Reactions 1.4-1.6[8-11]) the oxidation state of the metal again remains unaffected.

$$Fe(dpg)_2{\cdot}2py + CO \longrightarrow Fe(dpg)_2(CO)(py) + py$$

Reaction 1.4



Reaction 1.5



Reaction 1.6

When the metal in a complex is capable of being reduced to stable, low oxidation states, then reaction with a Lewis base may give rise to an internal redox reaction. Hence, low spin iron(III)(d^5) complexes are readily reduced to low spin iron(II)(d^6) complexes, copper(II)(d^9) complexes reduced to copper(I)(d^{10}) complexes and nickel(III)(d^7) or nickel(IV)(d^6) complexes easily reduced to square-planar nickel(II)(d^8) complexes (e.g. Reaction 1.7[12]). Some examples of this type of reaction where it has been established that internal redox reactions have occurred are given in Table 1.1.

$$Cu(2\text{-nqo})_2 \xrightarrow{Ph_3P} Cu(2\text{-nqo})(Ph_3P)_2 + \text{organic products}$$

Reaction 1.7

Table 1.1 **Lewis base promoted internal redox reactions of metal complexes.**

Metal complex	Lewis base	Metal complex formed	Other products	Refs.
$Fe(Et_2NCSS)_3$	RNC	$Fe(Et_2NCSS)_2(RNC)_2$	$(Et_2NCSS)_2$	1,4
$[Ni(Et_2NCSS)_3]PF_6$	RNC	$[Ni(Et_2NCSS)_2(RNC)_2]PF_6$	$(Et_2NCSS)_2$	4,25,26
$Fe(mexant)_3$	py	$Fe(mexant)_2 \cdot 2py$	not established	4,28
$Cu(1\text{-}nqo)_2$	Ph_3P	$Cu(1\text{-}nqo)(Ph_3P)_2$	Ph_3PO + a	12,29
$Cu(2\text{-}nqo)_2$	Ph_3P	$Cu(2\text{-}nqo)(Ph_3P)_2$	Ph_3PO + b	12,29
$Cu(\beta\text{-diketonate})_2$	Ph_3P	$Cu(\beta\text{-diketonate})(Ph_3P)_2$	not established	14
$Fe(1\text{-}nqo)_3$	py	$Fe(1\text{-}nqo)_2 \cdot 2py$	1-nqoH	23
$Fe(2\text{-}nqo)_3$	py	$Fe(2\text{-}nqo)_2 \cdot 2py$	2-nqoH	23
$Cu(5\text{-}MeOqo)_2$	Ph_3P	$Cu(5\text{-}MeOqo)(Ph_3P)_2$	Ph_3PO + c	24
$[Ni(Et_2NCSS)_3]BF_4$	Ph_3P	$Ni(Et_2NCSS)_2(Ph_3P)_2$ + $Ni(Et_2NCSS)_2$	$Ph_3PC(=S)NEt_2$ + Ph_3PS	25

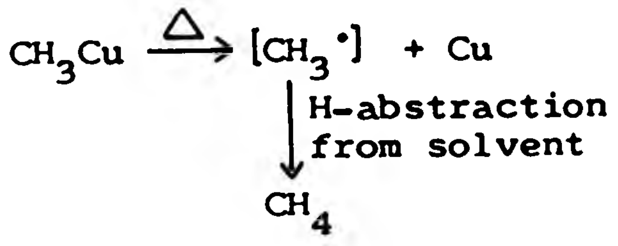
a = 1-amino-2-naphthol   b = 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine

c = 2-amino-7-methoxy-3H-phenoxazine-3-one

The nature of the Lewis base used also has an effect on whether or not reduction occurs. Thus Cu(1-nqo)$_2$ will react with pyridine to give a pyridine adduct of the copper(II) complex[13] but will react with triphenylphosphine to give the copper(I) complex, Cu(1-nqo)(Ph$_3$P)$_2$.[12] The behaviour of triphenylphosphine reflects its ability to stabilise low oxidation states.

With regard to the ligand in a metal complex, ML$_n$, it appears from examination of the systems considered so far that internal redox reactions are favoured by ligands having strong ligand fields and which are capable of stabilising low oxidation states e.g. quinoneoxime and dithiocarbamate ligands.

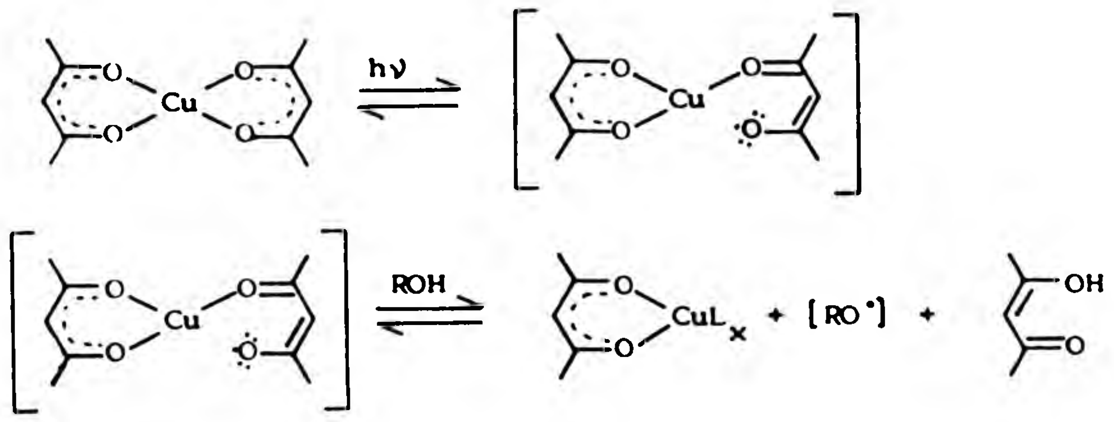
A number of reactions have been reported in which an internal redox reaction is initiated by photochemical or thermal means. Thus when methylcopper(I) is heated in heptane methane is obtained (Reaction 1.8)[15-17] and first row transition metal β-diketonate complexes readily undergo reduction upon irradiation (Scheme 1.1).[18-20]



Reaction 1.8

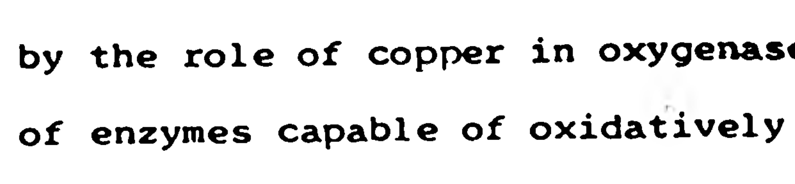
Photochemical and thermal reactions are often carried out in solvents capable of acting as Lewis bases. In such cases it is probable that the internal redox reaction is Lewis base induced, rather than thermally or photochemically initiated, or may occur via both mechanisms.

Scheme 1.1



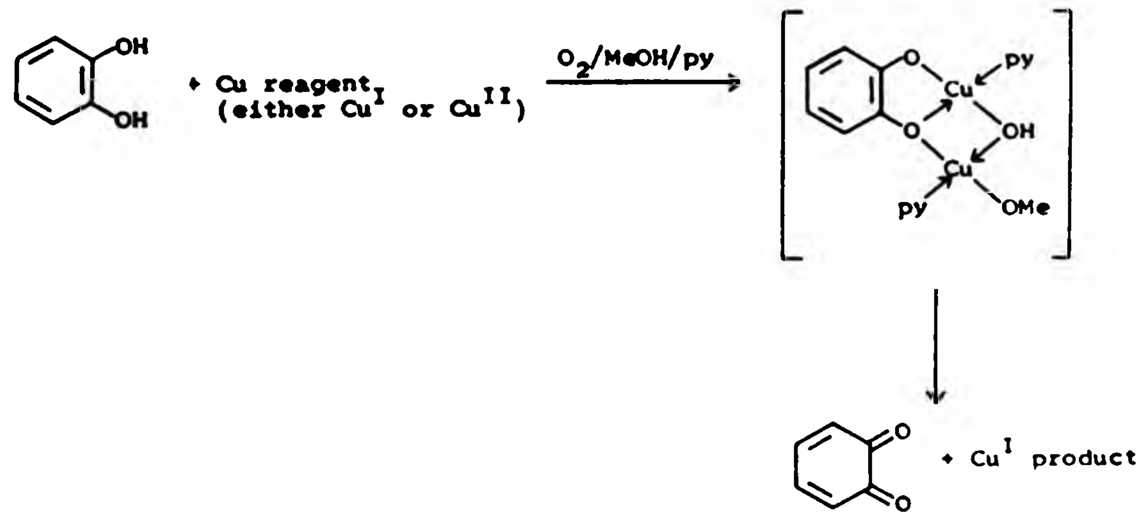
L = a ligand derived from the solvent

Internal redox reactions are important in a number of catalytic reactions (e.g. Reaction 1.9[21]) and play a key role in various biological systems. The catalytic aspects are discussed in Section 1.3.3.



Reaction 1.9

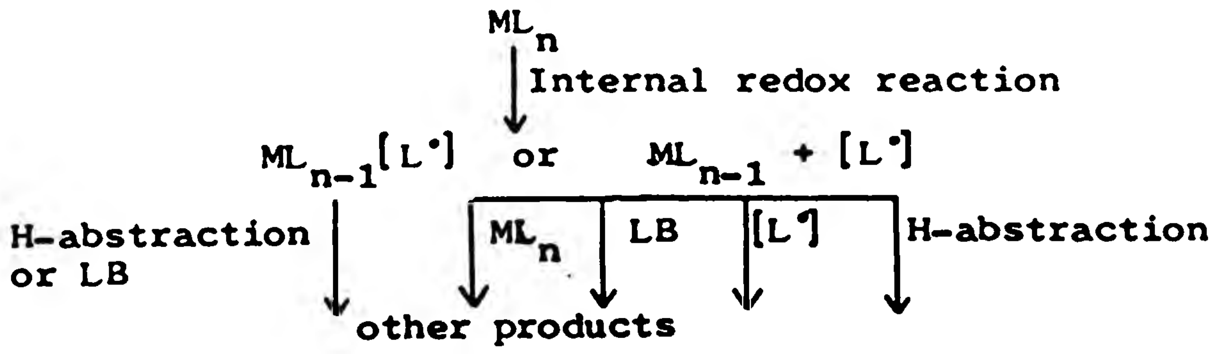
The biological significance of internal redox reactions is exemplified by the role of copper in oxygenases. These are a class of enzymes capable of oxidatively opening aromatic rings (of phenols and catechols) by inserting both atoms of an O_2 molecule into the substrate. Rogic and Demmin have shown that in model reactions using a copper(I) catalyst, in the presence of pyridine and methanol, for the oxygenation of catechols the actual species responsible for the oxygenation is a copper(II) complex.[22] The activation of molecular oxygen in the systems is achieved by the reaction of oxygen with the transition metal. Although these systems are extremely complex, it has been established that the initial stages of oxygenation involve complex formation between the catechol and the active copper(II) species. In the reactions that follow copper(II) is reduced to copper(I) and benzoquinone is produced during a step which involves an internal redox reaction (Reaction 1.10). The benzoquinone then reacts further with one or more of the copper species present to give rise to cis,cis muconic acid monomethyl ester.



Reaction 1.10

As noted earlier, internal redox reactions give rise to radicals in addition to reduced metal species. The radicals which are produced can react further in a variety of ways with the base and/or metal compound, or another radical, or solvent molecules (Scheme 1.2). In most studies of internal redox reactions quoted, only the metal containing products have been investigated and little attention has been paid to the fate of the ligand radicals. Because of this (i) the mechanistic understanding of the internal redox reactions and (ii) the realisation of their full importance and impact in synthesis, catalysis and in biologically important systems has been limited. As a consequence, the aims of this chapter are to clarify the internal redox reaction and consider the possible fate of the ligand radical, [L$^\bullet$], arising in these reactions.

Scheme 1.2



LB may be solvent

In order to achieve the above aims the literature on Lewis base promoted internal redox reactions, together with studies carried out for this thesis, have been carefully analysed. This has led to a classification of the different types of reaction that [L$^\bullet$] may undergo, which is given in Section 1.2. Section 1.3 deals with the uses of internal redox reactions in the synthesis of organic compounds. It includes reactions that are photochemically or thermally induced and reactions where catalysis is involved.

1.2 The fate of the ligand radical, [L•]

The reactions that ligand radicals (produced during internal redox reactions) may undergo can be subdivided in terms of the final products arising from them:

(i) [L•] abstracts hydrogen, either from the solvent or elsewhere, to give LH.

(ii) [L•] dimerises to give L-L. Suggestions of this type must be looked at carefully, as the possibility that two ligand radicals will interact with each other rather than with base or solvent molecules is extremely small. In reactions where L-L is obtained it is possible that it has arisen as a result of decomposition of a less stable compound.

(iii) [L•] reacts with the base or metal complex to give other products.

(iv) [L•] coordinates to the metal in the ML_{n-1} co-product.

1.2.1 H-abstraction by [L•]

The complexes $Fe(1\text{-nqo})_3$ and $Fe(2\text{-nqo})_3$ will react readily with Lewis bases such as pyridine[23] or nicotine (refer to Chapter 4) to give iron(II) complexes plus the free protonated ligand (1-nqoH or 2-nqoH). This can be easily explained if the mechanism in Scheme 1.3 operates. Attack of the Lewis base (e.g. pyridine) would lead to an internal redox reaction and homolytic breaking of an iron-ligand bond. Hydrogen

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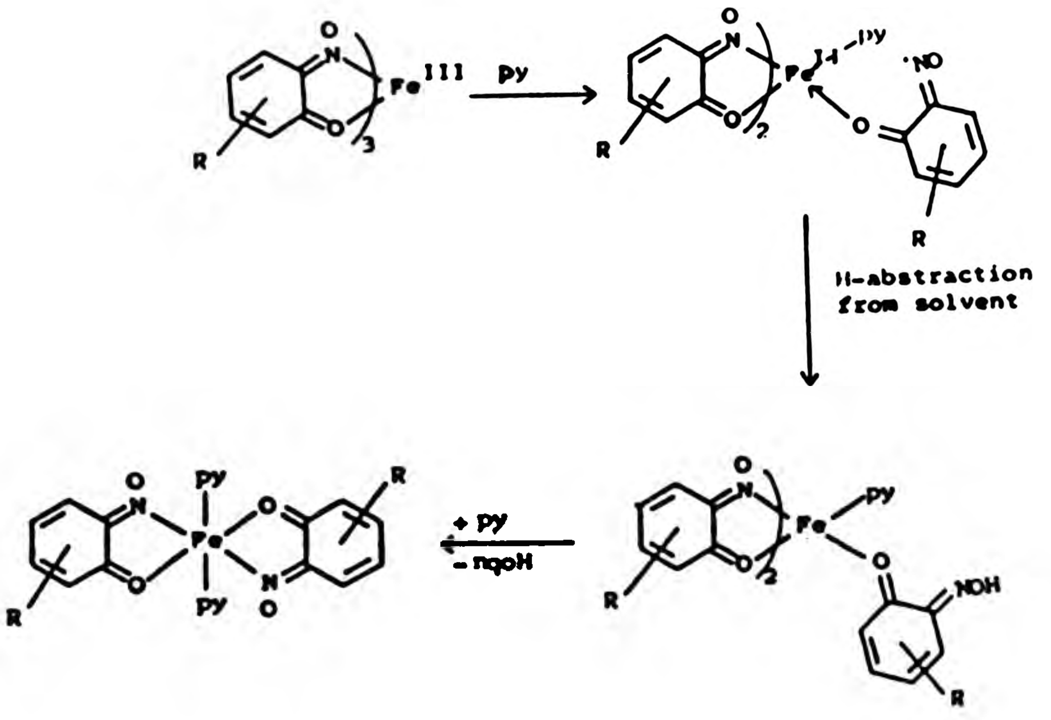
Scheme 1.3



Another reaction in which a similar mechanism is likely is that of $Cu(1\text{-}nqo)_2$ with triphenylphosphine.[13] However, here triphenylphosphine interacts further with the oxime group to give triphenylphosphine oxide and a nitrene ligand. This abstracts hydrogen to give 1-amino-2-naphthol as the major organic product (Reaction 1.11).

$$Cu(1\text{-}nqo)_2 \xrightarrow{Ph_3P} Cu(1\text{-}nqo)(Ph_3P)_2 + 1\text{-}nH_2 + Ph_3PO$$
$$+ \text{ other organic products}$$

Reaction 1.11

It must be noted that in the reaction above copper(II) is reduced to copper(I). However, in the reaction of $Cu(1\text{-}nqo)_2$ with pyridine[13] or nicotine (refer to Chapter 4) an adduct of the copper(II) complex is formed (Reaction 1.12).

$$Cu(1\text{-}nqo)_2 + LB \longrightarrow Cu(1\text{-}nqo)_2 \cdot LB$$

(LB = pyridine, nicotine)

Reaction 1.12

This behaviour can be explained in terms of the stabilisation of the copper(I) complex by triphenylphosphine. This stabilisation of metals in low oxidation states by triarylphosphines is well established.[30-34]

1.2.2 Dimerisation of $[L^{\bullet}]$.

Suggestions for ligand radical dimerisation have been reported in the literature.[1,4] One example concerns the reaction of $Fe(Et_2NCSS)_3$ with isonitriles (Reaction 1.13).[1]

$$2Fe(Et_2NCSS)_3 \xrightarrow{RNC} Fe(Et_2NCSS)_2(RNC) + 2(Et_2NCSS)_2$$

Reaction 1.13

It was concluded that a one electron redox process had occurred involving the reduction of $Fe^{III} \longrightarrow Fe^{II}$, with the liberation of diethyldithiocarbamyl radicals. The formation of radicals of type $[Et_2NCSS^{\bullet}]$ is supported by an earlier e.s.r. study of the redox reaction of piperidine with $Cu(Et_2NCSS)_2$.[36] In the reactions involving $Fe(Et_2NCSS)_3$ it has been suggested that the radicals combine to give diethylthiuram disulphide. However, as mentioned previously, this dimerisation is unlikely to occur. A more plausible explanation involves the formation of the dithiocarbamic acid. Thus if hydrogen abstraction occurs to give the acid, $[R^{\bullet}] \rightarrow RH$, this being unstable in air would then oxidise to give the thiuram disulphide, $RH \xrightarrow{[O]} R{-}R$.[4,35]

Another reaction in which diethylthiuram disulphide has been isolated as the major organic product is that of $Fe(Et_2NCSS)_3$ with pyridine, which has been investigated during this study (refer to Chapter 4). In this reaction an internal redox process occurs to yield the diethyldithiocarbamyl radicals. These then give rise to the thiuram disulphide. However, in this case the base adduct of $Fe(Et_2NCSS)_2$ is not obtained as the iron(II) complexes of dithiocarbamates are usually unstable.[4,37] and easily oxidise in air to iron(III) compounds.

Other related types of reaction are those of FeL_3 (L = e.g. methyl xanthate or $Ph_2P(S)SH$) with pyridine.[28] The yellow solids obtained from these reactions have been formulated as $FeL_2.2py$, but no isolation of any other products was attempted. However, Kuchen and Hertel have reported that thiophosphinic acid reacts with copper(II) to give a copper(I) compound and a dimerised thiophosphinic compound (Reaction 1.14).[38]

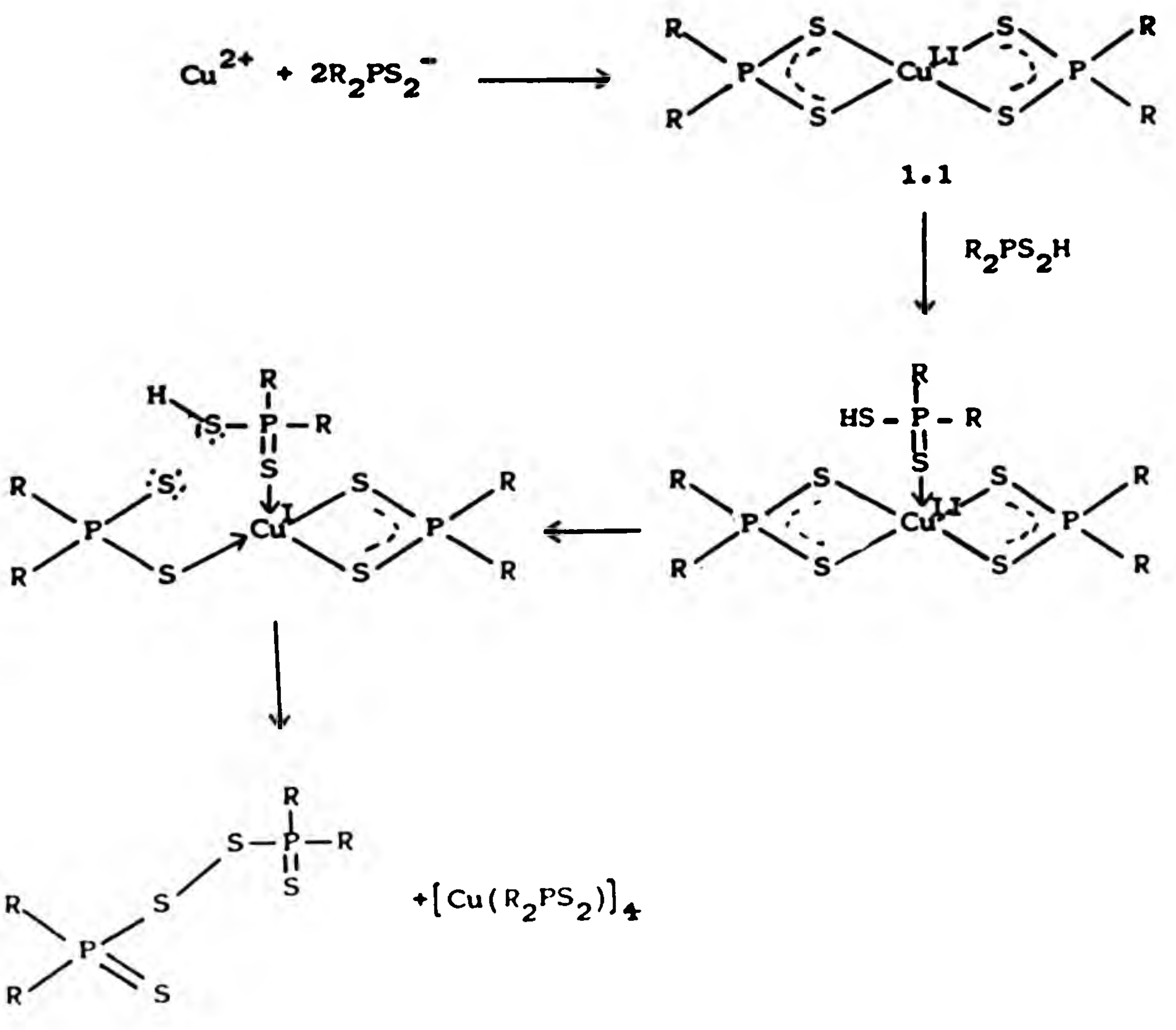
$$8R_2PS_2H + 4Cu^{2+} \longrightarrow [R_2PS_2Cu]_4 + 2R_2P(S)S_2P(S)R_2$$

Reaction 1.14

This reaction also occurs with $Au \xrightarrow{III} Au^{II}$. Thus it seems likely that in the reactions mentioned previously, especially where $LH = Ph_2P(S)SH$, the same process would occur, or alternatively, hydrogen abstraction by the radical may take place to give the protonated ligand, LH.

It is possible that Reaction 1.14 involves the formation of a copper(II) complex as an intermediate (1.1 in Scheme 1.4). This could then be attacked by another R_2PS_2H molecule (as a Lewis base) which could cause an internal redox reaction to occur. Ions of the type $R_2PS_2^-$ are extremely good at stabilising low oxidation states and thus once the copper is in oxidation state (I) expulsion of the dimer $R_2P(S)-S_2-P(S)R_2$ can occur. A possible mechanism for this is outlined in Scheme 1.4. The copper(I) complex formed, $Cu(R_2PS_2)$, then associates with three other $Cu(R_2PS_2)$ units to form an unreactive oligomeric structure, before further reactions with R_2PS_2H can occur.

Scheme 1.4



$Mn(acac)_3$ is used to oxidise thiols to give the disulphide as the major product.[39,40] The mechanism proposed for this reaction is shown in Scheme 1.5.

Scheme 1.5

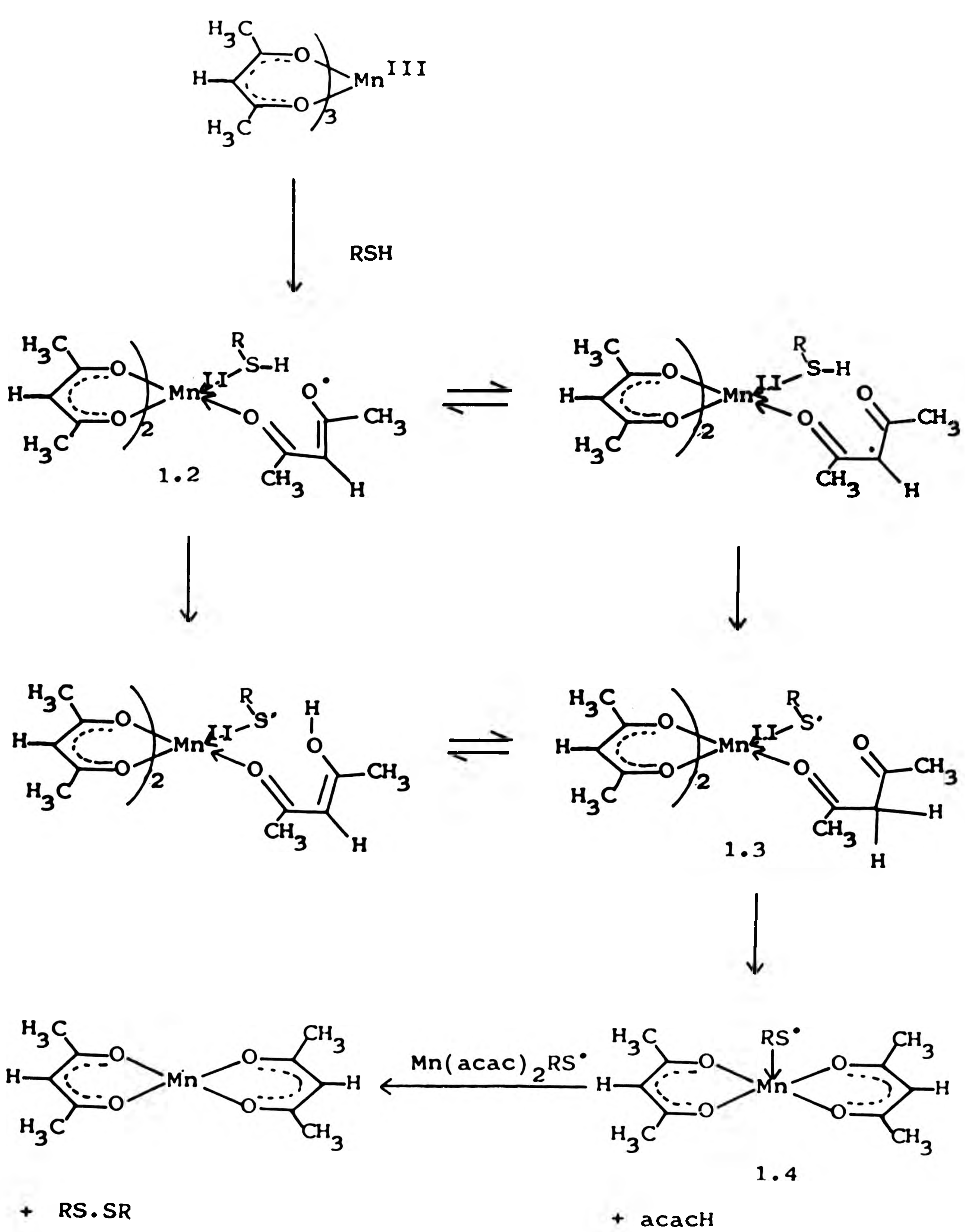
(i) $RS^- + Mn^{III} \longrightarrow [RS^\bullet] + Mn^{II}$

(ii) $[RS^\bullet] + Mn^{III} \longrightarrow RS^+ + Mn^{II}$

(iii) $RS^+ + RS^- \longrightarrow RSSR$

The manganese(II) product is the bisacetylacetonate. If step (i) in Scheme 1.5 is correct then an $acac^-$ ligand has been replaced by an RS^- ligand to give $Mn(acac)_2(RS)$, which then undergoes an internal redox reaction to give manganese(II) and $[RS^\bullet]$. It would be extremely unlikely that $[RS^\bullet]$ would attack another $Mn(acac)_3$ molecule to give $Mn(acac)_2$ and RS^+. The radical $[RS^\bullet]$ is much more likely to abstract hydrogen from elsewhere to give RSH. On this basis an alternative mechanism (Scheme 1.6) is for RSH to attack $Mn(acac)_3$ as a Lewis base, thus causing an internal redox reaction to occur with the formation of an acetylacetonyl radical (1.2 in Scheme 1.6). If this radical remains coordinated to the metal for a brief period it is possible for hydrogen abstraction from RSH to occur, thus forming an $[RS^\bullet]$ radical and acetyacetone (acacH) (1.3 in Scheme 1.6). The acetylacetone molecule then drops off to leave complex 1.4. It is possible for two complexes of type 1.4 to approach each other such that dimerisation of two $[RS^\bullet]$ radicals is possible, rather than $RS^\bullet$ abstracting hydrogen to give RSH and then RS•SR.

Scheme 1.6.



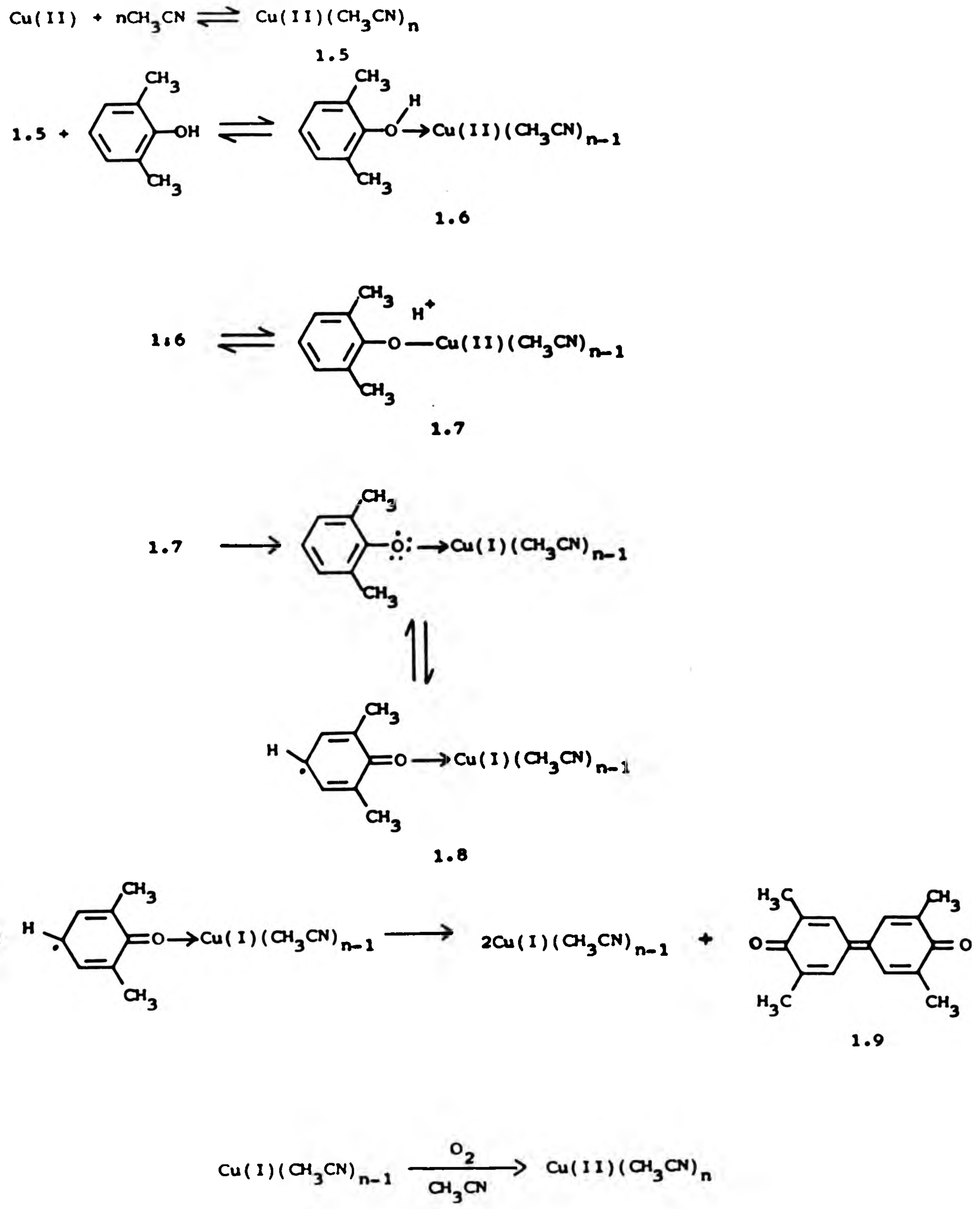
A reaction in which dimerisation occurs with ligands other than sulphur containing ones, is the copper(II) catalysed oxidative coupling of 2,6-dimethylphenol.[41] Here, copper(II) nitrate is added to acetonitrile so that the effective catalyst in the reaction is $Cu^{II}(CH_3CN)_n$ (1.5 in Scheme 1.7). It is thought that coordination of the phenolic group to copper(II) occurs, in a Lewis base type fashion, to give 1.6. Because of the electron deficiency on the oxygen atom of 2,6-dimethylphenol caused by the interaction with the copper(II) ion, species 1.6 may then lose a proton to give 1.7, which contains a phenolate anion as a ligand. An internal redox reaction then occurs to give copper(I) and a phenolate radical. Rearrangement follows to give 1.8, which leads to coupling to give 1.9. It was found that the copper(I) complex could be reoxidised to active copper(II) species with molecular oxygen.

From these examples it can be seen that when coupling of two ligand radicals occurs it is when the metal complex involved in the reaction acts as a substrate at which dimerisation can occur, or when the product expected from the more common reactions of ligand radicals (such as H-abstraction) is unstable and reacts further to give dimerisation products.

1.2.3 Reaction of [L•] with base or metal complex to give other products.

There are only a few examples of this type of reaction in the literature.[1,11,26,42] These reactions tend to occur

Scheme 1.7.


Cu(II) + nCH3CN ⇌ Cu(II)(CH3CN)n
1.5
1.5 +
1.6
1.6
1.7
1.7
1.8
2
2Cu(I)(CH3CN)n-1 +
1.9
Cu(I)(CH3CN)n-1
O2
CH3CN
Cu(II)(CH3CN)n

when the Lewis base used is of a reactive nature and is capable of attacking $[L^{\bullet}]$ such that the species $[LB\text{-}L^{\bullet}]$ formed during this reaction is still capable of reacting further as a radical. Such a Lewis base is triphenylphosphine which will readily attack oxygen or sulphur containing compounds in order to increase its valency to five. An example of such a reaction is that of $[Ni(Et_2NCSS)_3]^+$ with triphenylphosphine (Reaction 1.15).[26]

$$\begin{aligned}[Ni(Et_2NCSS)_3]PF_6 + Ph_3P \longrightarrow & \ Ni(Et_2NCSS)_2 + Ph_3PS \\ & + [Ph_3PC(=S)NEt_2]PF_6 \\ & + [Ni(Ph_3P)_2(Et_2NCSS)]PF_6\end{aligned}$$

Reaction 1.15

It can be seen from this reaction that an internal redox reaction has occurred in which a two electron reduction has taken place such that $Ni^{IV} \longrightarrow Ni^{II}$, with the release of diethyldithiocarbamyl radicals. The authors have proposed that initially the Ni(IV) complex reacts with triphenylphosphine to give an intermediate Ni(II) complex and diethyldithiocarbamyl radicals, which combine to give the thiuram disulphide (Reaction 1.16).

$$\begin{aligned}[Ni(Et_2NCSS)_3]PF_6 + 2Ph_3P \longrightarrow & \ [Ni(Ph_3P)_2(Et_2NCSS)]PF_6 \\ & + (Et_2NCSS)_2\end{aligned}$$

Reaction 1.16

The intermediate complex then reacts with the thiuram disulphide to give the final reaction products (Reaction 1.17).

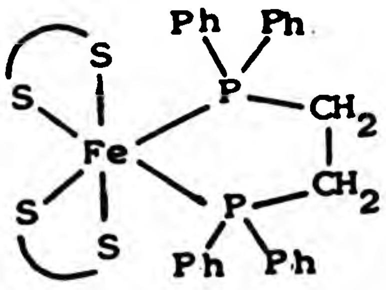
$$\begin{aligned}[\mathrm{Ni(Ph_3P)_2(Et_2NCSS)}]\ \mathrm{PF_6} + \mathrm{(Et_2NCSS)_2} &\longrightarrow \mathrm{Ni(Et_2NCSS)_2} \\ &\quad \mathrm{Ph_3PS} + [\mathrm{Ph_3PC(=S)NEt_2}]\ \mathrm{PF_6}\end{aligned}$$

Reaction 1.17

This mechanism was corroborated by reacting $(Et_2NCSS)_2$ with $[Ni(Ph_3P)_2(Et_2NCSS)]\ PF_6$, which resulted in the products shown in Reaction 1.17.

When Reaction 1.15 was carried out in a 1:2 ratio of complex to phosphine very little of the complex $[Ni(Ph_3P)_2(Et_2NCSS)]\ PF_6$ was isolated. However, when the phosphine concentration was increased the amount of $[Ni(Ph_3P)_2(Et_2NCSS)]\ PF_6$ obtained increased significantly. A likely explanation for this is that the excess phosphine reacts with the dithiocarbamyl radicals produced in the initial stage of Reaction 1.15 to give triphenylphosphine sulphide and a new ligand radical. This new radical then undergoes further reaction with triphenylphosphine to give rise to the other product isolated in the reaction, $[Ph_3PC(=S)NEt_2]\ PF_6$.

A similar reaction to 1.15 is that of $[Fe(Et_2NCSS)_3]\ BF_4$ with triphenylphosphine.[1] Again, triphenylphosphine sulphide was obtained together with $[Ph_3PC(=S)NEt_2]\ BF_4$ and $Fe(Et_2NCSS)_3$, representing a one electron reduction of $Fe^{IV} \longrightarrow Fe^{III}$. However, as iron(II) complexes of dithiocarbamates are usually unstable, it is possible that initially an iron(II) complex was formed which oxidised to an iron(III) complex. If this is the case then a similar mechanism as that proposed for Reaction 1.15 would operate, with triphenylphosphine reacting with ligand radicals produced during the internal redox reaction. If 1,2-di(diphenylphosphine)ethane (dppe) is used instead of triphenylphosphine, a stable iron(II) complex results (1.10) together with dppe dioxide and other, uncharacterised, products. In view of the reaction of [$Fe(Et_2NCSS)_3$] BF_4 with triphenylphosphine and the fact that no diethylthiuram disulphide was isolated in the reaction with dppe, it seems likely that these organic products have arisen by combination of a ligand radical with dppe.



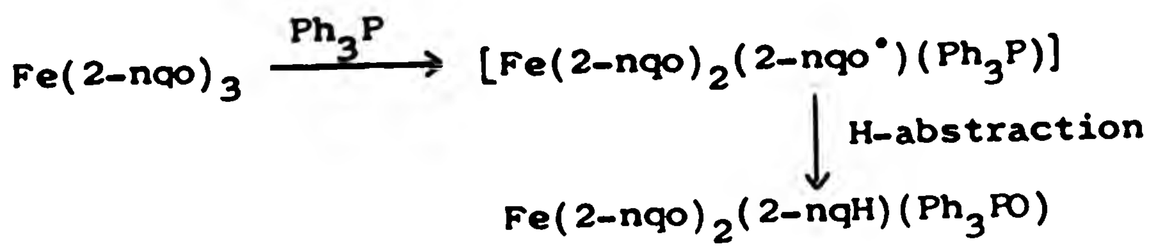
1.10

1.2.4 Coordination of [L•] to the metal.

Very few reactions of this type have been reported.[43-46] An electrochemical study (cyclic voltametry, d.c. polarography and differential pulse polarography) of iron(II) phthalocyanine was carried out in various solvents with supporting electrolytes.[46] Reduction to an iron(I) complex and an iron(I) phthalocyanine radical anion species was observed.

A study was then carried out by Smith et al on the reduction of the iron(III) complex of 3,10,17,24-tetrasulphonatophthalocyanine (tspc), using e.s.r.[45] Addition of $NaBH_4$ to an aqueous solution of iron(III)(tspc) containing 20% v/v of pyridine gave rise to a green solution which on standing for ten minutes turned violet. On the basis of the e.s.r. results and the previous results of Lever and Wilshire,[46] this was interpreted as being due to an iron(I) species with an anion radical species of the tspc. It was found that the system could be oxidised to iron(II)(tspc) and ultimately iron(III)(tspc) by molecular oxygen.

Another example of this type of behaviour has been noted during the present study. Thus the reaction of the complex $Fe(2\text{-}nqo)_3$ with triphenylphosphine leads to $Fe(2\text{-}nqo)_2(2\text{-}nqH)(Ph_3PO)$. The formation of this iron(II) product implies that the phosphine initiates an internal redox reaction to give rise to a reduced metal species and a ligand radical. This radical, whilst coordinated to the metal, reacts via hydrogen abstraction to give rise to the final iron(II) complex (Reaction 1.18).



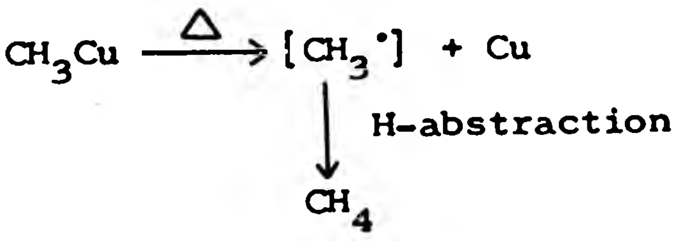
$$\begin{tikzcd} \mathrm{Fe(2\text{-}nqo)_3} \arrow[r, "\mathrm{Ph_3P}"] & {[\mathrm{Fe(2\text{-}nqo)_2(2\text{-}nqo^{\bullet})(Ph_3P)}]} \arrow[d, "\text{H-abstraction}"] \\ & \mathrm{Fe(2\text{-}nqo)_2(2\text{-}nqH)(Ph_3PO)} \end{tikzcd}$$

Reaction 1.18

1.3 The use of the internal redox reaction in organic synthesis.

1.3.1 Thermally initiated internal redox reactions.

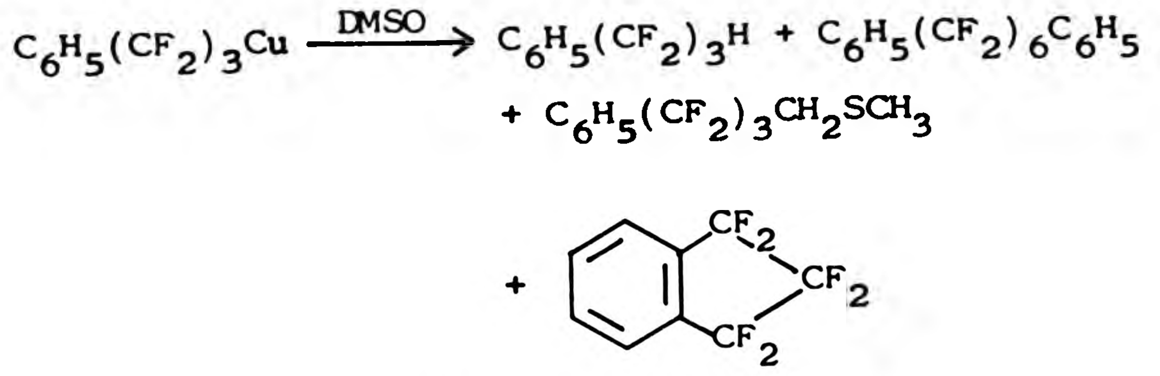
As noted earlier, methylcopper(I) undergoes an internal redox reaction upon heating to give either methane, or varying quantities of methane or ethane, according to the conditions of the decomposition.[15-17,47] Costa et al have found that the decomposition of pure, dry methylcopper(I) in a suspension in heptane gave methane, via methyl radicals, and copper metal only (Reaction 1.8, which is repeated here for clarity).[15-17]



Reaction 1.8

The thermal decomposition of methyl tris(triphenylphosphine)-copper(I) in the presence of a solvent is similar, but ethane is obtained as well as methane,[47-49] indicating that dimerisation has occurred by the interaction of two methyl radicals. There are a number of other organocopper reagents known which are unstable thermally and readily undergo internal redox reactions in a similar fashion.[47,50]

Perfluoroalkyl copper compounds when thermally decomposed in aprotic solvents give products that are mainly due to hydrogen abstraction. The decomposition of 3-phenylhexafluoropropyl copper(I) in dimethylsulphoxide has been examined in detail.[51] The major product arose as a result of hydrogen abstraction by the 3-phenylhexafluoropropyl radical. Accompanying products were the dimer and those resulting from a cyclisation and a reaction of the radical with the solvent (Reaction 1.19).



Reaction 1.19

No olefins from the elimination of fluorine by an ionic mechanism were isolated which is important since it has been suggested that perfluoro-tert-butylcopper(I) decomposes by a heterocyclic mechanism.[52]

The addition of organic compounds to solutions of metal compounds which decompose thermally has been used for the synthesis of new organic compounds. Thus, cerium(IV) acetate and manganese(III) acetate have been decomposed thermally in the presence of enolisable ketones together with olefins.[53] From acetone the radical $[\mathrm{MeCOCH_2}^{\bullet}]$ is formed, but the reaction (at least with Mn^{III}) is dependent on the enolisation rate of the ketone, so the exact mechanism of the oxidation of the enol remains obscure. Because of their low electron availability, the two oxo radicals formed are captured by olefin rather than by oxidant to give [$R\dot{C}H.CH_2.CH_2.COMe$]. Cerium(IV) is twelve times better at capturing this radical than manganese(III), but both give rise to a carbonium ion which may solvate or lose a proton.

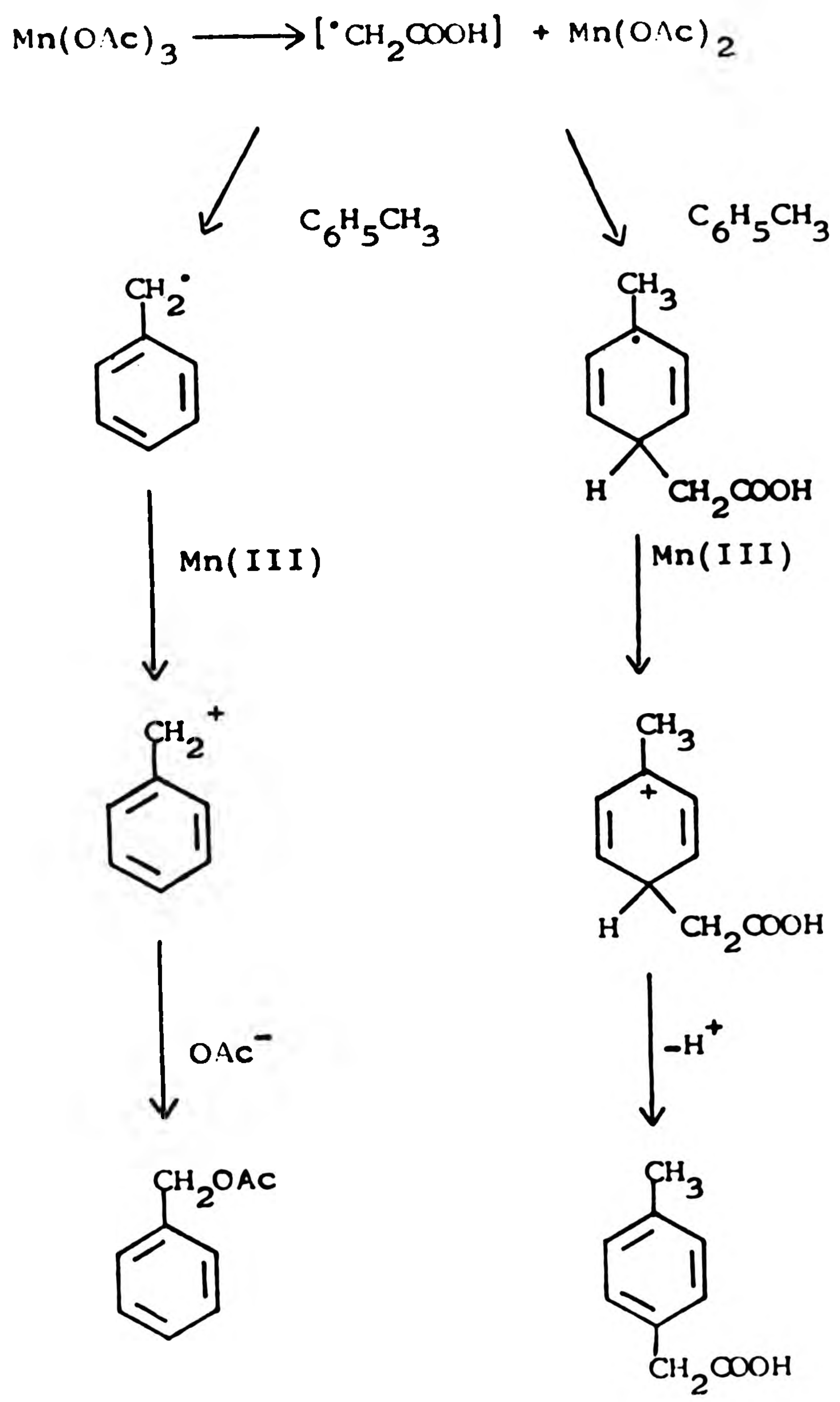
Heiba et al have shown that the manganese(III) acetate oxidation of aromatic hydrocarbons proceeds by two competing mechanisms;[54]

(i) a free radical mechanism resulting from the interaction of the aromatic hydrocarbon with the carboxymethyl radical, [$^\bullet CH_2COOH$], generated directly by the thermolysis of manganese(III) acetate.

(ii) An electron transfer mechanism which is of importance in the oxidation of aromatic hydrocarbons having ionisation potentials $\leqslant$8eV.

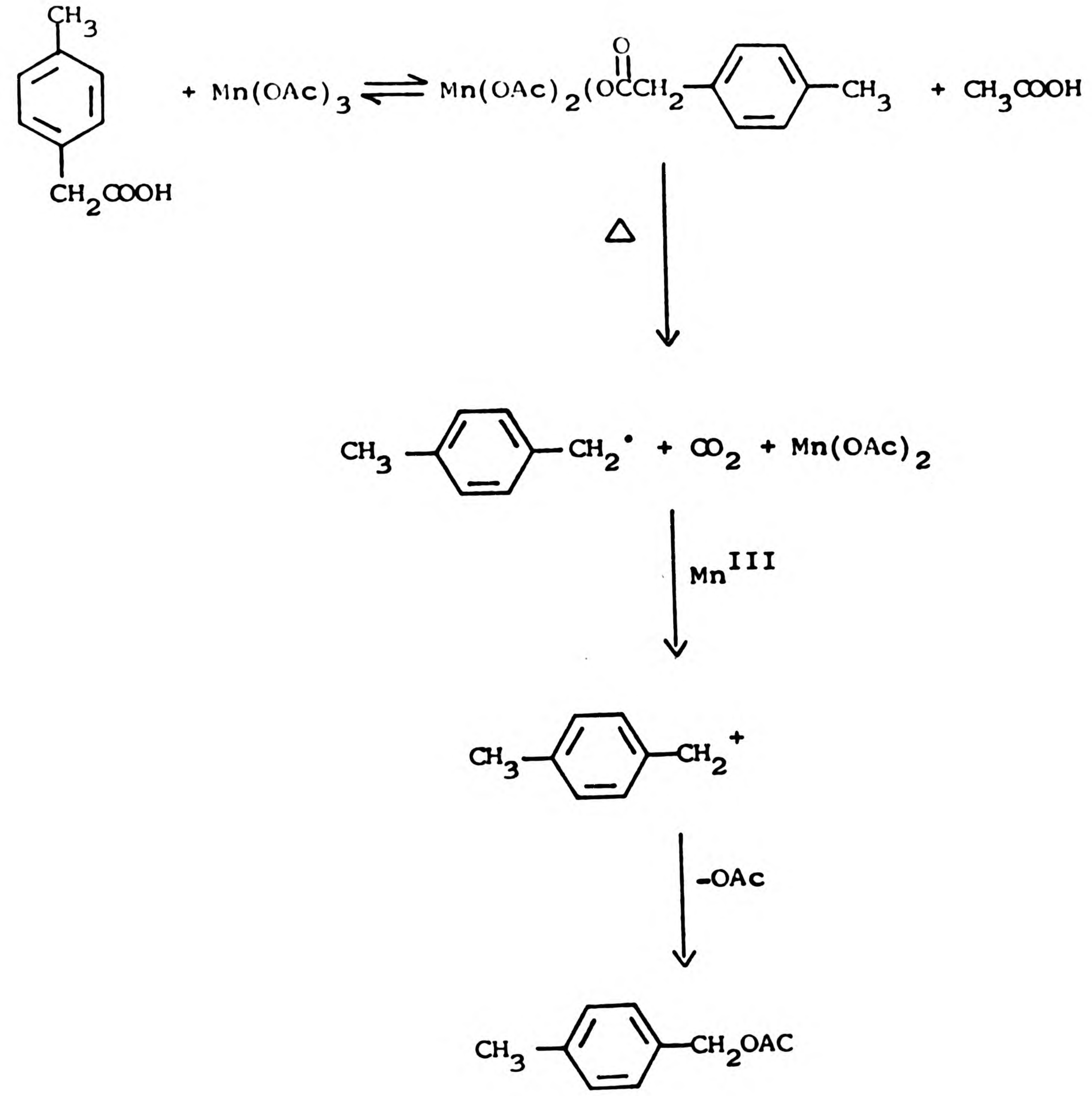
The relative extent of the electron transfer pathway can be suppressed by carrying out the reaction under anhydrous conditions or in the presence of potassium acetate. The [$^\bullet CH_2COOH$] radical reacts in two major ways (Scheme 1.8) to give the species 1.11 and 1.12. A further reaction can then occur between 1.12 and manganese(III) acetate to give a third product, 1.13,(Scheme 1.9). It is interesting to note that the radical formed after thermal decomposition of manganese(III) acetate is [$^\bullet CH_2COOH$] and not [$CH_3COO^\bullet$].The radical formed depends on the nature of R_1 and R_2 in $R_1R_2CHCOOH$. When R_1=R_2=H thermolysis proceeds almost exclusively to give [$^\bullet CH_2COOH$] (Reaction 1.20). If however R_1=R_2=an alkyl group, a further reaction (Reaction 1.21)

Scheme 1.8



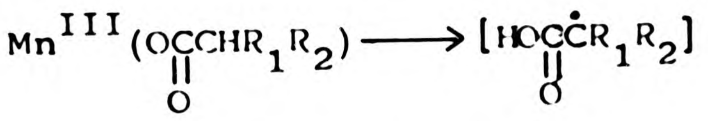
1.11 1.12

Scheme 1.9



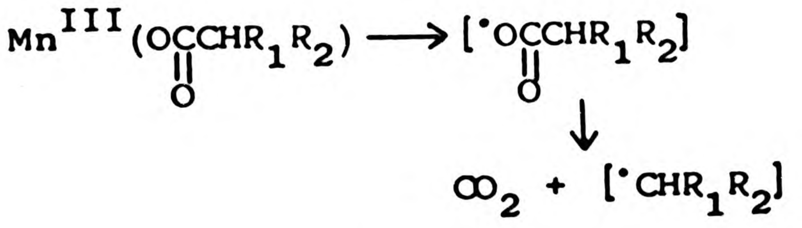
1.13

to give $[R_1R_2CHCOO^{\bullet}]$ is observed. When R_1 or R_2 is benzylic thermolysis proceeds predominantly via Reaction 1.21.



$$Mn^{III}(O\underset{\underset{O}{\|}}{C}CHR_1R_2) \longrightarrow [HO\underset{\underset{O}{\|}}{C}\dot{C}R_1R_2]$$

Reaction 1.20

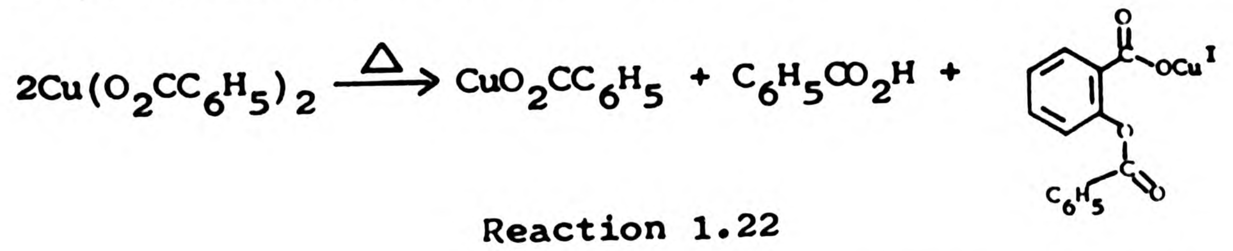


$$\begin{aligned} Mn^{III}(O\underset{\underset{O}{\|}}{C}CHR_1R_2) &\longrightarrow [{}^{\bullet}O\underset{\underset{O}{\|}}{C}CHR_1R_2] \\ &\qquad\qquad \downarrow \\ &\quad CO_2 + [{}^{\bullet}CHR_1R_2] \end{aligned}$$

Reaction 1.21

In either of these reactions an internal redox reaction occurs in which manganese(III) is reduced to manganese(II).

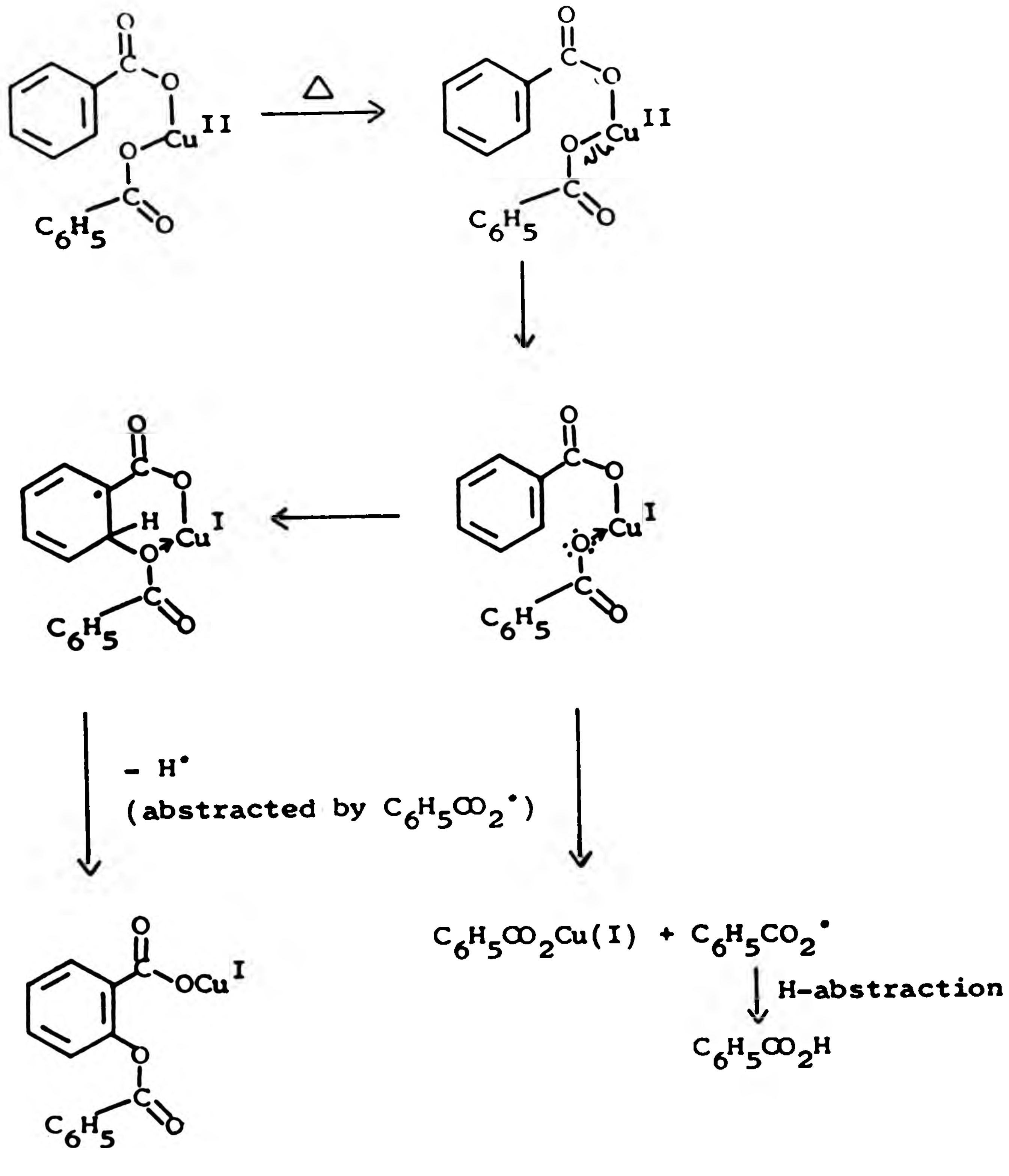
Thermolysis of the copper(II) compounds of aromatic carboxylic acids has been used as a method of oxidising the acids. An example of this is the thermolysis of cupric benzoate in an aprotic solvent (e.g. cyclohexane) to produce benzosalicyclic acid and two copper(I) compounds[55-58] (Reaction 1.22)



Reaction 1.22

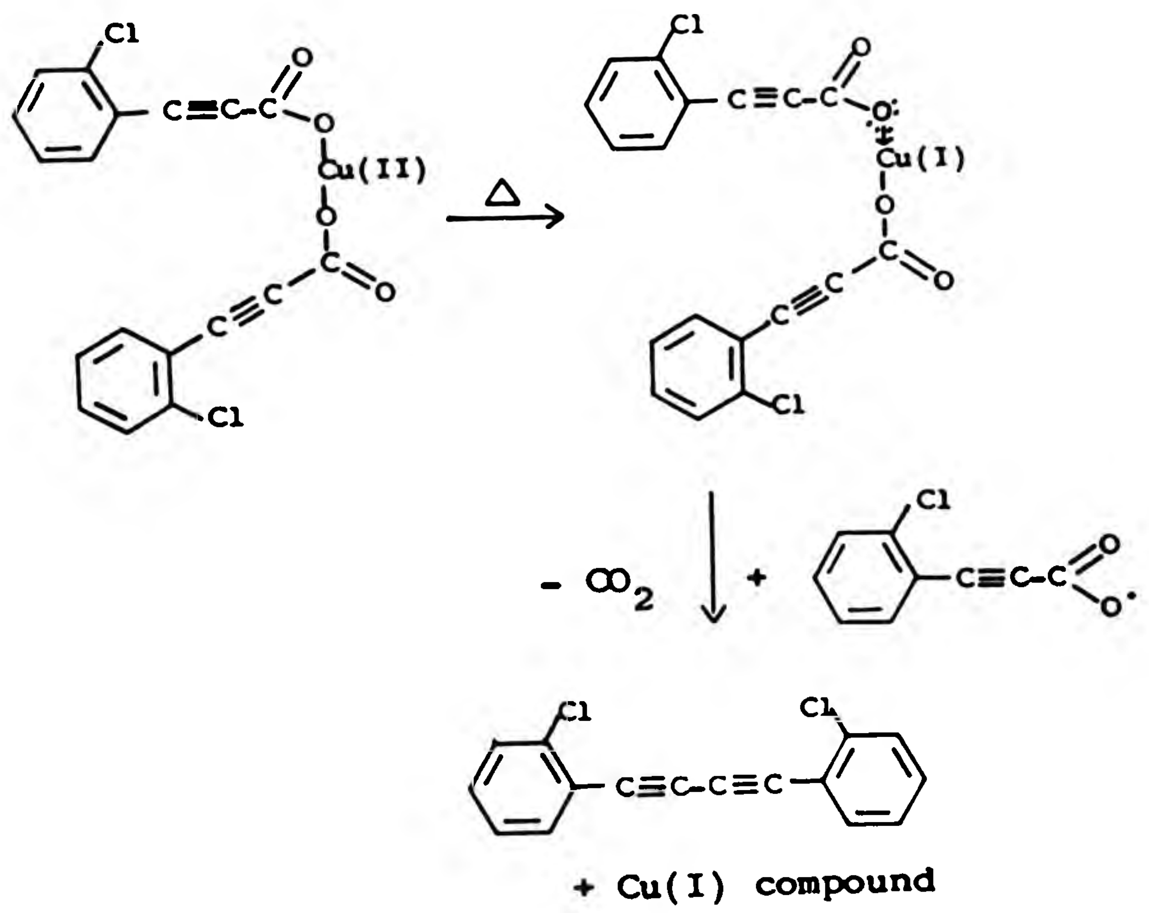
The products obtained in this reaction suggest that an internal redox reaction has occurred to produce a radical species which is able to coordinate to the metal in a Lewis base fashion. It thus remains in the vicinity of the metal and is able to attack the benzene ring ortho to the carboxylic acid group. A mechanism for this reaction is proposed in Scheme 1.10.

Scheme 1.10


Δ
Cu^{II}
Cu^{I}
C_6H_5
- H•
(abstracted by $C_6H_5CO_2^{\bullet}$)
OCu^{I}
$C_6H_5CO_2Cu(I)$ + $C_6H_5CO_2^{\bullet}$
H-abstraction
$C_6H_5CO_2H$

A similar reaction is that of copper(II) 2-chlorophenylpropiolate. This decomposes in refluxing pyridine to give carbon dioxide and bis(2-chlorophenyl)diacetylene.[59] This reaction can also be accounted for in terms of internal redox and a suitable mechanism is proposed in Scheme 1.11.

<u>Scheme 1.11</u>



As stated in Section 1.1, many of the reactions mentioned here involve systems where Lewis bases are present and thus it is probable that often the internal redox reaction is partially or wholly initiated by the base rather than thermally.

1.3.2 Photochemically initiated internal redox reactions.

This type of reaction has previously been described as an inner sphere, or intramolecular, redox process.[17] A large number of early studies have shown the synthetic use of metal compounds in reactions involving organic compounds, e.g. iron(III) compounds have been used in the oxidation of alcohols (Reactions 1.23 and 1.24).[60-69]

$$2FeCl_3 + RCH_2OH \xrightarrow{h\nu} 2FeCl_2 + RCHO + 2HCl$$

Reaction 1.23

$$2Fe(ClO_4)_3 + RCH_2OH \xrightarrow{h\nu} 2Fe(ClO_4)_2 + RCHO + 2HClO_4$$

Reaction 1.24

Two possible mechanisms have been proposed for these reactions, both involving internal redox reactions and radical formation. For Reaction 1.23 it has been proposed that the radical produced initially is $[Cl^\bullet]$,which then reacts further (Scheme 1.12).[60-62,64-66]

Scheme 1.12

(i) $Fe^{III}Cl_3 \xrightarrow{h\nu} Fe^{II}Cl_2 + [Cl^\bullet]$

(ii) $RCH_2OH + [Cl^\bullet] \longrightarrow [R\dot{C}HOH] + HCl$

(iii) $[R\dot{C}HOH] + Fe^{III}Cl_3 \longrightarrow RCHO + HCl + Fe^{II}Cl_2$

For reaction 1.24 it has been proposed that an iron complex is first formed with the alcohol, so that upon irradiation the initial radical formed is $[RCH_2O^\bullet]$ (Scheme 1.13).[63,68] By either mechanism the final products are the same. Step (iii) in both Schemes probably involve the formation of an intermediate adduct, 1.11, which facilitates the formation of the aldehyde (e.g. Scheme 1.14).

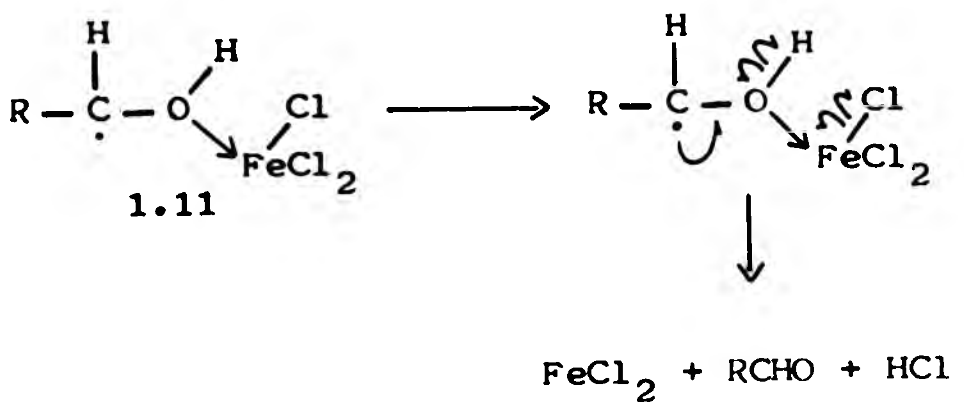
Scheme 1.13

(i) $[\mathrm{FeOCH_2R}]^{2+} \xrightarrow{h\nu} \mathrm{Fe}^{2+} + [\mathrm{RCH_2O^{\bullet}}]$

(ii) $[\mathrm{RCH_2O^{\bullet}}] + \mathrm{RCH_2OH} \longrightarrow \mathrm{RCH_2OH} + [{}^{\bullet}\mathrm{RCHOH}]$

(iii) $[{}^{\bullet}\mathrm{RCHOH}] + \mathrm{Fe^{III}(ClO_4)_3} \longrightarrow \mathrm{RCHO} + \mathrm{Fe^{II}(ClO_4)_2} + \mathrm{HCl}$

Scheme 1.14



Another photochemically induced internal redox reaction that has found use synthetically is that of copper(II) chloride being used as a chlorinating agent (Scheme 1.15).[58]

Scheme 1.15

(i) $\mathrm{CuCl_2} \xrightarrow{h\nu} \mathrm{CuCl} + [\mathrm{Cl^{\bullet}}]$

(ii) $\mathrm{C_6H_5CH_3} + [\mathrm{Cl^{\bullet}}] \longrightarrow [\mathrm{C_6H_5CH_2^{\bullet}}] + \mathrm{HCl}$

(iii) $[\mathrm{C_6H_5CH_2^{\bullet}}] + \mathrm{CuCl_2} \longrightarrow \mathrm{C_6H_5CH_2Cl} + \mathrm{CuCl}$

This reaction was modified by Kochi by the addition of lithium chloride.[70] The selectivity of this reagent in alkane chlorination was found to be the same as for photohalogenations by molecular chlorine, hence the mechanism given in Scheme 1.16 was postulated.

Scheme 1.16

(i) $CuCl_2 + nCl^- \longrightarrow CuCl_{n+2}^{n-}$

(ii) $CuCl_{n+2}^{n-} \xrightarrow{h\nu} CuCl_{n+1}^{n-} + [Cl^\bullet]$

(iii) $RH + [Cl^\bullet] \longrightarrow HCl + [R^\bullet]$

(iv) $CuCl_{n+2}^{n-} + [R^\bullet] \longrightarrow RCl + CuCl_{n+1}^{n-}$

Steps (ii) and (iv) involve internal redox reactions to produce copper(I) and $[Cl^\bullet]$ radicals.

Another photochemical reaction which gives rise to the formation of an aldehyde from an alcohol has recently been described by Ferraudi and Carrasco.[71] In this reaction $[FeL(OMe)MeOH)]^{2+}$ (LH = dimethylglyoxime) undergoes an internal redox reaction upon photolysis to give reduction of the metal and an $[{}^\bullet OMe]$ radical. This radical reacts further such that the final product obtained is $[FeL(MeOH)_2]^{2+}$ (Scheme 1.17).

Scheme 1.17

(i)
$$\begin{tikzcd}
{[FeL(OMe)(MeOH)]^{2+}} \arrow[r, "h\nu"] & \{[FeL(MeOH)], MeO^\bullet\} \arrow[dl] \arrow[dr] & \\
{[FeL(MeOH)_2]^{2+} + [{}^\bullet CH_2OH]} & & {[FeL(MeOH)_2]^{2+} + [CH_3O^\bullet]}
\end{tikzcd}$$

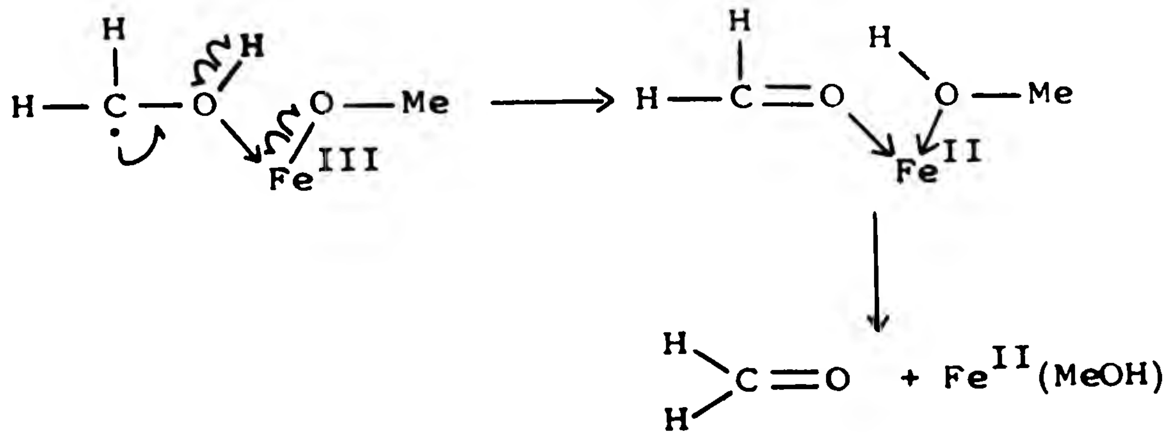
(ii) $[CH_3O^\bullet] + CH_3OH \longrightarrow CH_3OH + [{}^\bullet CH_2OH]$

(iii) $2[{}^\bullet CH_2OH] \longrightarrow CH_2O + CH_3OH$

(iv) $[{}^\bullet CH_2OH] + [FeL(OMe)(MeOH)]^{2+} \longrightarrow [FeL(MeOH)_2]^{2+} + CH_2O$

As described previously for Reactions 1.23 and 1.24, step (iv) of this mechanism is likely to involve an intermediate adduct between the radical [$^\bullet CH_2OH$] and the iron complex (Scheme 1.18).

Scheme 1.18



Organic acid complexes of iron also undergo photoreduction to give aldehydes (Scheme 1.19).[72-75]

Scheme 1.19

(i) $[Fe^{III}(RCHOHCOO^-)]^{2+} \xrightarrow{h\nu} Fe^{2+} + [RCHOHCOO^\bullet]$

(ii) $[RCHOHCOO^\bullet] + [Fe^{III}(RCHOHCOO^-)]^{2+} \longrightarrow Fe^{2+} + RCHO + H^+$
$+ RCHOHCOO^-$

The above mechanism is supported by kinetic[73,75] and stoichiometric[76,77] evidence.

Finally, an example of a photoreduction of a metal in which a two electron reduction occurs, is the photochemical reduction of alkylmercury(II) compounds. (Reaction 1.25).[78]

$$RHgOAc + BNAH \xrightarrow[AIBN]{h\nu} RH + [BNA]OAc + Hg$$

(BNAH = N-benzyl-1,4-dihydronicotinamide)
(AIBN = azobis(isobutyronitrile)

Reaction 1.25

The proposed mechanism for this reaction is outlined in Scheme 1.20.

Scheme 1.20

(i) $RHg^{II}OAC \xrightarrow{h\nu} [R^{\bullet}] + Hg^{I}OAc$

(ii) $AIBN \xrightarrow{h\nu} [R^{\bullet\prime}]$

(iii) $[R^{\bullet\prime}] + BNAH \longrightarrow R'H + [BNA^{\bullet}]$

(iv) $[R^{\bullet}] + BNAH \longrightarrow RH + [BNA^{\bullet}]$

(v) $[BNA^{\bullet}] + RHgOAC \longrightarrow BNA^{+} + RHg + OAc^{-}$

(vi) $RHg \xrightarrow{h\nu} [R^{\bullet}] + Hg$

A more likely mechanism, however, should include another step, either instead of or with step (v) of the mechanism (Reaction 1.26).

$$[BNA^{\bullet}] + Hg^{I}OAc \longrightarrow BNAOAc + Hg$$

Reaction 1.26

1.3.3 The use of internal redox reactions in catalysis.

A large number of catalytic reactions involving an internal redox mechanism comprise complex formation between the metal compound and the organic reactant, usually in the form of a Lewis base adduct. Because of this the major compounds formed from these reactions are generally produced in high yield, with little isomerisation of products occurring. One such reaction is the copper chloride catalysed reaction between aliphatic amines and carbon tetrachloride.[79] Asscher and Vofsi proposed the mechanism outlined in Scheme 1.21.

Scheme 1.21

initiation (i) $Cu^{2+} + RCH_2NR'R'' \longrightarrow Cu^{+} + [R\dot{C}HNR'R''] + H^{+}$

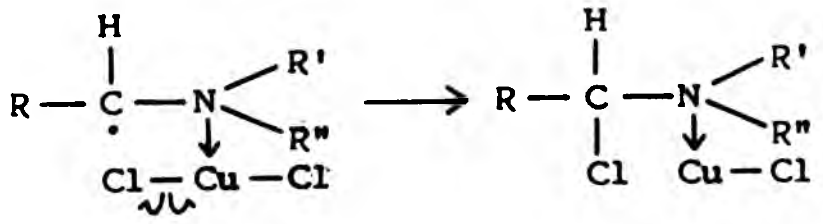
propagation (ii) $Cu^{+} + CCl_4 \longrightarrow [CuCl]^{+} + [{}^{\cdot}CCl_3]$

(iii) $[{}^{\cdot}CCl_3] + RCH_2NR'R'' \longrightarrow CHCl_3 + [R\dot{C}HNR'R'']$

(iv) $[R\dot{C}HNR'R''] + [CuCl]^{+} \longrightarrow RCHClNR'R'' + Cu^{+}$

termination (v) $2[R^{\cdot}] \longrightarrow$ products

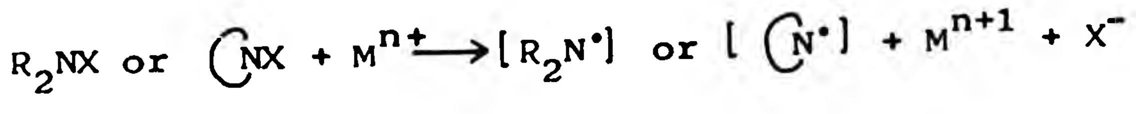
If a complex forms between $[R\dot{C}HNR'R'']$ and $[CuCl]^{+}$ this increases the possibility of chlorine abstraction occurring rather than hydrogen abstraction from elsewhere (Reaction 1.27).



Reaction 1.27

Thus, here an internal redox reaction has occurred such that $Cu^{II} \rightarrow Cu^{I}$ with the formation of a chlorine radical species, $[Cl^{\cdot}]$. This type of complexation probably occurs in the Sandmeyer and Meerwein reactions too. Both of these reactions have been shown to operate via a metal catalysed route,$^{80-83}$ such as the reactions discussed above.

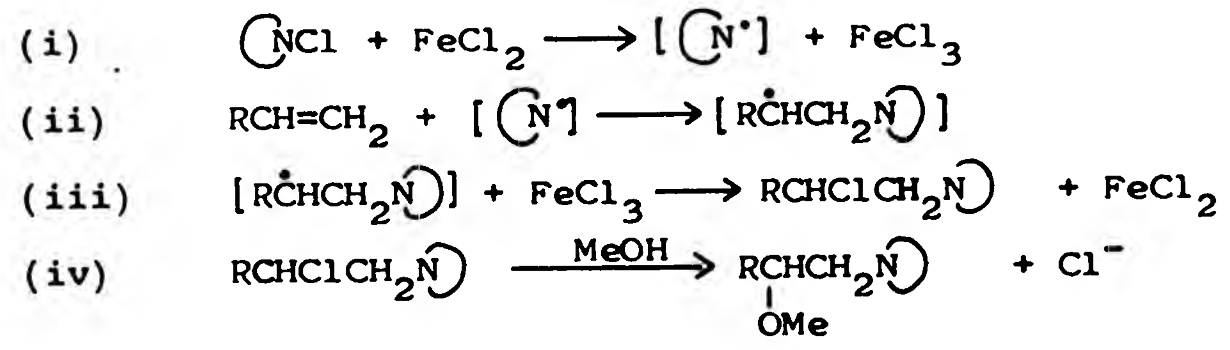
If instead of aliphatic amines N-haloalkylamines and N-haloheterocycloamines are used, then Reaction 1.28 occurs.



Reaction 1.28

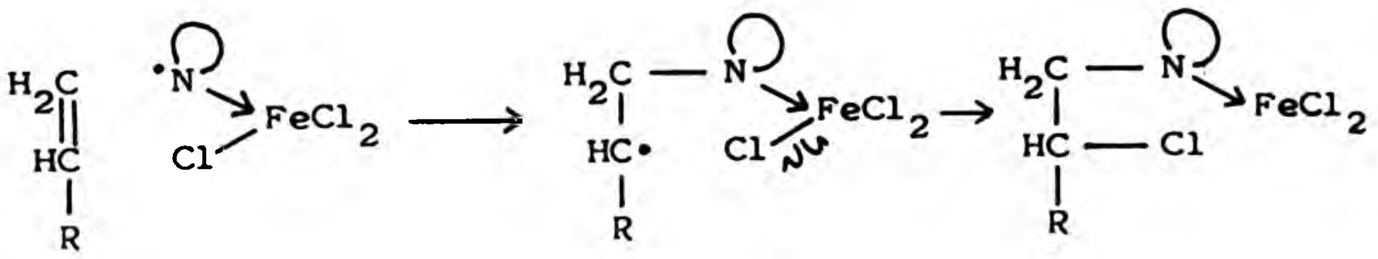
For example, the reaction of N-chloropiperidine with styrene or p-chlorostyrene in the presence of iron chlorides resulted in adducts which were converted into amino-ethers.[84] (Scheme 1.22).

Scheme 1.22



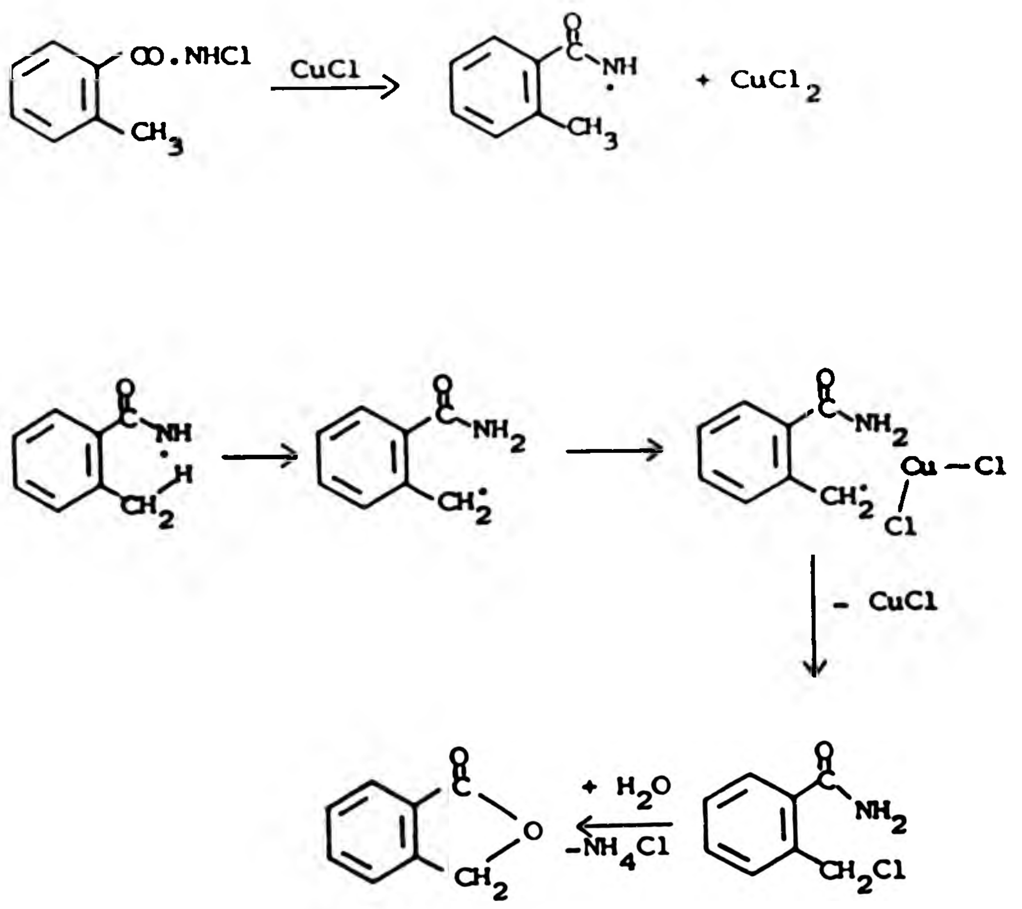
As in reactions mentioned previously, this probably involves an intermediate metal-radical complex such that steps (ii) and (iii) are almost simultaneous (Scheme 1.23).

Scheme 1.23

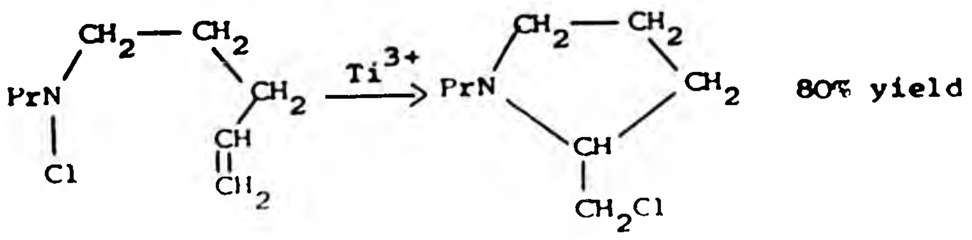


This also occurs in the addition of N-chloropiperidine to cyclohexene.[85,86] In acidic medium the reaction gives a mixture of cis and trans products, whereas in a non-acidic medium it gives mainly the cis isomer. This stereoselectivity can be explained if a coordination of unprotonated amino group to an iron(III) centre takes place (as in previous reactions mentioned). Thus when the internal redox reaction occurs to give [Cl•] it is alligned in a cis fashion. In acidic medium the N-chloropiperidine is protonated, so no coordination to iron can occur. Hence a less stereospecific reaction occurs. A similar reaction is used in the preparation of lactones (e.g. Scheme 1.24).[21]

Scheme 1.24



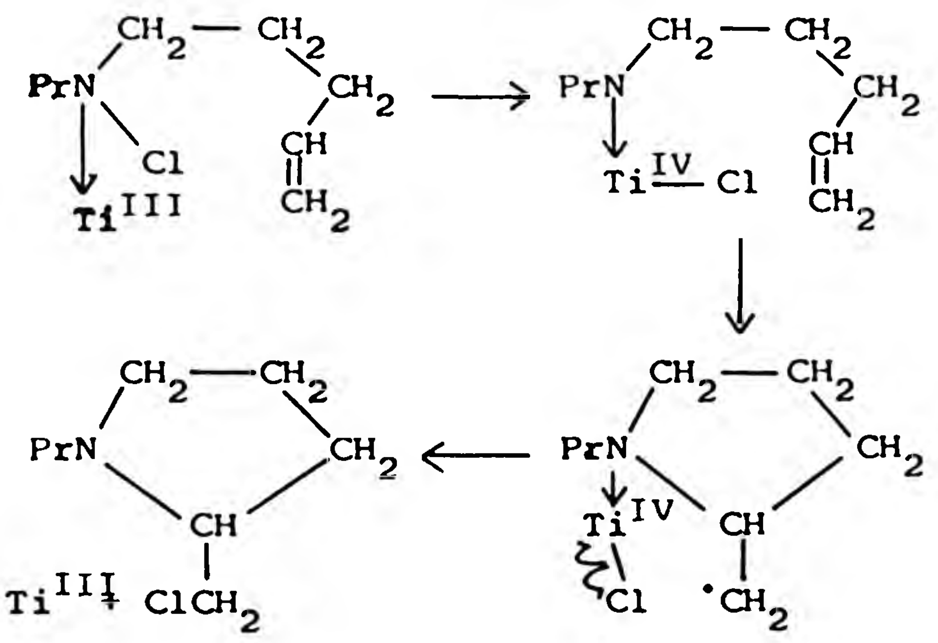
Although the majority of these reactions involve iron or copper catalysts, a ring closure involving a titanium catalyst has been reported (Reaction 1.29).[87]



Reaction 1.29

It seems likely that this too would involve the formation of an intermediate complex and an internal redox process (Scheme 1.25).

Scheme 1.25



Oxygen containing compounds can act as Lewis bases also. Thus it has been suggested that several systems involving peroxides and hydroperoxides with copper or iron catalysts also involve intermediate complexes. Scheme 1.26 shows a generalised mechanism for the copper catalysed reactions.

Scheme 1.26

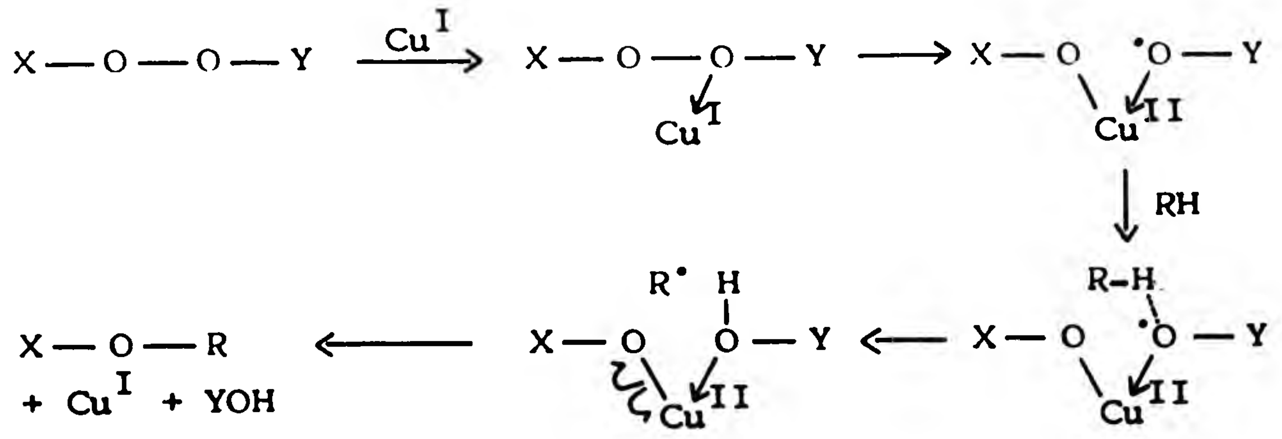
(i) $XOOY + Cu^{I} \longrightarrow XOCu^{II} + [YO^{\bullet}]$

(ii) $RH + [YO^{\bullet}] \longrightarrow [R^{\bullet}] + YOH$

(iii) $[R^{\bullet}] + XOCu^{II} \longrightarrow ROX + Cu^{I}$ e.t.c.

A possible mechanism for this reaction, involving adduct formation is outlined in Scheme 1.27.

Scheme 1.27



Another important section in catalysis which involves internal redox reactions is that which deals with the metal catalysed addition of organic polyhalides to olefins. Organic polyhalides such as carbon tetrachloride, trichloroacetate or chloroform are known to generate radical species on reaction with metal compounds, which then add to olefins (Reaction 1.30).[80,88-90]

$$CCl_3X + CH_2{=}\overset{R}{C}{-}Y \xrightarrow{\text{metal compound}} X{-}CCl_2{-}CH_2{-}\overset{R}{\underset{Cl}{C}}{-}Y$$

Reaction 1.30

The first detailed study of this type of reaction was carried out by Asscher and Vofsi.[88] The addition of carbon tetrachloride to olefins had been extensively investigated by Kharasch et al, who proposed a free radical chain mechanism (Scheme 1.28).[91] In this mechanism, step (iii) is of minor importance for non-polymerisable olefins, but in reactions of styrene, butadiene, acrylates and acrylonitrile this step predominates over step (ii) to the extent that polymers are obtained, even for carbon tetrachloride-monomer ratios as high as 100:1.[92] Each polymeric chain incorporates the elements of one molecule of carbon tetrachloride.

Scheme 1.28

(i) $[CCl_3^{\bullet}] + CHR{=}CHR' \longrightarrow [CCl_3\text{-}CHR\text{-}CHR'^{\bullet}]$

(ii) $[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + CCl_4 \longrightarrow CCl_3\text{-}CHR\text{-}CHR'Cl + [CCl_3^{\bullet}]$

(iii) $[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + CHR{=}CHR' \longrightarrow [CCl_3\text{-}CHR\text{-}CHR'\text{-}CHR\text{-}CHR'^{\bullet}]$

e.t.c.

Asscher and Vofsi found that good yields of 1:1 adducts are obtained from carbon tetrachloride and olefins in molar ratios of 2:1 or less if the reaction is catalysed by one mole % of copper(I) or copper(II) chloride. With iron(II) or iron(III) chloride a 1:1 adduct or telomers (telomer denotes an oligomer with a residue from the chain-transfer agent attached at each end) or both are obtained, depending on the nature of the olefin and on the reaction conditions.[93] This was attributed to the fact that step (iii) in Scheme 1.28 is superseded by the reduction-oxidation steps (i) and (ii) in Scheme 1.29.[88]

Scheme 1.29

(i) $[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + MCl^+ \longrightarrow CCl_3\text{-}CHR\text{-}CHR'Cl + M^+$

(ii) $M^+ + CCl_4 \longrightarrow MCl^+ + [CCl_3^{\bullet}]$

(M^+ stands for cuprous or ferrous ion and MCl^+ for cupric or ferric ion with at least one chlorine ligand in the oxidation shell.)

It can be seen that step (i) in Scheme 1.29 is in fact an internal redox reaction (Scheme 1.30).

Scheme 1.30

$$[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + Cl\overset{\curvearrowright\curvearrowright}{-}M^{n}$$
$$\downarrow$$
$$[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + [Cl^{\bullet}] + M^{n-1}$$
$$\downarrow$$
$$CCl_3\text{-}CHR\text{-}CHR'Cl + M^{n-1}$$

Step (i) in Scheme 1.29 had already been postulated by Minisci and Pallini for the formation of the 1:1 adduct of carbon tetrachloride with acrylonitrile,[94] which they and their co-workers obtained in low yield on heating the components in a steel autoclave at 160 °C (Scheme 1.31).[95]

Scheme 1.31

(i) $CCl_4 \xrightarrow{Fe^{2+}} [CCl_3^{\bullet}]$

(ii) $[CCl_3^{\bullet}] + CH_2\text{=}CH\text{-}CN \longrightarrow [CCl_3\text{-}CH_2\text{-}CH(CN)^{\bullet}]$

(iii) $[CCl_3\text{-}CH_2\text{-}CH(CN)^{\bullet}] + [FeCl]^{2+} \longrightarrow CCl_3\text{-}CH_2\text{-}CHCl\text{-}CN + Fe^{2+}$

Step (ii) in Scheme 1.29 can be considered as the initiating step in this reaction when iron(II) or copper(I) salts are used. However, if iron(III) or copper(II) salts are used, the initiating step is that in which reduction to iron(II) or copper(I) takes place. It was observed that copper(II) chloride is slowly reduced by methanol, but iron(III) chloride required the addition of benzoin or tin(II) chloride before reduction would occur.

Asscher and Vofsi also investigated the addition of chloroform to olefins using iron(III) and copper(II) chlorides.[80] They found that whilst non-polymerisable olefins yield 1:1 adducts with carbon tetrachloride, both in peroxide induced and redox reactions, for chloroform the case is different. Ordinary sources of free radicals induce addition across the double bond in the sense CCl_3-H, as the radical formed in step (i) in Scheme 1.32 abstracts hydrogen from chloroform.[91,96-98]

Scheme 1.32

(i) $[CCl_3^{\bullet}] + R\text{-}CH{=}CHR' \longrightarrow [CCl_3\text{-}CHR\text{-}CHR'^{\bullet}]$

(ii) $[CCl_3\text{-}CHR\text{-}CHR'^{\bullet}] + CHCl_3 \longrightarrow CCl_3\text{-}CHR\text{-}CH_2R' + [CCl_3^{\bullet}]$

Redox transfer however leads to specific chlorine activation by the propagating sequence shown in Scheme 1.33, with an internal redox reaction in step (iii) giving rise to the final organic product.

Scheme 1.33

(i) $M^{+} + CHCl_3 \longrightarrow MCl^{+} + [CHCl_2^{\bullet}]$

(ii) $[CHCl_2^{\bullet}] + R\text{-}CH{=}CHR' \longrightarrow [CHCl_2\text{-}CHR\text{-}CHR'^{\bullet}]$

(iii) $[CHCl_2\text{-}CHR\text{-}CHR'^{\bullet}] + MCl^{+} \longrightarrow CHCl_2\text{-}CHR\text{-}CHR'Cl + M^{+}$

Thus isomeric adducts can be formed selectively by mechanisms which are both of the radical chain type. The relative unimportance of any side reactions in the synthesis involving redox steps is a direct outcome of the effeciency of the internal redox reaction occurring in step (iii) of Scheme 1.33. This was also found by Murai et al in the copper compound induced addition of ethyl trichloroacetate to olefins (Reaction 1.31).[89]

$$R\text{-}CH{=}CH_2 + CCl_3\text{-}COOC_2H_5 \xrightarrow{Cu^{+}} R\text{-}CHCl\text{-}CH_2\text{-}CCl_3\text{-}COOC_2H_5$$

($R = CN$, $COOC_2H_5$ or C_6H_{13})

Reaction 1.31

They proposed that the same mechanism as outlined previously occurred here also (Reaction 1.32).

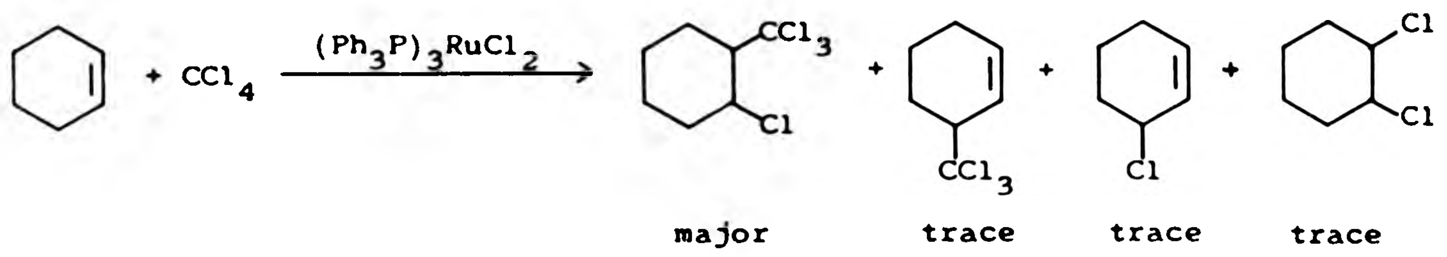
$$[\mathrm{R{-}\underset{\bullet}{C}H{-}CH_2{-}CCl_3{-}COOC_2H_5}] + \mathrm{CuCl}^{+} \longrightarrow \mathrm{R{-}CHCl{-}CH_2{-}CCl_3{-}COOC_2H_5} + \mathrm{Cu}^{+}$$

Reaction 1.32

Because of the high effeciency of the internal redox reaction in this synthesis the telomer formation was suppressed and 1:1 adducts were obtained exclusively.

More recently, Burton and Kehoe have used this type of reaction to add polyhaloalkanes, such as $CF_2BrCFClBr$, to alkenes and found that increasing reactivity of the halogenated alkane directly parallels the ease with which a halogen atom is abstracted from the molecule.[99-101] Also, trichloro- and dichloroacetonitriles have been successfully added to olefins to give high yields of 2,2,4-trichloro- and 2,4-dichlorobutyronitriles.[102]

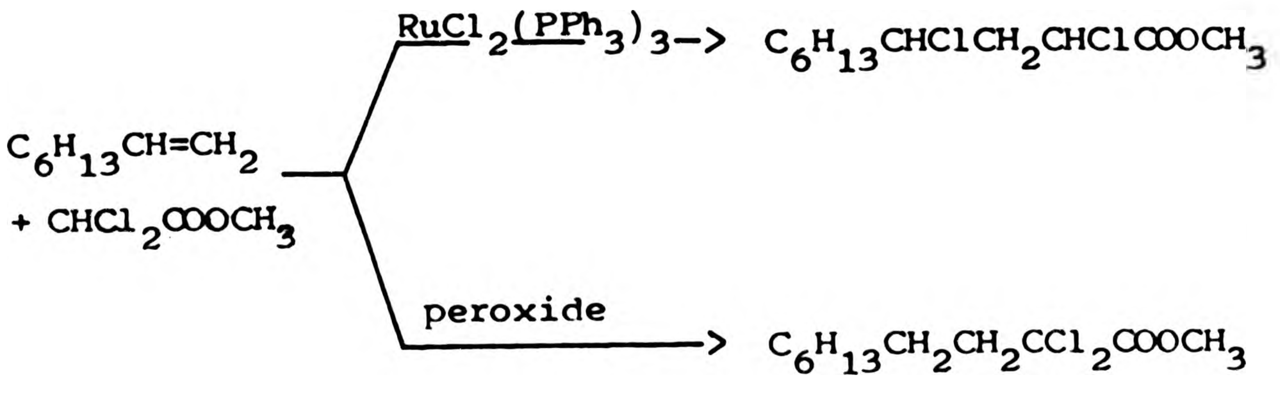
As well as iron and copper compounds, another catalyst that has found use in recent years is dichlorotris(triphenylphosphine)ruthenium(II). This catalyst has been used in the addition of chloroform or carbon tetrachloride to a variety of 1-olefins, cyclohexene and cis-cyclooctene.[103-106] It was found that carbon tetrachloride would react with cyclohexene by peroxide initiation to give the expected adduct in low yield.[107] However, in the presence of the ruthenium catalyst a highly stereoselective addition of carbon tetrachloride to cyclohexene takes place that produces trans-1-trichloromethyl-2-chlorocyclohexene in good yield (Reaction 1.33).[104]



Reaction 1.33

The products in this reaction indicate that a similar mechanism as that outlined previously in Scheme 1.33 is operating (Scheme 1.34).

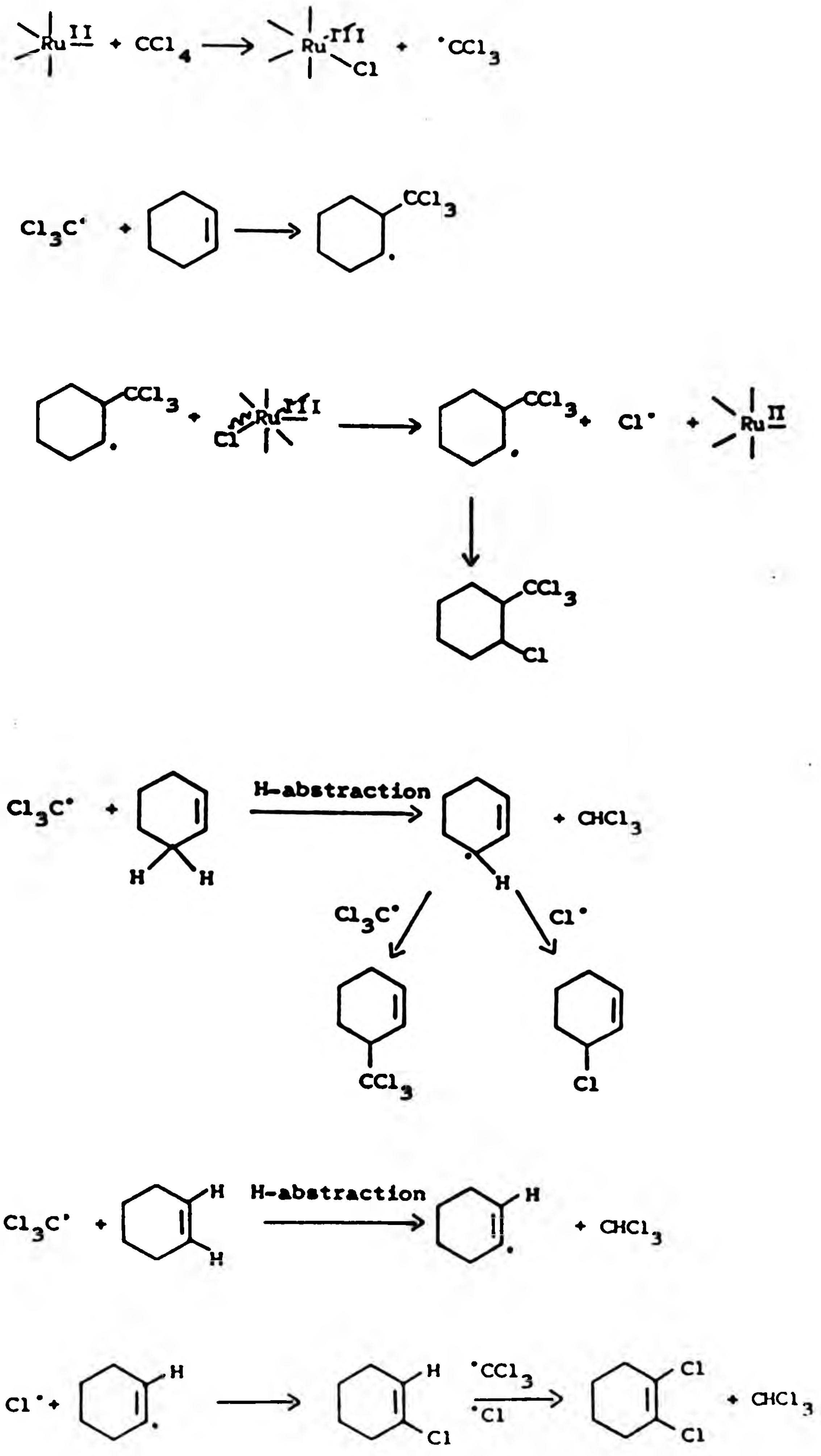
The ruthenium catalyst has also been used in the reactions of dichloro- and trichloroacetic acid esters with 1-olefins.[105] It was found that when methyl dichloroacetate was reacted with 1-octene in the presence of 0.7 mole % of the ruthenium complex, 2,4-dichlorodecanoate was obtained in 95% yield. This is in contrast to the peroxide catalysed reaction in which the main product is 2,2-dichlorodecanoate (Reaction 1.34).[108]



Reaction 1.34

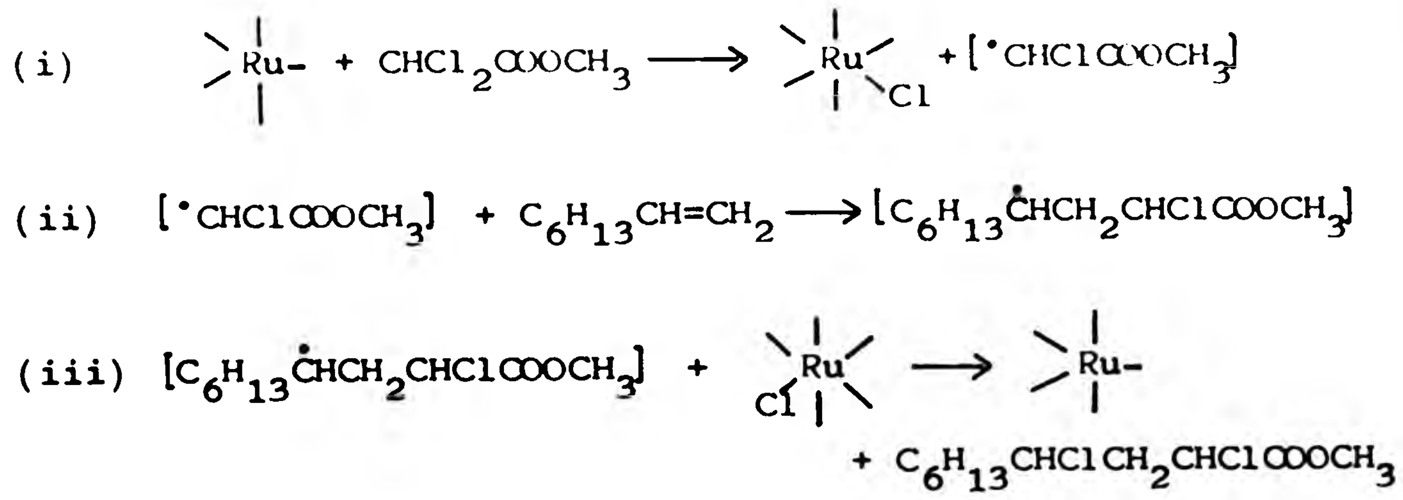
This result can be rationalised in terms of the mechanism outlined in Scheme 1.35, which involves internal redox behaviour.

Scheme 1.34.



Ru II
CCl4
Ru III
Cl
·CCl3
Cl3C·
CCl3
Cl·
Cl
H-abstraction
H
CHCl3
Cl3C·
·CCl3
·Cl

Scheme 1.35



This reaction is likely to involve the internal redox reaction in step (iii) of Scheme 1.35, in which the adduct radical abstracts a chlorine atom from the ruthenium complex. The chlorine abstraction in the catalyst is associated with lower energy requirements (due to the ease with which the internal redox can occur) compared to the hydrogen abstraction from the starting ester. It follows that the formation of methyl-2,4-dichlorodecanoate becomes a predominate pathway in this reaction.

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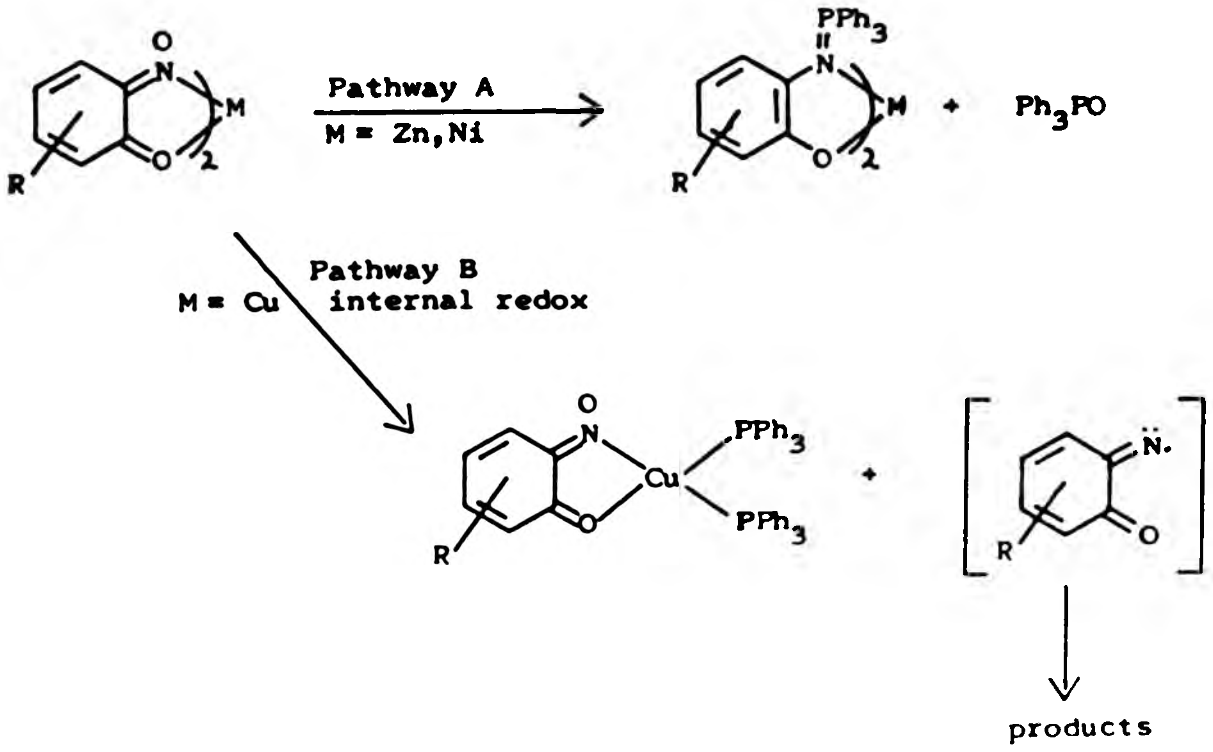
CHAPTER 2

2. The reactions of triphenylphosphine with the iron complexes derived from the monooximes of 1,2-naphthoquinone.

2.1. Previous studies of reactions of triphenylphosphine with metal complexes derived from monooximes of 1,2-quinones.

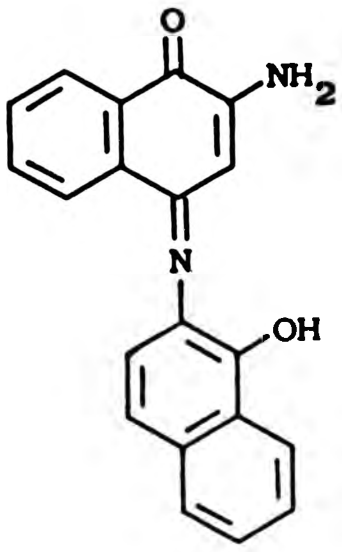
Previous work on the interaction of triphenylphosphine with various nickel, copper and zinc complexes derived from monooximes of 1,2-quinones has shown that two types of reaction may occur, both of which involve formation of triphenylphosphine oxide (Scheme 2.1).[1-6]

Scheme 2.1

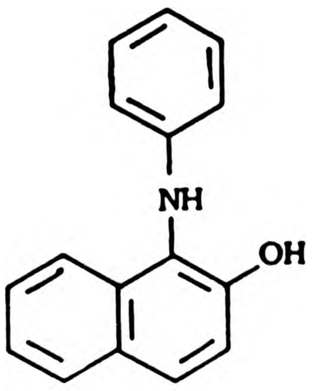


For the nickel(II) and zinc(II) complexes an iminophosphorane-type complex is produced, in which the metal remains in the same oxidation state (Scheme 2.1, pathway A). For the copper(II) complexes an internal redox reaction occurs. In this case the metal is reduced and a ligand radical is released (Scheme 2.1, pathway B). The radical reacts further to give products whose nature depends on the metal complex and the reaction conditions.

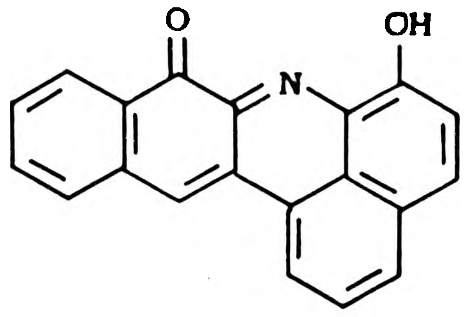
In the systems involving copper complexes, the products arising from the subsequent reactions of the released ligand radical are often complex. For example, the reaction of Cu(2-nqo)$_2$ with the phosphine leads to the formation of 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone-monoimine (2.1). In the case of the complex Cu(1-nqo)$_2$ the main product is 1-amino-2-naphthol, with traces of 1-phenylamino-2-naphthol (2.2) and 6-hydroxydibenz[b,kl]-acridin-8-one (2.3).



2.1



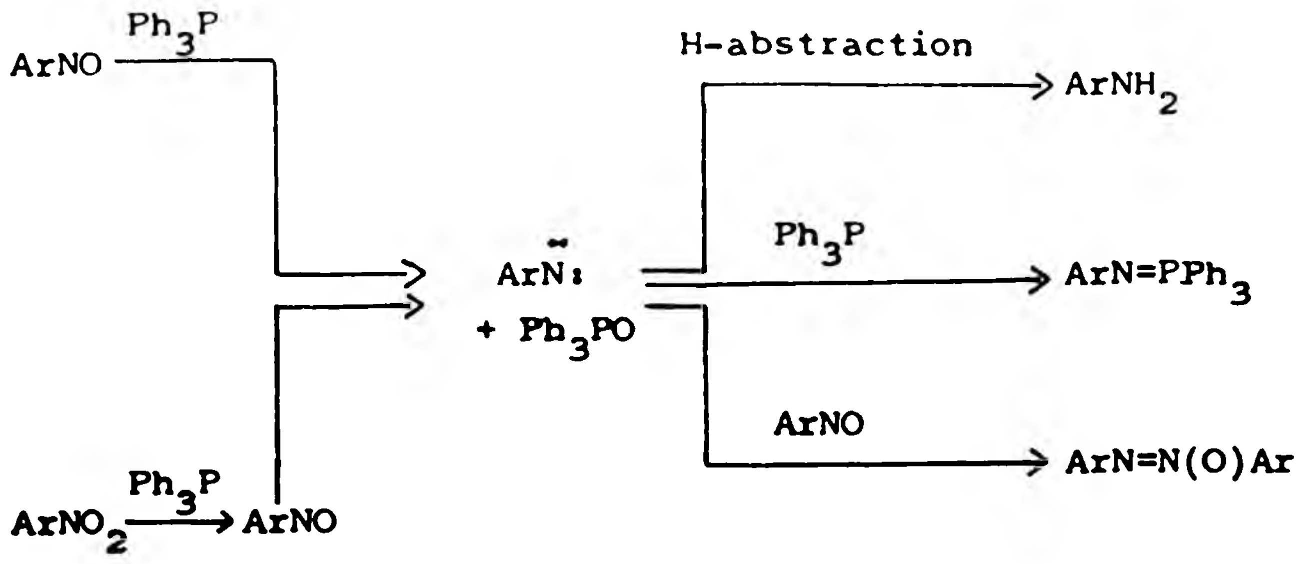
2.2



2.3

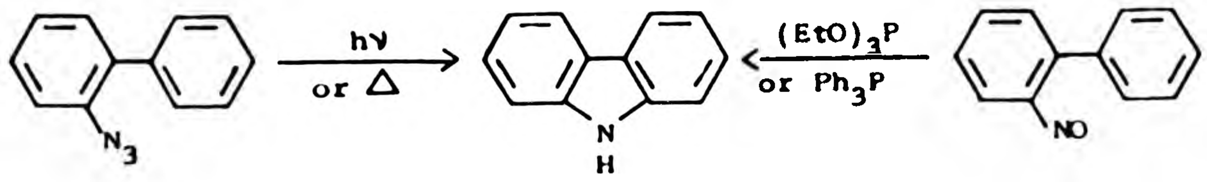
The products arising from these reactions have been rationalised in terms of deoxygenation and the formation of nitrene intermediates. The occurrence of deoxygenation is indicated by the formation of triphenylphosphine oxide, but the involvement of nitrene intermediates is less firmly established. A large number of reactions are known in which aromatic nitroso- and nitro- compounds are deoxygenated by tervalent phosphorus derivatives, to give various organic products and pentavalent phosphorus oxo derivatives.[7-19] Although the nature of the deoxygenated product depends on the initial organic compound, it has been suggested that nitrene intermediates are involved.[20-31] These can react to give N-aryliminophosphoranes, azoxy compounds, amines, or other products arising from interaction of the nitrene species with other substances (Scheme 2.2).

Scheme 2.2



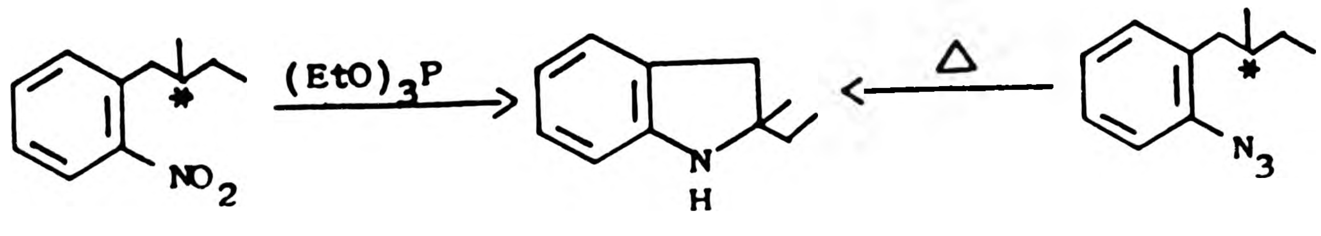
Even though there is no direct evidence for the intermediacy of nitrenes in these reactions, their involvement in the formation of amines and heterocyclic compounds, from the thermal degradation of azides, is supported by kinetic evidence.[32-36] Thus carbazole is formed in high yield from the pyrolysis of 2-azidobiphenyl.[37] It is also the major product from the reaction of 2-nitrosobiphenyl with either triethylphosphite or triphenylphosphine (Scheme 2.3).[10]

Scheme 2.3



This suggests that both reactions occur via an intermediate nitrene species, a view supported by Smolinsky in his study of the pyrolysis of 2,4,6-trimethyl-2'-azidobiphenyl.[38] Also, nitrene or carbene species are known for their ability to insert into C-H bonds. Hence the isolation of such insertion products from deoxygenation reactions has been seen as evidence for the intermediacy of nitrenes. Thus, the reaction of (+)-(S)-2-nitro-1-(2-methylbutyl)benzene (2.4 in Scheme 2.4) with triethylphosphite leads to the formation of partially active (50%) indoline (2.5 in Scheme 2.4).[14] This compares favourably with an earlier study in which indoline of 65% optical purity was obtained by the pyrolysis of the azide (2.6 in Scheme 2.4).[39] In both cases it was postulated that a nitrene intermediate was involved which inserted into the C-H bond of the side chain to give the product.

<u>Scheme 2.4</u>



2.4 2.5 2.6

The reactions of complexes of the type M(qo)$_n$ with triphenylphosphine present not only interesting mechanistic aspects, but they are also synthetically valuable. Thus the reactions of $Ni(qo)_2$ complexes provide a convenient synthetic route to nickel(II) complexes of (2-hydroxyphenylimino)-phosphoranes.[1,4] These reactions also offer a useful method for the preparation of N-(2-hydroxyphenyl)iminophosphoranes-benzoxazaphospholes[5] and are advantageous as the reactions use non-hazardous reagents and do not have to be carried out in anhydrous media. The reactions of the copper(II) complexes, such as $Cu(5\text{-}MeOqo)_2$ give rise to organic products which are not readily available by other synthetic means, e.g. 2-amino-7-methoxy-3H-phenoxazin-3-one.[5] In addition, these reactions are not only important for synthetic reasons, but can also lead to a fuller understanding of internal redox reactions and the mechanisms involved, through the identification of the products arising from them. As a consequence the studies on the reactions of $M(qo)_n$ complexes with triphenylphosphine have been extended to other metals. In the case of both iron(III) and cobalt(III) complexes, preliminary studies indicated that internal redox reactions occur. All of the reactions involving iron(III) afforded well defined iron(II) complexes, whereas the cobalt complex afforded an ill-defined metal species. Both the cobalt and iron complexes gave several other products whose nature was not fully established. These reactions and others involving $M(qo)_n$ type complexes are summarised in Table 2.1.

In this thesis a more detailed and systematic investigation of the reactions of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with triphenylphosphine has been carried out.

Table 2.1 Previous studies of the reactions of triphenylphosphine with metal complexes derived from the monooximes of 1,2-quinones

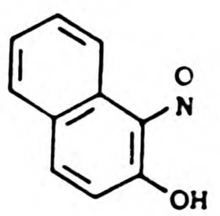
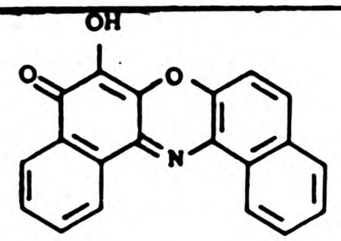
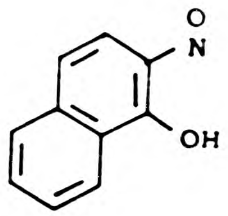
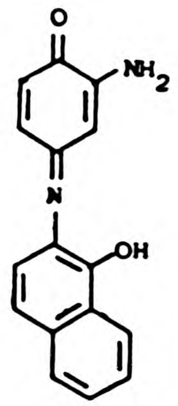
Ligand(LH)	Complex	Metal containing product	Main organic products (other than Ph_3PO)	Refs
	CuL_2	$CuL(Ph_3P)_2$ [a]	$1\text{-}nH_2$	2
	ZnL_2	$ZnL_2.2py$ [a,c]	none	2
	ZnL_2	$Zn(1\text{-}nqPPh_3)_2$ [b,c]	none	2
	FeL_3	$FeL_2.2py$ [a,d]		3
	FeL_3	FeL_2 [a,c]		3
	CuL_2	$CuL(Ph_3P)_2$ [a,c]		2
	CoL_3	Ill-defined[b,e]		6

Table 2.1 cont.

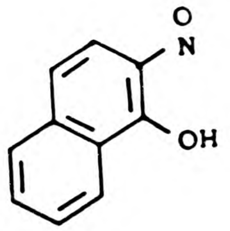
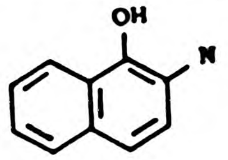
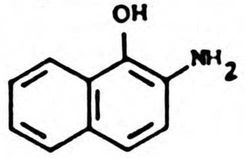
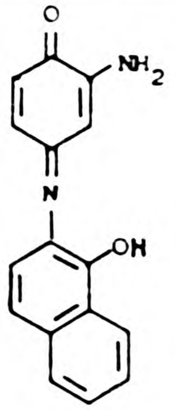
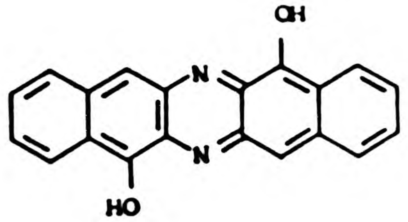
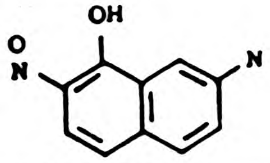
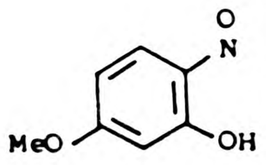
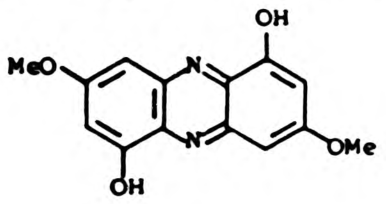
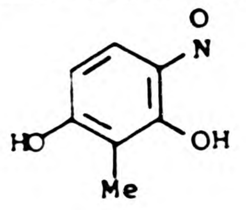
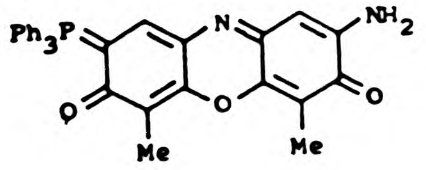
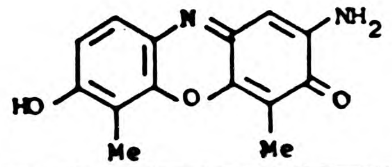
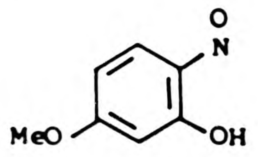
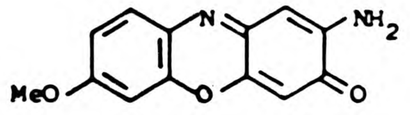
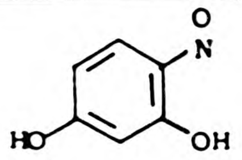
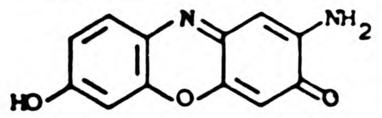
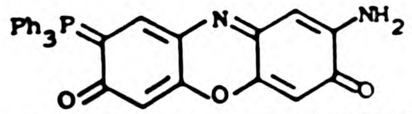
Ligand(LH)	Complex	Metal containing product	Main organic products (other than Ph_3PO)	Refs
	FeL_3	$FeL_2.2py^{a,d}$	    	3
	FeL_3	$FeL_2^{a,c}$		3
	ZnL_2	$ZnL_2.2py^{a,c}$	none	2
	ZnL_2	$Zn(2\text{-}nqPPh_3)_2^{b,c}$	none	2
	NiL_2	$Ni(5\text{-}MeOqPPh_3)_2^{a,d}$	none	1,4
	CuL_2	$CuL(PPh_3)_2$		

Table 2.1 cont.

Ligand(LH)	Complex	Metal containing product	Main organic products (other than Ph_3PO)	Refs
	CuL_2	Ill-defined[b,c]	 	5
	CuL_2	$CuL(PPh_3)_2$[b,c]		5
	$CuL_2.H_2O$	Ill-defined	 	5

a = At 20 ^{o}C

b = Reflux conditions

c = In pyridine

d = In chloroform

e = In methanol

2.2 Properties and structure of iron complexes of 1,2-quinone monooximes.

Before describing the results obtained from the study of the interaction of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with triphenylphosphine, an outline of the structure and properties of iron quinone monooximato complexes will be given here. Particular attention will be paid to those complexes which aid the understanding of the results obtained during this study.

There are two main methods for the preparation of metal complexes of 1,2-quinone monooximes:

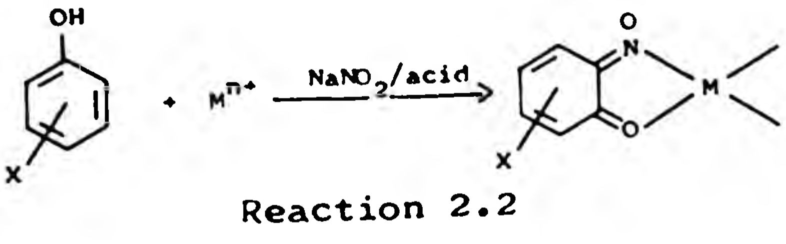
a) The direct interaction of the 1,2-quinone monooxime with the metal salt in a suitable solvent (Reaction 2.1).[1,38-52]

$$x\text{qoH} + MX_x \longrightarrow M(\text{qo})_x + xHX$$

Reaction 2.1

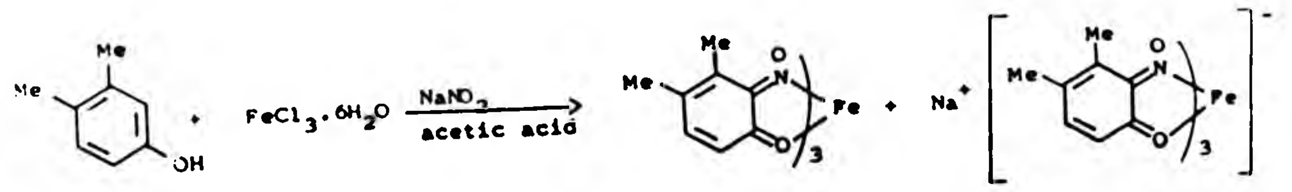
This has been found suitable for the preparation of many complexes, but is restricted by the limited availability of 1,2-quinone monooximes.

b) Nitrosation of an appropriate phenol in the presence of metal ions (reaction 2.2).[3,53-55]



Reaction 2.2

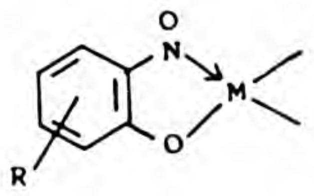
Both methods have been used previously in this laboratory for the preparation of iron 1,2-quinone monooximato complexes. However, use of the second method can lead to a mixture of chelate complexes. For example, the reaction involving 3,4-dimethylphenol and iron(III) chloride leads to the formation of an anionic iron(II) complex as well as the iron(III) trischelate (Reaction 2.3).[3]



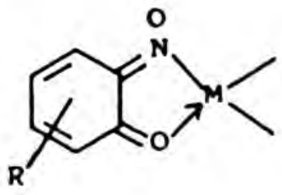
Reaction 2.3

Due to the strong ligand field strength of the quinoneoximato ligand, the iron(III) complexes and most of the iron(II) complexes formed in these reactions are low spin. The high ligand field strength is also indicated by the magnitude of the Mössbauer parameters and by the electronic spectra of the complexes Fe(qo)$_2$. These spectra are noted for intense charge transfer bands. As a result of this d-d bands, which often appear as shoulders on these bands, tend to have artificially high extinction coefficients, compared with those normally observed for d-d-transitions.

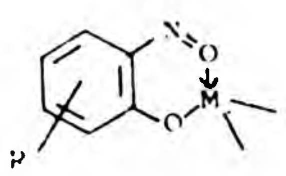
The metal complexes derived from 1,2-quinone monooximes can be described in valence bond terms as involving resonance between a quinone oximic and a nitrosophenolic structure (2.7). Also, there is the possibility that the nitroso/oximato group can coordinate to the metal through the nitrogen or the oxygen atom (2.8).



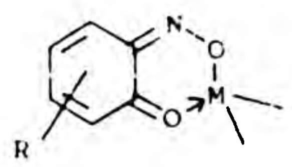
2.7a



2.7b



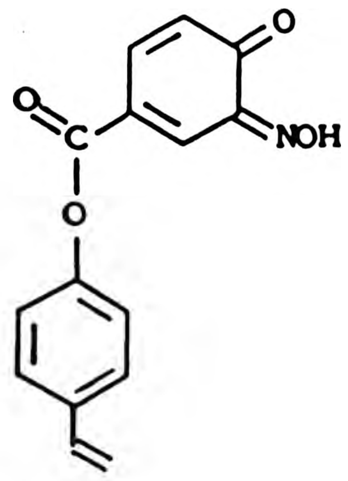
2.8a



2.8b

The structures of a number of first and second row transition metal complexes of this type have been determined. In each case the ligand is essentially quinoneoximic in character and is bound to the metal through the nitrogen of the oximato group and the oxygen of the quinone group. For example, crystal structures of the complexes $Cu(2\text{-}nqo)_2 \cdot H_2O$[56] and ferroverdin (2.9)[57] have shown this to be the case.

Na[Fe(qo)$_3$] where qoH =



2.9

However, recent X-ray studies on some complexes involving heavier metals have shown that a different type of bonding can sometimes occur. In the complexes diaquobis(1,2-naphthoquinone-2-oximato)dioxouranium(VI)-½trichloromethane and aquobis(1,2-naphthoquinone-1-oximato)-(triphenylphosphine oxide)dioxouranium(VI), the quinoneoximato ligand is bound to the metal through the nitrogen and the oxygen of the oximato group.[58]

Henceforth in this thesis, structures of iron complexes derived from 1,2-naphthoquinone monooxime will be given in the quinone oximic form. Arrows denoting donor bonds and also donor arrows, i.e. N→ M will be omitted in most cases.

As stated previously, octahedral complexes derived from 1,2-quinone monooximes are low spin, where possible, due to the strong ligand field strength of the ligand. Whilst the magnetic moments of the complexes $Fe(nqo)_3$, $Fe(nqo)_2.2py$ and $M[Fe(qo)_3]$ are in agreement with this, those for the $Fe(nqo)_2$ complexes are not. $Fe(1\text{-}nqo)_2$, $Fe(2\text{-}nqo)_2$ and related compounds such as $Fe(5\text{-}MeOqo)_2$, are green, rather insoluble complexes and have magnetic moments of approximately 3 B.M. Mössbauer and other studies indicate that these complexes have an oligomeric structure (Fig. 2.1).

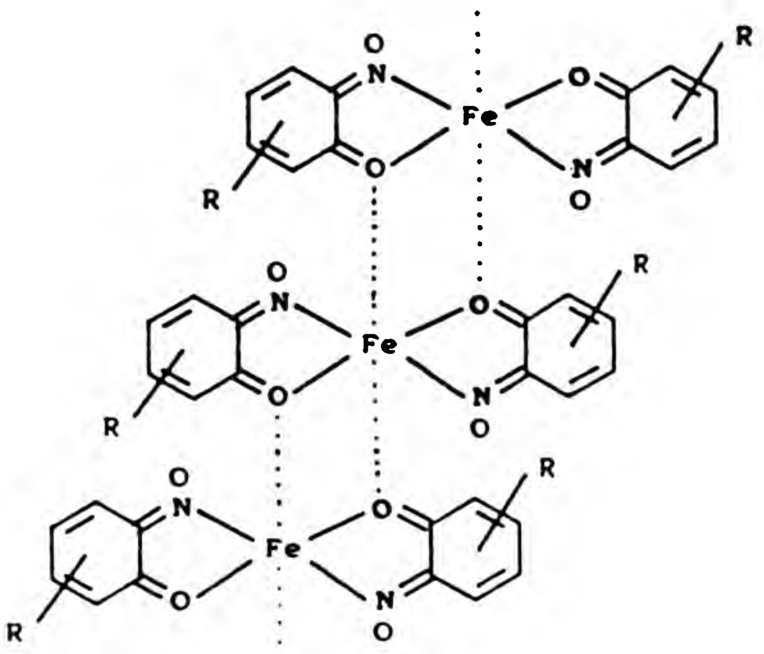
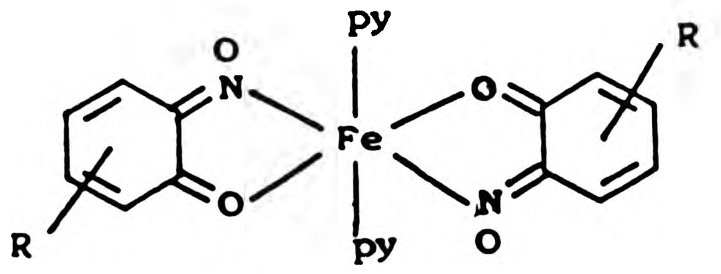


Fig. 2.1

In the oligomers there are both low spin iron(II) and high spin iron(II) species. The former correspond to meso six coordinate iron sites and the latter to the terminal five coordinate iron species, thus giving rise to the anomalous magnetic behaviour. This oligomeric structure accounts for the insolubility of the complexes and also for their thin layer chromatographic behaviour. The complexes have R_f=0 in all solvents, except pyridine, on silica, cellulose and alumina plates. One solvent in which the bischelates will readily dissolve is pyridine. This is due to the breaking of the association by pyridine to give rise to the pyridine adduct of the bischelate (2.10).



2.10

The pyridine adducts are diamagnetic, soluble in a range of solvents and move on silica, cellulose and alumina t.l.c. plate

In contrast to the bischelates, iron(III) trischelates are brown/purple in colour, readily soluble in a range of solvents and will move on a t.l.c. plate in various solvents. The trischelates will readily undergo an internal redox reaction in the presence of a Lewis base to give the iron(II) bischelates, or a Lewis base adduct of these, as well as organic products obtained from the released ligand radical. Thus the pyridine adducts of the

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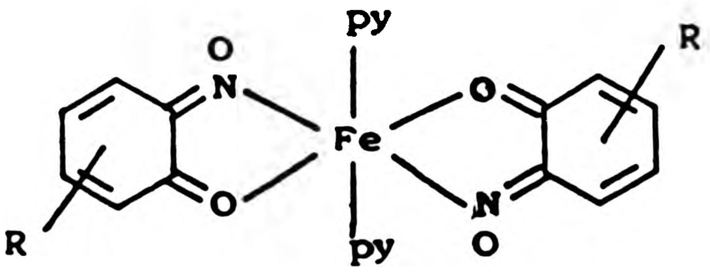

2.10

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$$Fe(nqo)_3 + py \longrightarrow Fe(nqo)_2.2py + nqoH$$

Reaction 2.4

These internal redox reactions of the trischelates provide a facile and convenient route to the pyridine adduct of $Fe(nqo)_2$. This contrasts with the bischelates, which are slow to react completely with pyridine and require heating. Because of the ready reaction of the trischelates with Lewis bases, it has been observed during the course of this study that they decompose to the bischelates in solvents such as methanol and ethanol, which are capable of acting as Lewis bases, but are stable in solvents which are not capable of acting as Lewis bases, such as toluene. The trischelates were also found to be reasonably stable in acetone.

2.3 Preliminary studies of the interaction of $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ with triphenylphosphine.

The reactions of $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ with triphenylphosphine were found to be complex, with a variety of factors affecting the final products obtained. It was established that the reactions proceed via intermediate complexes and that the choice of reaction media depends on the stability of both the trischelates and the intermediates in a particular solvent (Scheme 2.5). Thus it was found that the trischelates decompose to the bischelates in certain solvents. This occurs readily in methanol and together with the relative insolubility of the trischelates in this solvent, precluded its use in this study. In a previous study of the interaction of $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ with triphenylphosphine[3], chloroform was used as the solvent. From these reactions the bischelates and a number of organic products, accounted for in terms of deoxygenation of a ligand, were obtained e.g. dibenzo[b,i]phenoxazine-1-hydroxy-2-one and 2-nitrene-1-naphthol. However, in the present study it was found that the intermediate products formed during the reactions of the trischelates with triphenylphosphine are unstable in chloroform and decompose to the bischelates and organic products. Thus, it is probable that some of the organic products obtained when the reactions were carried out in chloroform arose as a result of interaction with the solvent. Similar behaviour was noted in other solvents. Hence it was necessary to find a solvent in which

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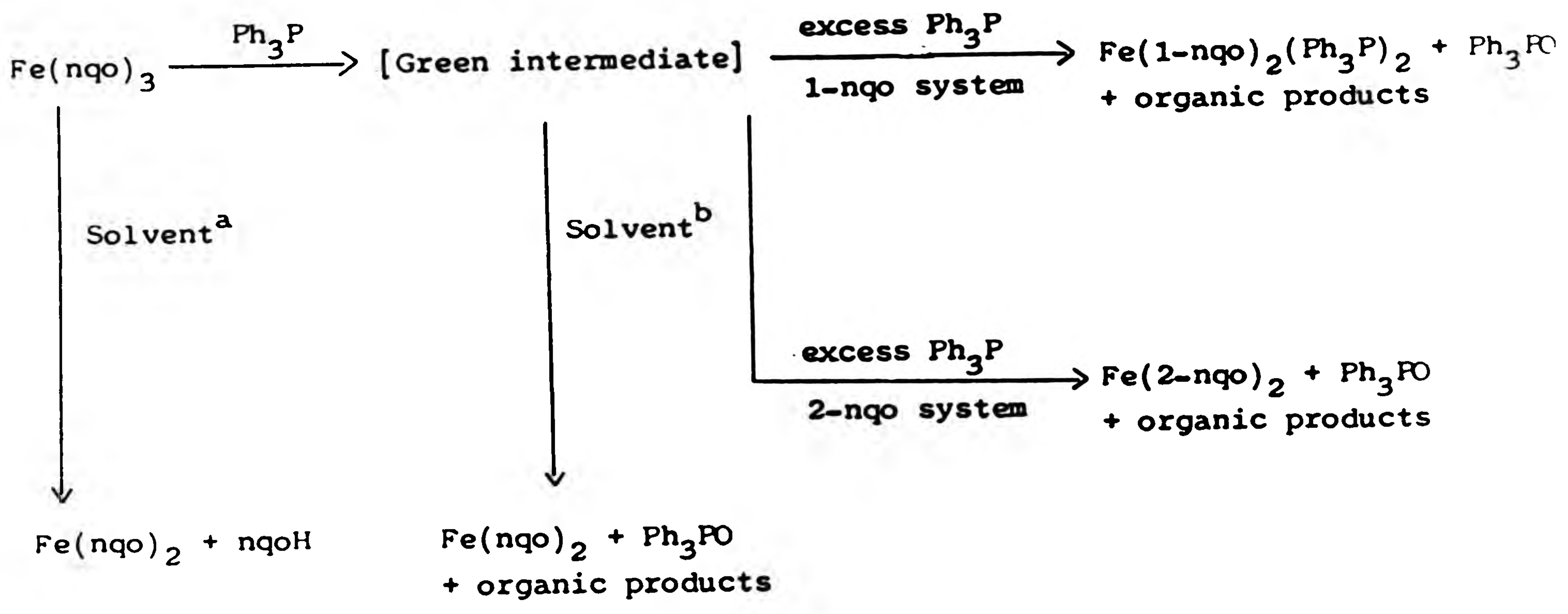
The reactions of $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ with triphenylphosphine were found to be complex, with a variety of factors affecting the final products obtained. It was established that the reactions proceed via intermediate complexes and that the choice of reaction media depends on the stability of both the trischelates and the intermediates in a particular solvent (Scheme 2.5). Thus it was found that the trischelates decompose to the bischelates in certain solvents. This occurs readily in methanol and together with the relative insolubility of the trischelates in this solvent, precluded its use in this study. In a previous study of the interaction of $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ with triphenylphosphine[3], chloroform was used as the solvent. From these reactions the bischelates and a number of organic products, accounted for in terms of deoxygenation of a ligand, were obtained e.g. dibenzo[b,i]phenoxazine-1-hydroxy-2-one and 2-nitrene-1-naphthol. However, in the present study it was found that the intermediate products formed during the reactions of the trischelates with triphenylphosphine are unstable in chloroform and decompose to the bischelates and organic products. Thus, it is probable that some of the organic products obtained when the reactions were carried out in chloroform arose as a result of interaction with the solvent. Similar behaviour was noted in other solvents. Hence it was necessary to find a solvent in which decomposition, both of the trischelates and of the intermediates, was minimal. Acetone was found to give the best results and was used for further studies.

The mole ratio of complex to triphenylphosphine and the reaction time were also found to be important in determining the types of product obtained. It was found that when the reactions were carried out in a 1:1 mole ratio the final products were different to those obtained in either a 1:3 or a 1:5 mole ratio reaction. In the 1:1 reactions, the iron(II) bischelates were the major iron-containing products, together with a number of organic products. In the 1:3 or 1:5 reactions the green intermediates were the major iron-containing products and only traces of organic products were observed. Also, if the reactions were monitored by t.l.c. examination and stopped as soon as no trace of trischelate could be seen, then the 'intermediates' were the major iron-containing products. However, if the reactions were allowed to proceed further, then other products resulted (Table 2.2).

On the basis of these results, detailed studies of the reactions of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with triphenylphosphine were undertaken, using 1:3 mole ratios of complex to phosphine and keeping reaction time to a minimum (approx. 30 min in the 2-nqo system and 5 h in the 1-nqo system).

Scheme 2.5



a e.g. MeOH

b e.g. $CHCl_3$, ether

Table 2.2 Preliminary experiments of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with triphenylphosphine at room temperature in acetone.

Iron complex (1 mol eq)	Ph_3P (n mol eq)	Reaction time	T.l.c. examination of iron-containing solid (major products only)	μ_{eff}(BM)^{a,b} of iron-containing mixture
$Fe(2\text{-}nqo)_3$	1	20h^c	Complex A + $Fe(2\text{-}nqo)_2$	1.60
$Fe(2\text{-}nqo)_3$	3	45min^d	Complex A + $Fe(2\text{-}nqo)_2$	0.95
$Fe(2\text{-}nqo)_3$	3	30min^c	Complex A + $Fe(2\text{-}nqo)_2$	0.50
$Fe(2\text{-}nqo)_3$	5	20min^c	Complex A + $Fe(2\text{-}nqo)_2$	0.40
$Fe(1\text{-}nqo)_3$	1	7 days^c	Complex B + $Fe(1\text{-}nqo)_2$	1.80
$Fe(1\text{-}nqo)_3$	3	20h^c	$Fe(1\text{-}nqo)_2(PPh_3)_2$ + $Fe(1\text{-}nqo)_2$	0.80
$Fe(1\text{-}nqo)_3$	3	5h^c	Complex B + $Fe(1\text{-}nqo)_2$	0.60

[a] μ_{eff} for $Fe(nqo)_2 \simeq 3$; μ_{eff} for $Fe(nqo)_2L_x = 0$

[b] calculated by % iron in solid

[c] acetone removed at 25 °C/0.3mm

[d] acetone removed by evaporation under a stream of nitrogen

2.4 The isolation and characterisation of the intermediate complex arising from the interaction of $Fe(2\text{-}nqo)_3$-with triphenylphosphine.

2.4.1 The isolation of the intermediate complex.

Various separation techniques were used in an attempt to isolate the iron complexes formed from the reaction of $Fe(2\text{-}nqo)_3$ (1 mol eq) with triphenylphosphine (3 mol eq). The separation proved to be difficult and it was found that the best results were obtained if it was carried out in stages. In stage 1 the solvent was removed at low temperature and pressure. In stage 2, extraction of the solid remaining, with light petrol, gave unreacted triphenylphosphine, together with small amounts of triphenylphosphine oxide and organic products. The amount of triphenylphosphine recoverdd shows that for every mole of complex used approximately one mole of triphenylphosphine has been consumed. T.l.c. examination of the iron-containing solid that remained after extraction, on both silica and cellulose plates, showed the presence of just two components, $Fe(2\text{-}nqo)_2$ and the Complex A.

The low magnetic moment of this mixture and the green colour of Complex A indicates that Complex A is a low spin, iron(II) species. This implies that an internal redox reaction has occurred in which iron(III) has been reduced to iron(II). If this were the case then it would be expected that a ligand radical would be released, which would ultimately give rise to organic products. However, in the t.l.c. examination of

2.4 The isolation and characterisation of the intermediate complex arising from the interaction of Fe(2-nqo)$_3$- with triphenylphosphine.

2.4.1 The isolation of the intermediate complex.

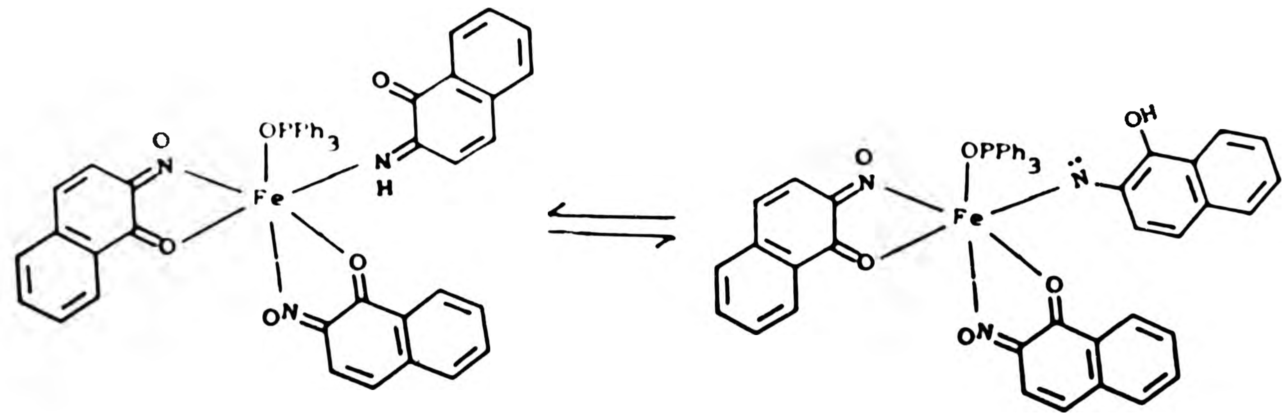
Various separation techniques were used in an attempt to isolate the iron complexes formed from the reaction of Fe(2-nqo)$_3$ (1 mol eq) with triphenylphosphine (3 mol eq). The separation proved to be difficult and it was found that the best results were obtained if it was carried out in stages. In stage 1 the solvent was removed at low temperature and pressure. In stage 2, extraction of the solid remaining, with light petrol, gave unreacted triphenylphosphine, together with small amounts of triphenylphosphine oxide and organic products. The amount of triphenylphosphine recoverdd shows that for every mole of complex used approximately one mole of triphenylphosphine has been consumed. T.l.c. examination of the iron-containing solid that remained after extraction, on both silica and cellulose plates, showed the presence of just two components, Fe(2-nqo)$_2$ and the Complex A.

The low magnetic moment of this mixture and the green colour of Complex A indicates that Complex A is a low spin, iron(II) species. This implies that an internal redox reaction has occurred in which iron(III) has been reduced to iron(II). If this were the case then it would be expected that a ligand radical would be released, which would ultimately give rise to organic products. However, in the t.l.c. examination of the iron-containing mixture there was no indication of any of the expected organic products and only traces were seen in the light petrol extract. The separation of Complex A from the bischelate was found to be more difficult than was expected initially, with the yields of the complexes dependent on the conditions used in the separation. As Fe(2-nqo)$_2$ is insoluble in diethyl ether, it was thought that the iron-containing mixture could be stirred in diethyl ether and filtered. The insoluble bischelate could be removed by filtration, leaving Complex A in solution and readily obtainable by evaporation of the ether. This was attempted on a portion of the iron-containing solid. However, decomposition of Complex A occurred to give Fe(2-nqo)$_2$ in quantitative yield and a complex mixture of organic products. Attempts to use solvents other than diethyl ether for the separation also led to decomposition, although t.l.c. examination of the original mixture did not indicate any decomposition of Complex A in the solid state.

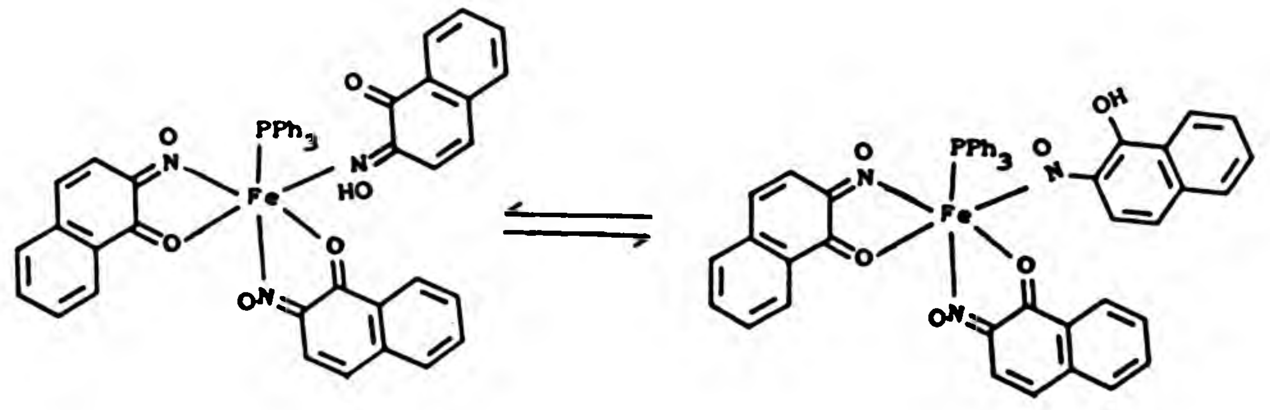
It was then decided to try column chromatography for the third stage of the separation and purification technique. Standard chromatography led to decomposition. However, it was found that if a short column with a rapid flow of eluant, followed by fast removal of solvent from the eluate at low temperature was used, then a pure sample of Complex A could be obtained. Elemental analysis of Complex A gave an empirical formula of $C_{48}H_{34}FeN_3O_6P$. This suggests that for each iron there are the elements of three quinoneoximato groups and one triphenylphosphine. The complex was found to be diamagnetic with a well defined i.r. spectrum. The n.m.r. spectrum of Complex A could not be obtained due to decomposition to Fe(2-nqo)$_2$ in solution. Structural characterisation of Complex A was achieved using a variety of techniques. On the basis of the results obtained from the characterisation techniques and elemental analysis, the most probable structure of Complex A is 2.11 , which contains two quinone oxime type ligands, a quinone imine type ligand and triphenylphosphine oxide. Henceforth, Complex A will be assigned structure 2.11, although it must be noted that there are other, less likely structures which are possible (see next section).

2.4.2 The characterisation of Complex A: bis(1,2-naphthoquinone-2-monooxime)(1,2-naphthoquinone-2-monoimine)(triphenylphosphine oxide)iron(II).

As stated previously, elemental analysis of Complex A gave an empirical formula of $C_{48}H_{34}FeN_3O_6P$ and it has also been established that the reaction of Fe(2-nqo)$_3$ with triphenylphosphine requires one mole of the phosphine per mole of complex. In addition, the complex is green and diamagnetic, indicating the presence of an iron(II) species. This is supported by the Mössbauer spectrum of the complex. Comparison of the spectrum with those of iron(II) quinone-oximato complexes indicates that a low spin iron(II) species is present, also with a quinone oximato type structure. On this basis the two most probable structures of the complex are 2.11, a quinone imine complex, or 2.12, which contains triphenylphosphine and three quinoneoximato type ligands.



2.11a 2.11b



2.12a 2.12b

It was thought that comparison of the spectrum of the complex with those of triphenylphosphine, triphenylphosphine oxide, Fe(2-nqo)$_3$ and Fe(2-nqo)$_2$ might distinguish between these two structures. The region of the spectrum between 1070 and 1200 cm^{-1} was chosen for the comparison, as this contains the triphenylphosphine oxide P=O stretch at ν = 1120. The results are summarised in Table 2 .3. This comparison indicated that the complex contained triphenylphosphine oxide, rather than triphenylphosphine, and thus has the quinone imine structure. However, the

Table 2.3 Comparison of the i.r. spectra of triphenylphosphine, triphenylphosphine oxide, $Fe(2\text{-nqo})_2$ and $Fe(2\text{-nqo})_3$ with the quinoneimine complex isolated from the reaction of $Fe(2\text{-nqo})_3$ with triphenylphosphine.

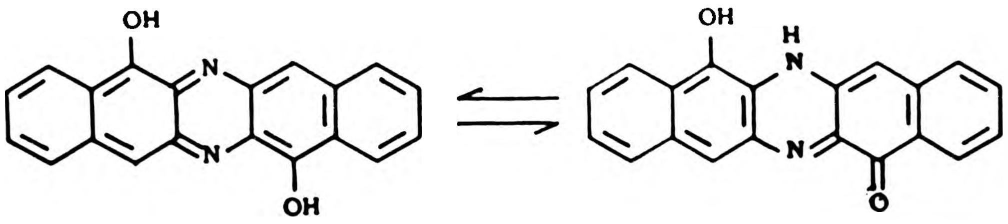
Compound	ν/cm^{-1}													
$Fe(2\text{-nqo})_2$			1090(m)	1100(m)		1135(s)		1150(s)						1200(s)
$Fe(2\text{-nqo})_3$		1080(w)			1125(m)		1145(m)						1193(m)	
Ph_3P	1070(s)		1090(s)						1155(m)		1180(m)			
Ph_3PO	1070(m)		1090(m)		1120(s)					1165(m)		1185(s)		
$Fe(2\text{-nqo})_2(2\text{-nqH})(Ph_3PO)$ (Complex A)	1070(w)		1090(m)		1120(s)	1135(m)		1150(m)			1180(m)		1190(m)	1200(m)

evidence is not conclusive. As the quinoneimine complex could not be recrystallised due to decomposition in solution, the chemical reactivity of the complex toward a number of compounds was used to gain further information on its structure. Thus reactions with pyridine, hydrogen sulphide, hydrochloric acid, triphenylphosphine and methyl iodide were carried out with the objective of gaining information on the ligands bonded to the iron in the complex.

For the reaction with methyl iodide it was expected that if triphenylphosphine was a ligand in the complex then triphenylmethylphosphonium iodide would be obtained. This would not be observed if a pentavalent phosphorus ligand, such as triphenylphosphine oxide, was present.

For the reactions with the other reagents it was hoped that decomposition of the complex would occur to yield the ligands bonded to the metal. However, it was found that these reactions are very complex and give multicomponent mixtures. Partial separation of these mixtures, using chromatographic techniques and recrystallisation, allowed the isolation of the iron-containing product formed in reactions and triphenylphosphine oxide. The types and amounts of organic products obtained enabled some conclusion to be drawn on the types of ligand present.

It was found that the quinoneimine complex reacted with pyridine to give $Fe(2\text{-}nqo)_2.2py$ and a number of organic products, the major ones of which were identified as 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine (2.1), triphenylphosphine oxide and dibenzo[b,i]phenazine-5,12-diol (2.13). In previous studies the latter has been assigned the phenazinone structure (2.13b) rather than the diol structure (2.13a) on the basis of its u.v./visible spectrum.[2]



2.13a 2.13b

In the reaction with hydrochloric acid, similar organic products were obtained and in addition 2-nitroso-1-naphthol was isolated.

When hydrogen sulphide was bubbled through a solution of the complex (either in toluene or methanol) a multicomponent mixture resulted. Filtration of the solution yielded a black, iron-containing solid. The amount of this solid obtained made it clear that it was not just iron sulphide that was present. This was confirmed by analysis of its iron content. This could have been due to either;

(i) incomplete reaction, i.e. the solid could contain some Fe(2-nqo)$_2$, or;

(ii) insoluble organic products could have been formed.

Separation of the organic products obtained from the filtrate gave triphenylphosphine oxide, 2-nitroso-1-naphthol and dibenzo[b,i] phenazine-5,12-diol as the major products. The isolation of triphenylphosphine oxide is in contrast to the reaction of hydrogen sulphide with 1,2-naphthoquinone-1-oximatobis(triphenylphosphine)copper(I)[2] In this complex the triphenylphosphine ligands are adducted to the copper. When hydrogen sulphide is bubbled through a suspension of the complex, triphenylphosphine sulphide is obtained. That no triphenylphosphine sulphide was obtained in the reaction of the quinoneimine complex with hydrogen sulphide is in agreement with the proposed structure, as here the ligand is triphenylphosphine oxide rather than triphenylphosphine. However, the study involving the copper complex is incomplete and as neither triphenylphosphine or triphenylphosphine oxide will react with hydrogen sulphide, it is possible that in the copper complex system some sort of catalytic cycle involving the metal centre is operating, which is not present in the iron system. Also, the copper system involves the complex derived from the 1-oxime, whereas the quinoneimine complex is derived from the 2-oxime and this study has shown clearly that there are significant differences in the reactivity of the iron complexes derived from the two isomers.

It was found that the quinoneimine complex reacted readily with methyl iodide to give a complex mixture. Separation of this mixture was not attempted.

The results of the various reactions of the quinoneimine complex are summarised in Table 2.4. In the reactions with pyridine, hydrochloric acid, triphenylphosphine and hydrogen sulphide, each mole of complex gives rise to one mole of triphenylphosphine oxide and approximately one mole of organic products. In addition, in the reaction with triphenylphosphine and pyridine the iron(II) bischelate, Fe(2-nqo)$_2$, or its pyridine adduct, Fe(2-nqo)$_2$.2py is obtained. In the reactions with hydrochloric acid and hydrogen sulphide, further breakdown of the iron complex occurs to give 2-nitroso-1-naphthol. Thus these reactions appear to back up the proposed quinoneimine structure of Complex A, i.e. the complex is a derivative of the bischelate and contains triphenylphosphine oxide as a ligand together with a ligand derived from a deoxygenated quinoneoximato group. This is supported by the reaction with methyl iodide, in which triphenylphosphine oxide was also observed, but not triphenylmethylphosphonium iodide. However, it was also shown that 2-nitroso-1-naphthol will react rapidly with triphenylphosphine to give similar products, but in different yields. Thus, although these reactions, together with the spectroscopic evidence, imply that the complex has structure 2.11 and contains triphenylphosphine oxide as a ligand, the evidence is not conclusive.

Table 2.4 Products and yields obtained from the reactions of bis(1,2-naphthoquinone-2-monooxime)(1,2-naphthoquinone-2-monoimine)-(triphenylphosphine oxide)iron(II).

Reagent	Iron-containing product	Products derived from the quinone oximato ligands.		Ph_3PO	Ph_3P
		2-nqoH	Other		
Pyridine	Fe(2-nqo)$_2$.2py	—	85% from 2.13 & 2.1	96%	—
aq.HCl	—	74%	89% from 2.13 & 2.1	99%	—
Ph_3P	Fe(2-nqo)$_2$	—	84% from 2.13 & 2.1	98%	94% recovered
H_2S	Ill-defined metal containing product (incomplete decomposition)	13%	64% from 2.13 & 2.1	97%	—

For structures of 2.1 and 2.13 see text

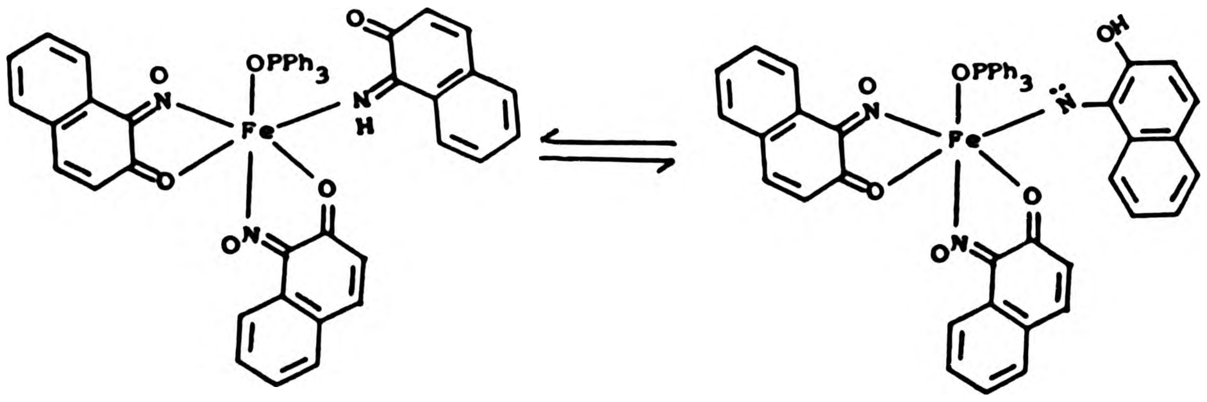
2.5 The isolation and characterisation of the intermediate complex arising from the interaction of Fe(1-nqo)$_3$ with triphenylphosphine.

2.5.1 The isolation of the intermediate complex(Complex B).

The techniques used to isolate the intermediate complex were similar to those used in the Fe(2-nqo)$_3$/Ph$_3$P system. The amount of triphenylphosphine recovered shows that for every mole of Fe(1-nqo)$_3$ used one mole of triphenylphosphine is required and, as in the Fe(2-nqo)$_3$/Ph$_3$P system, there was no indication of any of the expected products arising from the shedding of a ligand radical. Rapid column chromatography gave a pure sample of Complex B. Elemental analysis of this complex gives an empirical formula of $C_{48}H_{34}FeN_3O_6P$, i.e. the same as for the quinone imine complex obtained from the reaction of Fe(2-nqo)$_3$ with triphenylphosphine. Complex B is also diamagnetic, with a well defined i.r. spectrum. The n.m.r. spectrum could not be obtained due to decomposition to Fe(1-nqo)$_2$ in solution. The same physical and chemical techniques used in the characterisation of Complex A were used to enable structural characterisation of Complex B to be made. These are outlined in section 2.5.2 and led to Complex B being assigned structure 2.14 , although other structures are possible.

An unexpected complex obtained from the chromatographic separation of the iron-containing mixture of Fe(1-nqo)$_2$

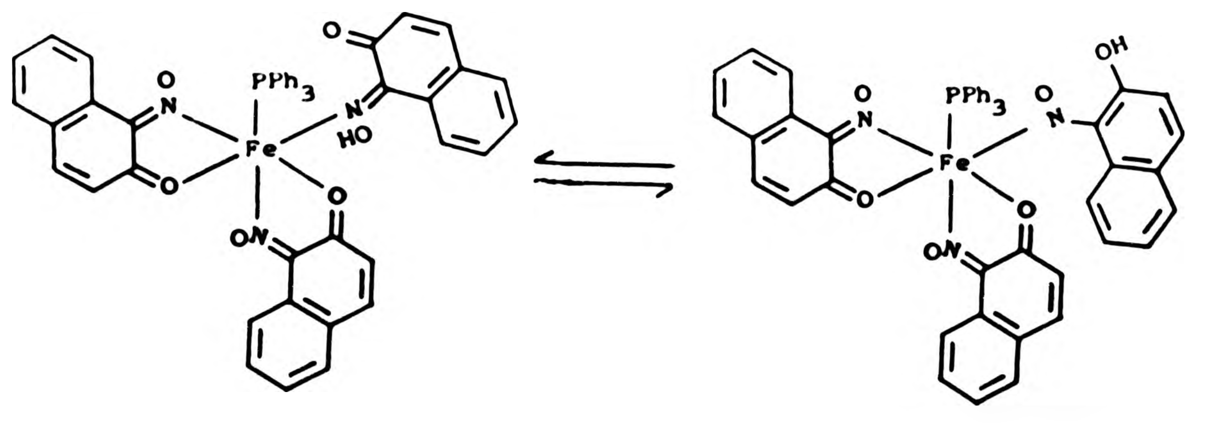
and Complex B was Fe(1-nqo)$_3$. In a t.l.c. examination of the mixture carried out previous to the column separation, Fe(1-nqo)$_3$ was not apparent. However, the compound was obtained in low yield and may have arisen as a result of the column work up.



2.14a 2.14b

2.5.2 The characterisation of bis(1,2-naphthoquinone-1-monooxime)(1,2-naphthoquinone-1-monoimine)-(triphenylphosphine oxide)iron(II) (Complex B).

On the basis of elemental analysis, experimental results and Mössbauer and magnetic moment studies, it was established that Complex B contains the elements of three quinoneoximato groups, one triphenylphosphine group and an iron(II) species. On this basis the most probable structure for the complex is either 2.14 or 2.15. As with Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO), decomposition of the complex occurs in solvents such as diethyl ether and chloroform to give Fe(1-nqo)$_2$, triphenylphosphine oxide and organic products, the major one of which was identified as 1-amino-2-naphthol. Thus Complex B could not be recrystallised.



2.15a 2.15b

Comparison of the i.r. spectrum of Complex B with those of triphenylphosphine, triphenylphosphine oxide, Fe(1-nqo)$_3$ and Fe(1-nqo)$_2$ was carried out in the region 1065-1200 cm^{-1} (Table 2.5). As with Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO), there is some evidence here to suggest that triphenylphosphine oxide is present as a ligand in the complex, implying that the complex is of the form Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO). Henceforth this is the structure assigned to Complex B. However, the band at 1118 cm^{-1} in the i.r. spectrum of the complex, which is indicative of a P=O stretch is not as strong as would be expected and thus is not conclusive proof.

The products from the reactions of the complex with pyridine, hydrochloric acid and triphenylphosphine are summarised in Table 2.6. Unlike Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO), the quinoneimine complex of the 1-nitroso-system did not

Table 2.5 Comparison of the i.r. spectra of triphenylphosphine, triphenylphosphine oxide, $Fe(1\text{-}nqo)_2$ and $Fe(1\text{-}nqo)_3$ with the quinone imine complex isolated from the reaction of $Fe(1\text{-}nqo)_3$ with triphenylphosphine.

Compound	ν/cm^{-1}							
$Fe(1\text{-}nqo)_2$		1085(s)			1130(s)		1155(s)	
$Fe(1\text{-}nqo)_3$		1080(w)				1140(m)	1155(m)	
Ph_3P	1070(s)	1090(s)					1155(m)	1180(m)
Ph_3PO	1070(m)	1090(m)		1120(s)			1165(m)	1185(s)
$Fe(1\text{-}nqo)_2(nqH)(Ph_3PO)$ (Complex B)	1065(s)		1100(m)	1118(m)	1130(s)	1142(s)		1180(w)

Table 2.5 **Comparison of the i.r. spectra of triphenylphosphine, triphenylphosphine oxide, $Fe(1\text{-}nqo)_2$ and $Fe(1\text{-}nqo)_3$ with the quinone imine complex isolated from the reaction of $Fe(1\text{-}nqo)_3$ with triphenylphosphine.**

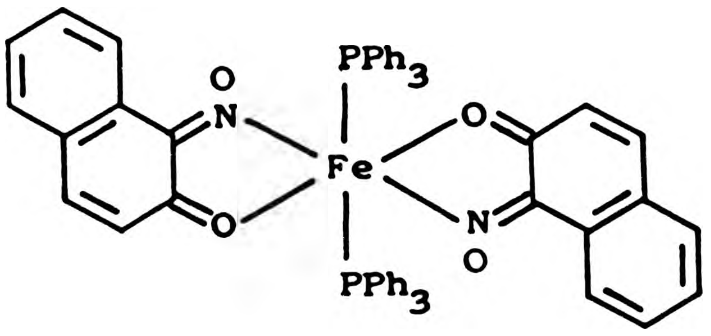
Compound	ν/cm^{-1}							
$Fe(1\text{-}nqo)_2$		1085(s)			1130(s)		1155(s)	
$Fe(1\text{-}nqo)_3$		1080(w)				1140(m)	1155(m)	
Ph_3P	1070(s)	1090(s)					1155(m)	1180(m)
Ph_3PO	1070(m)	1090(m)		1120(s)			1165(m)	1185(s)
$Fe(1\text{-}nqo)_2(nqH)(Ph_3PO)$ (Complex B)	1065(s)		1100(m)	1118(m)	1130(s)	1142(s)		1180(w)

Table 2.6 Products and yields obtained from the reactions of bis(1,2-naphthoquinone-1-monooxime)(1,2-naphthoquinone-1-monoimine)-(triphenylphosphine oxide)iron(II).

Reagent	Iron-containing product	Products derived from the quinone oximato ligands.		Ph_3PO	Ph_3P
		2-nqoH	Other		
Pyridine	$Fe(1\text{-}nqo)_2\cdot 2py$	—	50% $1\text{-}nH_2$	96%	—
aq. HCl	—	65%	77% $1\text{-}nH_2$	93%	
Ph_3P	$Fe(1\text{-}nqo)_2(Ph_3P)_2$	—	81% $1\text{-}nH_2$	97%	78% recovered

$1\text{-}nH_2$ = 1-amino-2-naphthol

react with hydrogen sulphide, although some decomposition due to the solvent was observed. The reaction of $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$ with methyl iodide was carried out for the same reasons as those given in Section 2.4.2. As with the quinoneimine complex of the 2-nitroso-system, this reaction gave a complex mixture of products. However, t.l.c. examination indicated the presence of triphenylmethylphosphonium iodide. Attempts at separation resulted in the isolation of an insignificant amount of the iodide in a pure form. Further amounts were shown to be present in mixtures of products by t.l.c. The reactions with pyridine and triphenylphosphine were similar to those of the 2-nitroso-system in that they gave one mole of triphenylphosphine oxide, one mole of iron complex and one mole of organic products per mole of quinoneimine complex. However, in the reaction of $Fe(2\text{-}nqo)_2(2\text{-}nqH)(Ph_3PO)$ with triphenylphosphine decomposition of the complex to $Fe(2\text{-}nqo)_2$, triphenylphosphine oxide and organic products were found and triphenylphosphine was recovered quantitatively. In the reaction of $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$ with triphenylphosphine the iron-containing product isolated was $Fe(1\text{-}nqo)_2(Ph_3P)_2$. This was also observed in the preliminary reactions used to establish reaction conditions. Thus, it was found that if the reaction between $Fe(1\text{-}nqo)_3$ and triphenylphosphine, in a 1:3 mole ratio, was allowed to continue for 20h then the amount of quinoneimine complex present in the reaction mixture was minor. T.l.c. examination of the reaction mixture showed it to contain triphenylphosphine oxide, 1-amino-2-naphthol and traces of triphenylphosphine and other organic compounds. In addition, Fe(1-nqo)$_2$ and another green iron complex were shown to be present. Column chromatography was employed as a separation technique and gave a pure sample of the unidentified complex. Analysis suggested that it was Fe(1-nqo)$_2$(Ph$_3$P)$_2$, 2.16 , Treatment of the complex with pyridine gave Fe(1-nqo)$_2$.2py and triphenylphosphine, which supports the formulation of the complex as the triphenylphosphine adduct.



2.16

The reaction of the quinoneimine complex with hydrochloric acid gave similar results to those obtained for Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO). The organic products isolated in these reactions, other than 1-nitroso-2-naphthol, are analogous to those obtained from the reaction of triphenylphosphine with 1-nitroso-2-naphthol, although the product yields are markedly different. In all the reactions involving Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO) the major organic product derived from the deoxygenated ligand is 1-amino-2-naphthol. In the reaction of triphenylphosphine with 1-nitroso-2-naphthol the major product is 1-phenylamino-2-naphthol. Also, in this reaction a more complex mixture results and the weight of products is greater than the weight of reactants, implying that interaction with the solvent, acetone, occurs. This is not observed in the reactions of the quinoneimine complex (apart from the decomposition of the complex in chloroform). This difference in product yields, together with the spectroscopic evidence, implies that the complex does contain triphenylphosphine oxide as a ligand rather than triphenylphosphine and that the quinoneimine structure is correct. However, this is contradicted by the reaction of the complex with methyl iodide, in which the presence of triphenylmethylphosphonium iodide and hence triphenylphosphine initially, was indicated. Thus, although the majority of the evidence is in favour of the structure containing triphenylphosphine oxide, it is not conclusive.

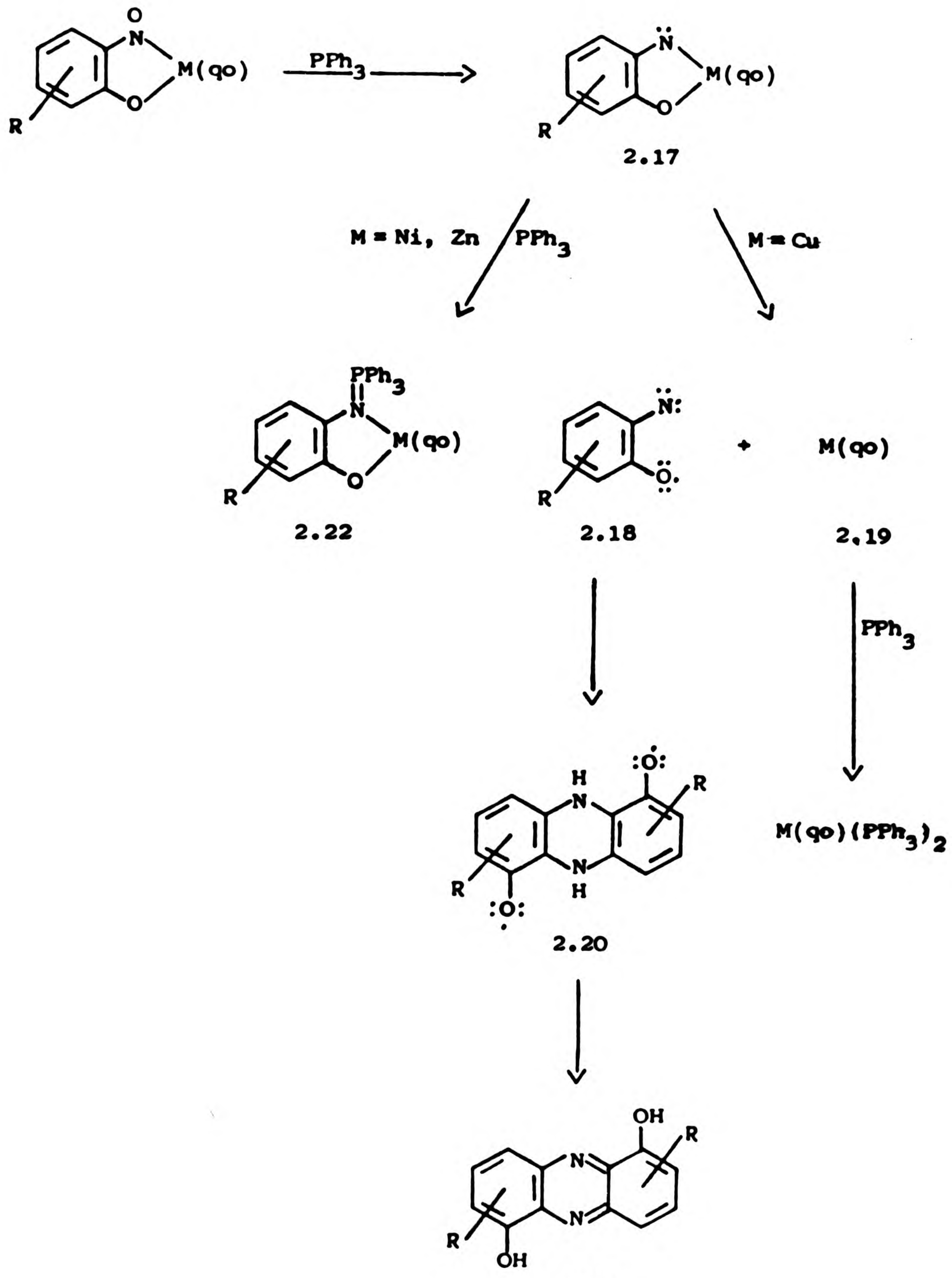
2.6 Mechanistic rationalistion for the reaction of triphenylphosphine with Fe(1-nqo)$_3$ or Fe(2-nqo)$_3$.

2.6.1 Introduction.

Two mechanisms have previously been proposed for the interaction of triphenylphosphine with M(qo)$_n$ complexes. Workers in this laboratory have proposed that M(qo)$_2$ complexes are initially deoxygenated by triphenylphosphine to yield an intermediate complex containing both quinoneoxime and nitrene/quinoneimine ligands (2.17 in Scheme 2.6).[1] Then, if the metal is easily reduced, the nitrene ligand is released as the radical species, 2.18. This could then react in a number of ways. It may interact with M(qo)$_2$ or the intermediate, 2.19, or it may dimerise to yield a species such as 2.20, which can then rearrange to give the phenazine, 2.21. This would result in a triphenylphosphine adduct of the complex M(qo). If the metal is not easily reduced then 2.17 interacts with triphenylphosphine to give an iminophosphorane complex, 2.22.

It has been proposed that in the presence of triphenylphosphine an easily reduced metal complex undergoes a redox process.[2] A quinone oxime ligand is then discharged as a free radical (2.23 in Scheme 2.7). Abstraction of hydrogen by this radical, from the solvent or another reactive species, would then yield 2.24. Deoxygenation of this by triphenylphosphine could then give the nitrene intermediate, 2.25, and triphenylphosphine oxide. The nitrene intermediate could then hydrogen abstract or

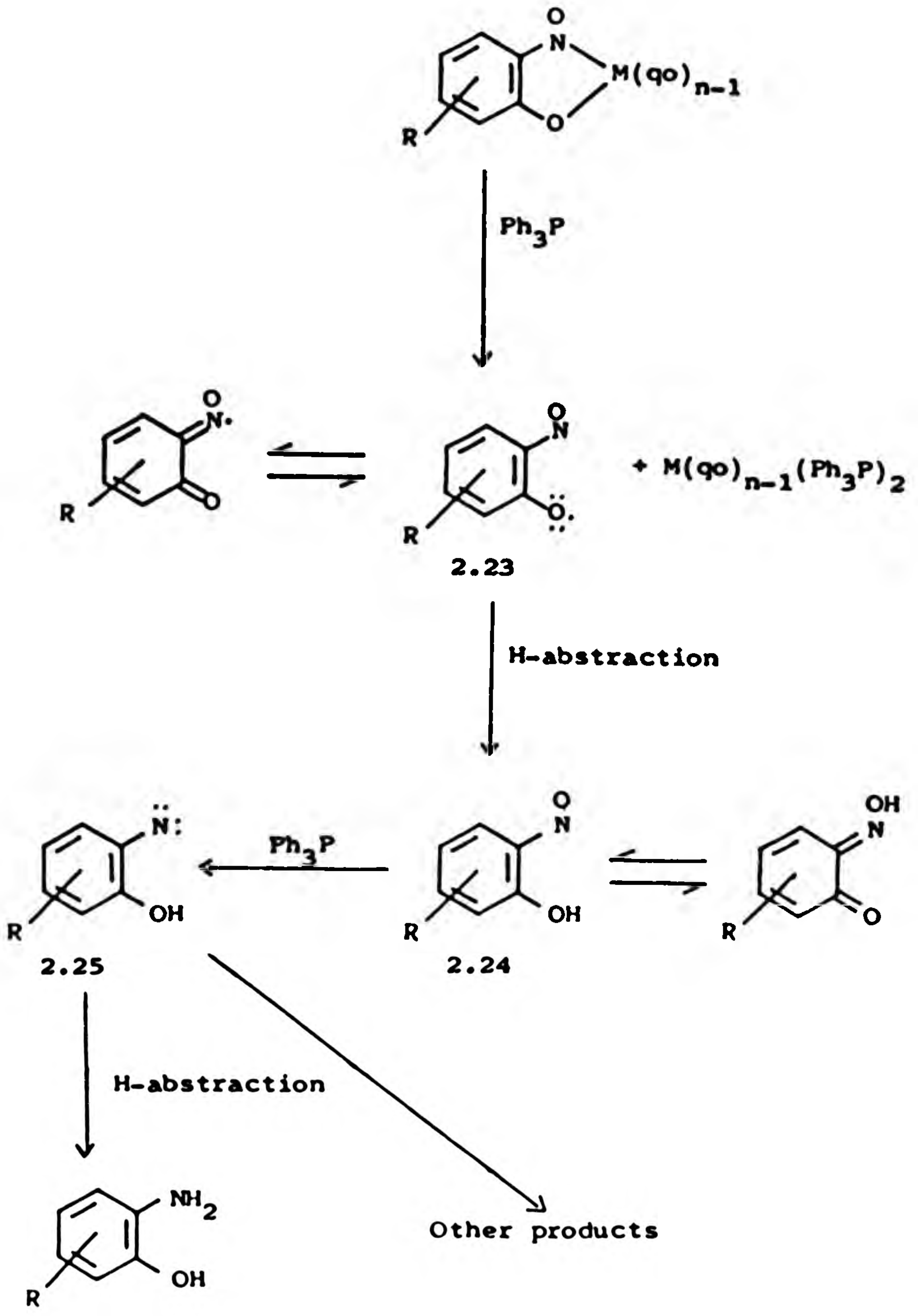
Scheme 2.6


M(qo)
PPh$_3$
2.17
M = Ni, Zn
PPh$_3$
M = Cu
2.22
2.18
+ M(qo)
2.19
PPh$_3$
M(qo)(PPh$_3$)$_2$
2.20
2.21
R
OH

react in other ways to give rise to the organic products obtained from the reactions.

For the reactions of Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ with triphenylphosphine it appears that neither of these mechanisms is applicable. In order to clarify the reaction mechanisms kinetic studies were undertaken and in addition the reactions were carried out in different solvents.

<u>Scheme 2.7</u>



2.6.2 A kinetic investigation of the reaction of Fe(1-nqo)$_3$ or Fe(2-nqo)$_3$ with triphenylphosphine in acetone.

2.6.2.1 Introduction.

Before the kinetic investigation was carried out the visible spectra of Fe(1-nqo)$_3$, Fe(1-nqo)$_2$, Fe(1-nqo)$_2$(Ph$_3$P)$_2$, Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO), Fe(2-nqo)$_3$, Fe(2-nqo)$_2$ and Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO) were obtained using standard solutions. The extinction coefficients are presented in Table 2.7.

Table 2.7

Complex	λ_{max}(nm)	ε (10^{-2} mol^{-1} m^2)
Fe(1-nqo)$_3$	400 590	29600 3500
Fe(1-nqo)$_2$	390 700	20100 12000
Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO)	400 670 735	22200 9250 9370
Fe(1-nqo)$_2$(Ph$_3$P)$_2$	380 700	17200 9550
Fe(2-nqo)$_3$	455	8300
Fe(2-nqo)$_2$	440 670	11000 9900
Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO)	660 800	7950 9540

2.6.2.2 The reaction of $Fe(2\text{-}nqo)_3$ with triphenylphosphine.

a) In 1 mm reaction cells.

The reaction between $Fe(2\text{-}nqo)_3$ and triphenylphosphine was studied in 1 mm cells at 25 °C ± 0.2 °C at different concentrations of triphenylphosphine (ranging from 3 fold to 17 fold excess). It was monitored by recording the increase in absorbance at 660 nm and 800 nm and was considered complete when no significant change could be observed at these wavelengths over a certain period of time. In a typical experiment a solution of the phosphine in acetone was added to a solution of $Fe(2\text{-}nqo)_3$ in acetone, to give a mixture in which the initial concentration of phosphine was 1.67×10^{-3} mol dm^{-3} and that of the complex was 5.66×10^{-4} mol dm^{-3}. The spectrum obtained is shown in Fig. 2.2. The absorbance due to $Fe(2\text{-}nqo)_3$ at 350 nm started to decrease with a parallel increase in absorbance at 660 nm and 800 nm and a decrease and shift in absorbance at $\lambda = 456$ nm to $\lambda = 430$ nm. An isosbestic point was found at 598 nm. The final spectrum obtained was the same as that of the quinoneimine complex, $Fe(2\text{-}nqo)_2(2\text{-}nqH)(Ph_3PO)$, isolated from the macroscale reaction of triphenylphosphine with $Fe(2\text{-}nqo)_3$. T.l.c. examination of the kinetic solution confirmed the presence of this complex. A plot of $\log(A_\infty - A_t)$ for the absorbance at 800 nm against time gave a straight line, indicating the reaction to be first order with respect to the concentration of trischelate (Fig. 2.3).

When the reaction was studied at other concentrations of triphenylphosphine the system behaved in an analogous

2.6.2.2 The reaction of $Fe(2\text{-}nqo)_3$ with triphenylphosphine.

a) In 1 mm reaction cells.

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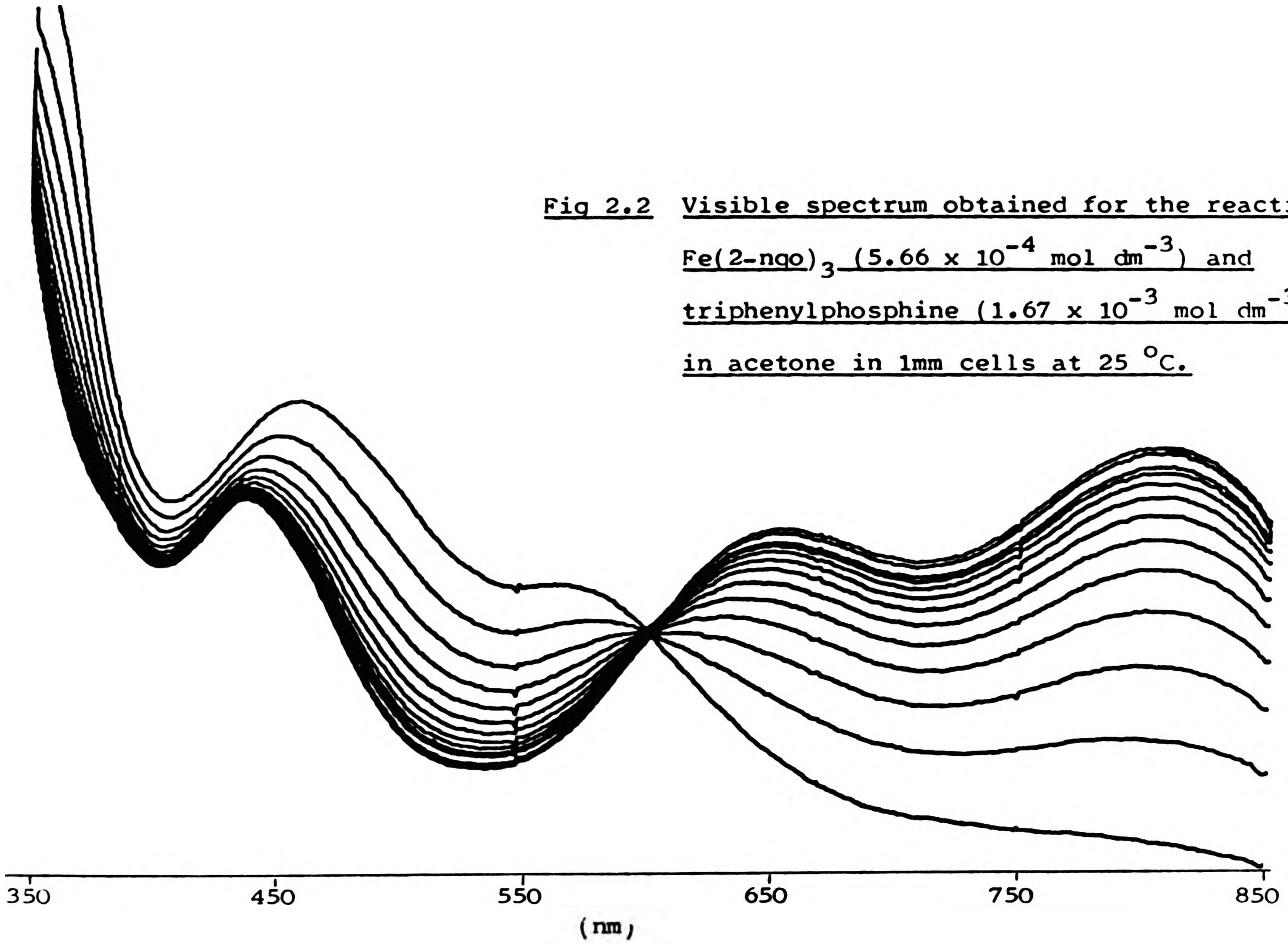


Fig 2.2 Visible spectrum obtained for the reaction of $Fe(2\text{-}nqo)_3$ (5.66×10^{-4} mol dm^{-3}) and triphenylphosphine (1.67×10^{-3} mol dm^{-3}) in acetone in 1mm cells at 25 °C.

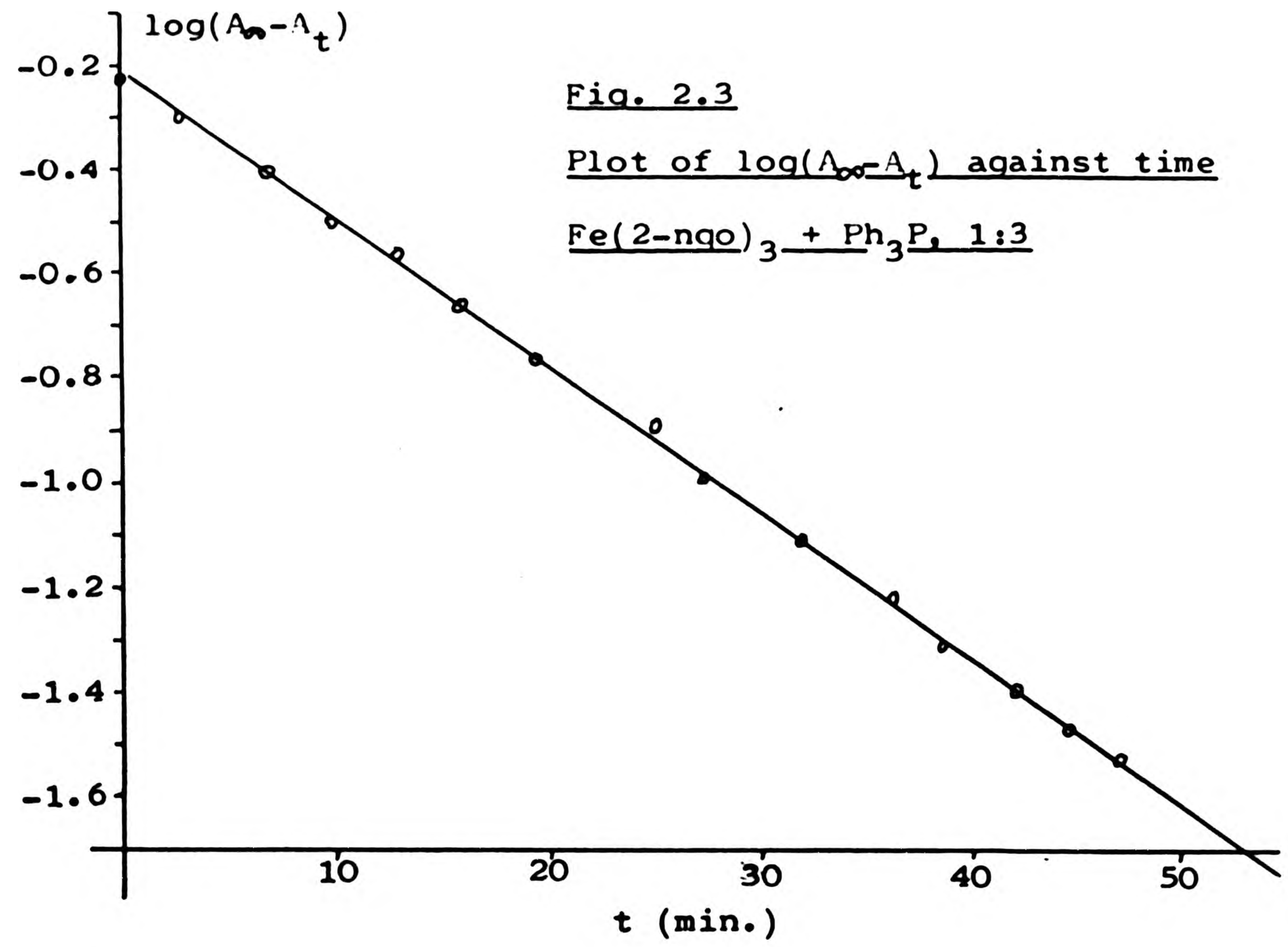


Fig. 2.3

Plot of log(A_∞-A_t) against time

Fe(2-nqo)$_3$ + Ph_3P, 1:3

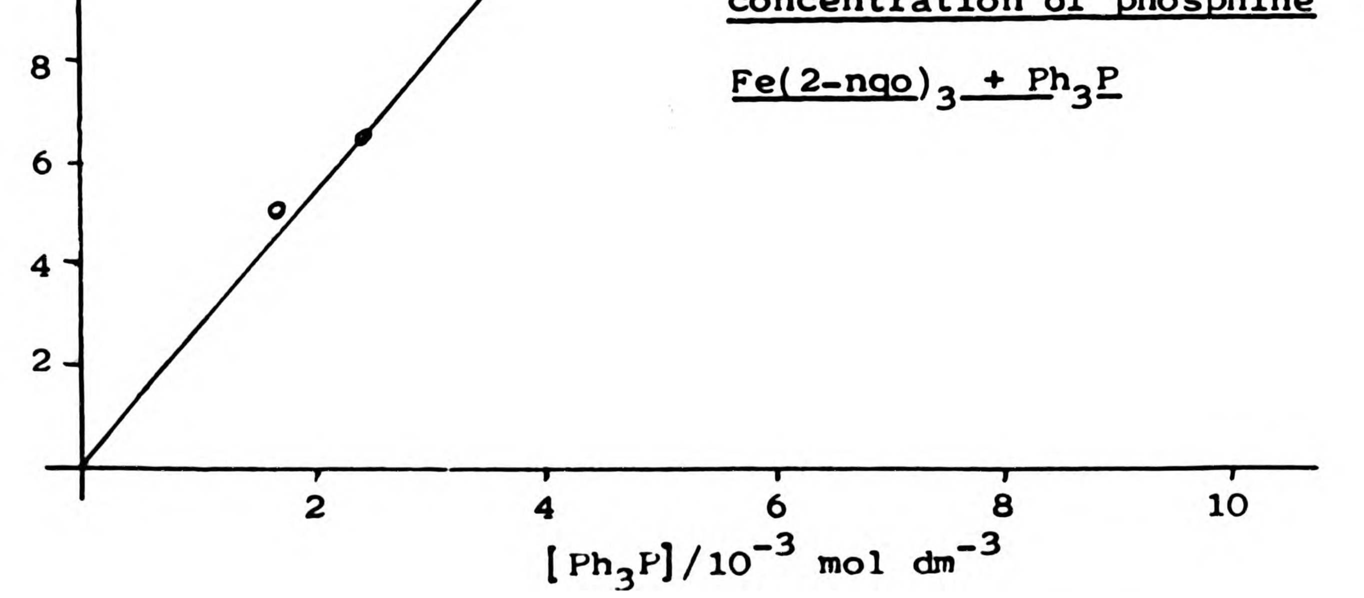


Fig 2.4

Plot of k_{obs} against initial concentration of phosphine

Fe(2-nqo)$_3$ + Ph_3P

fashion. The rate constants for the reaction at different concentrations of phosphine are given in Table 2.8.

Table 2.8

Initial conc. $Fe(2\text{-}nqo)_3/10^{-4}$ mol dm^{-3}	Initial conc. $Ph_3P/10^{-3}$ mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
5.66	1.70	4.90
5.67	2.40	6.33
5.59	3.91	11.17
5.60	4.65	11.63
5.69	5.69	14.78
5.66	8.49	17.04
5.67	9.87	17.09

A plot of k_{obs} versus initial concentration of phosphine gave a straight line which could be extrapolated back through zero and which levelled off to a constant value of k_{obs} at an approximate phosphine concentration of 8.5×10^{-3} mol dm^{-3}, which corresponds to a fifteen fold excess of the phosphine (Fig. 2.4).

T.l.c. examination of the solutions after completion of reaction showed the presence of the quinoneimine complex, together with small amounts of $Fe(2\text{-}nqo)_2$. The concentrations of the bischelates were then estimated using the extinction coefficients of the bischelate and the quinoneimine complex, together with the initial concentrations of $Fe(2\text{-}nqo)_3$ (Table 2.9).

Table 2.9

Initial conc. $Ph_3P/10^{-3}$ mol dm^{-3}	Conc. quinoneimine complex/10^{-4} mol dm^{-3}	Conc. $Fe(2\text{-nqo})_2$/ 10^{-4} mol dm^{-3}
1.70	4.66	1.00
2.40	4.58	1.09
3.91	4.71	0.88
4.65	4.35	1.25
5.69	4.57	1.12
8.49	4.61	1.05
9.87	4.59	1.08

However, the concentration of $Fe(2\text{-nqo})_2$ does not appear to be consistent. This is not unexpected as there are a number of factors which affect the amount of bischelate produced. These include:

i) Time:- The longer that the quinoneimine complex is in solution the more it is converted to $Fe(2\text{-nqo})_2$ by decomposition.This was observed in the macroscale reactions and also in the kinetic study. If the kinetic solutions were left to stand then decomposition to $Fe(2\text{-nqo})_2$ occurred with a shift of the isobestic point to a higher wavelength and a decrease in absorbance at 660 nm and 800 nm.

ii) The concentration of triphenylphosphine:- In the macroscale reactions of $Fe(2\text{-nqo})_3$ with triphenylphosphine it was found that the quinoneimine complex decomposes to $Fe(2\text{-nqo})_2$ in solution and that this process is speeded up in the presence of excess phosphine. The decomposition of the quinoneimine complex in solution was too slow to follow kinetically, due to evaporation of acetone from the uv/vis cells. However, when triphenylphosphine was added the decomposition was much more rapid and hence it was decided to carry out a kinetic investigation of the reaction between the quinoneimine complex and triphenylphosphine. This is outlined in Section 2.6.2.3.

b) The reaction of $Fe(2\text{-nqo})_3$ and triphenylphosphine in 1 cm reaction cells.

The reaction between $Fe(2\text{-nqo})_3$ and triphenylphosphine was also studied in 1 cm reaction cells using 10, 20 and 50 fold excesses of phosphine to complex and was monitored similarly to the reactions in the 1 mm cells. Because 1 cm cells were being used the initial concentration of complex was lower by a factor of ten compared to the initial concentration in the 1 mm cells. In a typical experiment a solution of the phosphine in acetone was added to a solution of $Fe(2\text{-nqo})_3$ in acetone, such that the initial concentration of phosphine was 1.1×10^{-3} mol dm^{-3} and that of complex was 5.6×10^{-5} mol dm^{-3}. The spectrum obtained is shown in Fig. 2.5. An isobestic point was found at 610 nm. A plot of $\log(A_{\infty}-A_t)$ for the absorbance at 800 nm against time gave a straight line, indicating the reaction to be first order with respect to the concentration of $Fe(2\text{-nqo})_3$. When the reaction was studied at other concentrations of triphenylphosphine the system behaved in

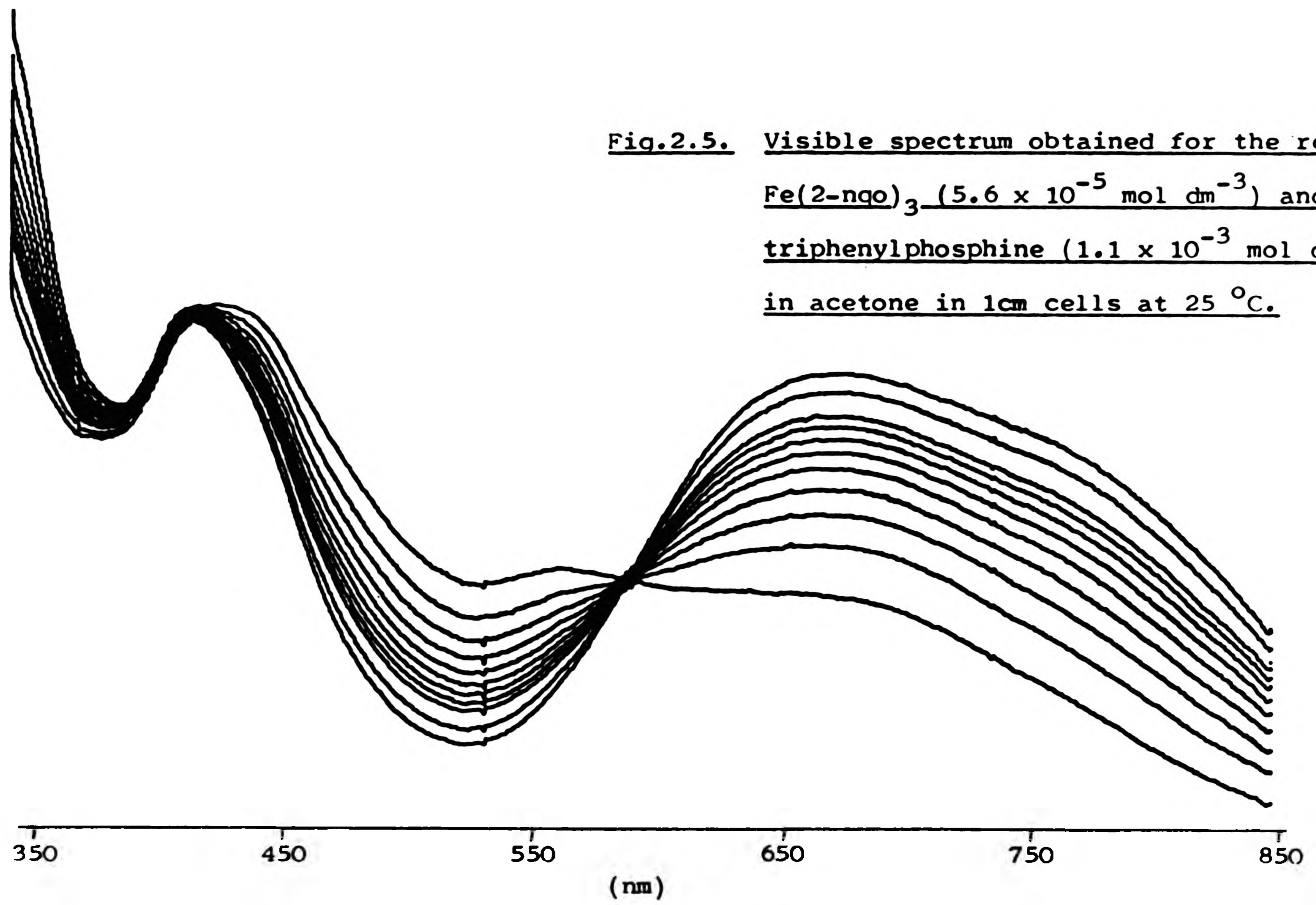


Fig.2.5. **Visible spectrum obtained for the reaction of Fe(2-nqo)$_3$ (5.6 x 10^{-5} mol dm^{-3}) and triphenylphosphine (1.1 x 10^{-3} mol dm^{-3}) in acetone in 1cm cells at 25 ^{o}C.**

an analogous fashion. The rate constant for the reaction at different concentrations is given in Table 2.10.

Table 2.10

Initial conc. $Fe(2\text{-}nqo)_3/10^{-5}$ mol dm^{-3}	Initial conc. $Ph_3P/10^{-3}$ mol dm^{-3}	$k_{obs}/10^{-4}$ s^{-1}
5.61	0.56	2.65
5.60	1.10	6.03
5.63	2.83	8.27

Comparison of the rate constants obtained from the reactions in the 1 mm and 1 cm cells shows that the same concentration of phosphine gives a similar rate constant in both types of cell. However, the final spectra of the reactions in the 1 cm cells are different to those obtained in the 1 mm cells. T.l.c. examination of the 1 cm cell solutions after completion of the reactions showed them to contain $Fe(2\text{-}nqo)_2$ as the major product, together with the quinoneimine complex and organic products. Thus it seems that in the 1 cm cell reactions decomposition of the quinoneimine complex occurs to finally give $Fe(2\text{-}nqo)_2$ and organic products. As similar first order rate constants for a given concentration of phosphine are obtained in both the 1 mm and 1 cm cell reactions, the rate determining step in the 1 cm cells is likely to be the formation of the quinoneimine complex. However, because of the complexity of the reaction system in 1 cm cells less importance should be attached to the values of k_{obs} obtained in these cells.

2.6.2.3 The reaction of $Fe(2\text{-nqo})_2(2\text{-nqH})(Ph_3PO)$ with triphenylphosphine.

As the quinoneimine complex, $Fe(2\text{-nqo})_2(2\text{-nqH})(Ph_3PO)$, was found to decompose faster in solution in the presence of triphenylphosphine, it was decided to carry out a kinetic investigation of this reaction. The decomposition was followed by recording the decrease in absorbance at 800 nm and was considered complete after 24h. A solution of the phosphine in acetone was added to a solution of the quinoneimine complex in acetone, such that the initial concentration of phosphine was 5.75×10^{-2} mol dm^{-3} and that of complex was 5.71×10^{-4} mol dm^{-3}. The spectrum obtained is shown in Fig. 2.6. A plot of $\log(A_\infty - A_t)$ against time for the decrease in absorbance at 800 nm gave a straight line, indicating the reaction to be first order with respect to the concentration of the quinoneimine complex. T.l.c. examination of the final reaction solution showed it to contain $Fe(2\text{-nqo})_2$, triphenylphosphine oxide and a number of organic products, similar to those isolated in the macroscale reaction of the quinoneimine complex with pyridine.

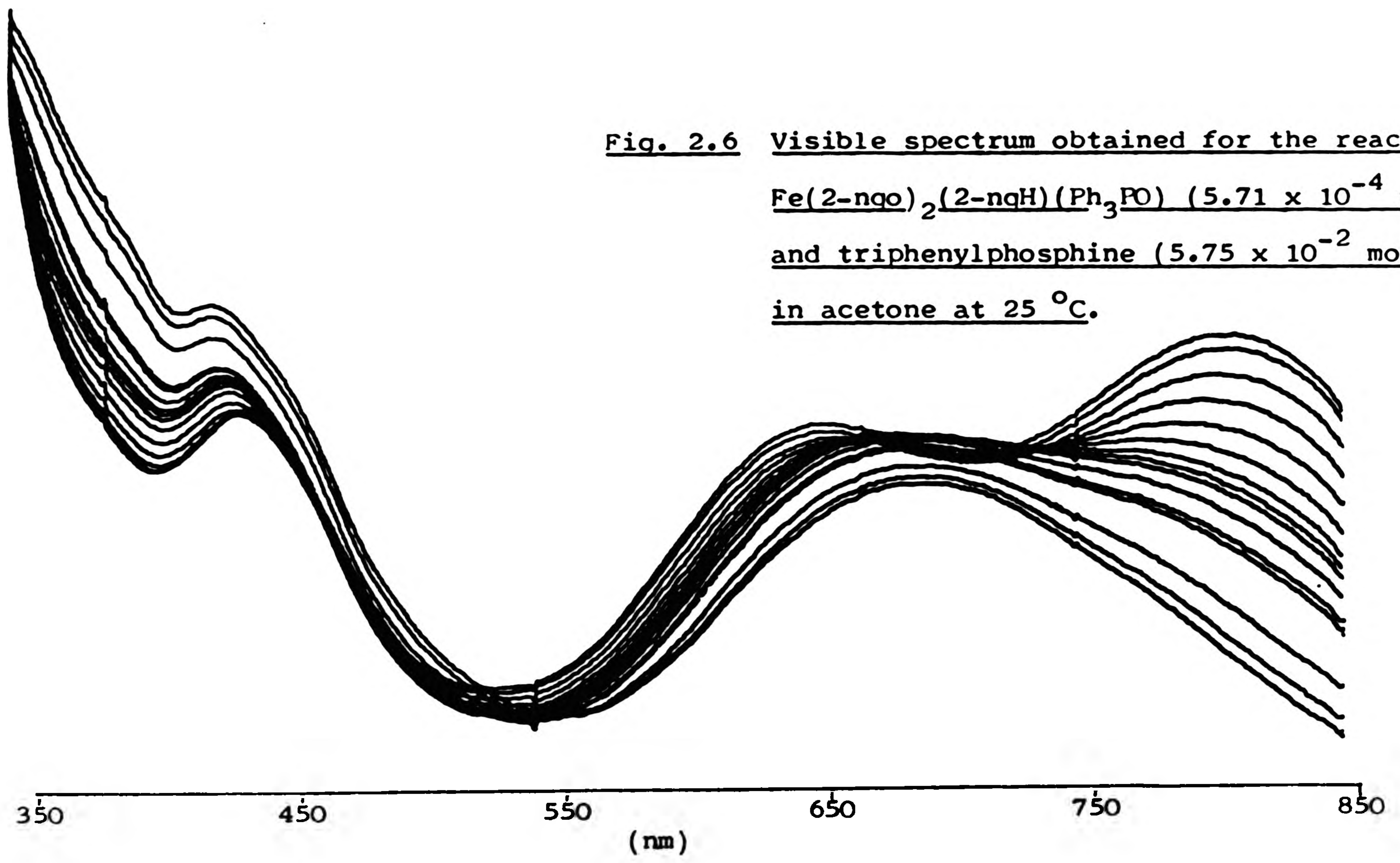


Fig. 2.6 **Visible spectrum obtained for the reaction of $Fe(2\text{-}nqo)_2(2\text{-}nqH)(Ph_3PO)$ (5.71×10^{-4} mol dm^{-3}) and triphenylphosphine (5.75×10^{-2} mol dm^{-3}) in acetone at 25 °C.**

2.6.2.4 The reaction of $Fe(1\text{-}nqo)_3$ with triphenylphosphine.

The reaction between $Fe(1\text{-}nqo)_3$ and triphenylphosphine was studied at 33 °C ± 0.2 °C at variable concentrations of the phosphine (ranging from 5 fold to 100 fold excess) in 1 mm cells. It was monitored by recording the increase in absorbance at 735 nm and the decrease in absorbance at 400 nm and was considered complete when no further change in absorbance could be observed at these wavelengths. For the five fold excess of phosphine reaction, a solution of the phosphine in acetone was added to a solution of $Fe(1\text{-}nqo)_3$ in acetone, such that the initial concentration of phosphine was 3.28×10^{-3} mol dm^{-3} and that of complex was 5.56×10^{-4} mol dm^{-3}. The spectrum obtained is shown in Fig. 2.7. The absorbance due to $Fe(1\text{-}nqo)_3$ at 400 nm and 450 nm started to decrease with a parallel increase in absorbance at 735 nm, 670 nm and 350 nm. Isobestic points were found at 368 nm and 595 nm. The final spectrum obtained was the same as that of the quinoneimine complex, $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$, isolated from the macroscale reaction of triphenylphosphine with $Fe(1\text{-}nqo)_3$. T.l.c. examination of the kinetic solution confirmed the presence of this complex. A plot of $\log(A_\infty - A_t)$ against time for the absorbance at 735 nm gave a straight line indicating the reaction to be first order with respect to the concentration of $Fe(1\text{-}nqo)_3$ (Fig. 2.8).

However, when the reaction was studied at higher concentrations of phosphine different results were obtained. At ratios of phosphine to complex of 10:1 and 50:1 a plot

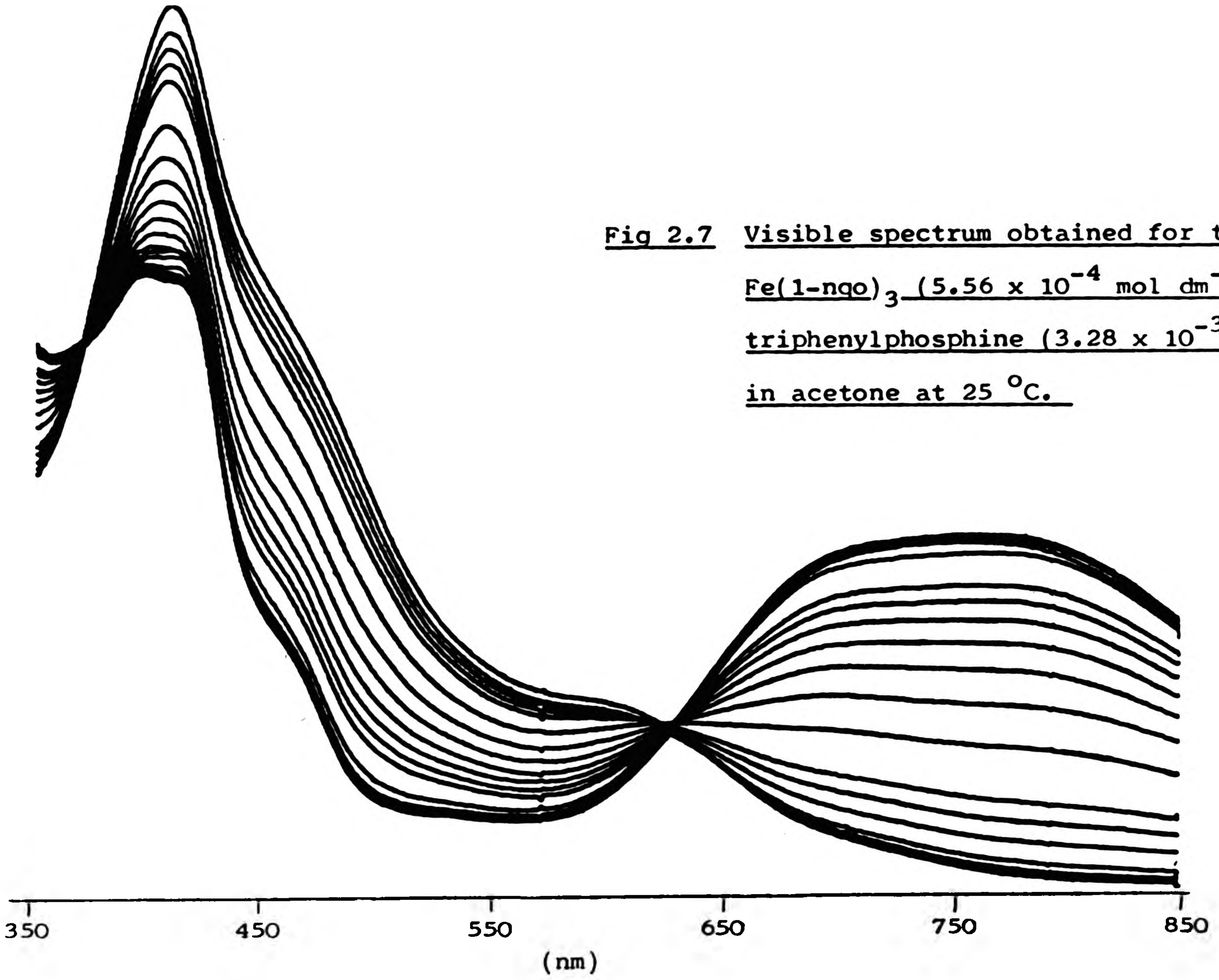


Fig 2.7 Visible spectrum obtained for the reaction of Fe(1-nqo)$_3$ (5.56 x 10^{-4} mol dm^{-3}) and triphenylphosphine (3.28 x 10^{-3} mol dm^{-3}) in acetone at 25 °C.

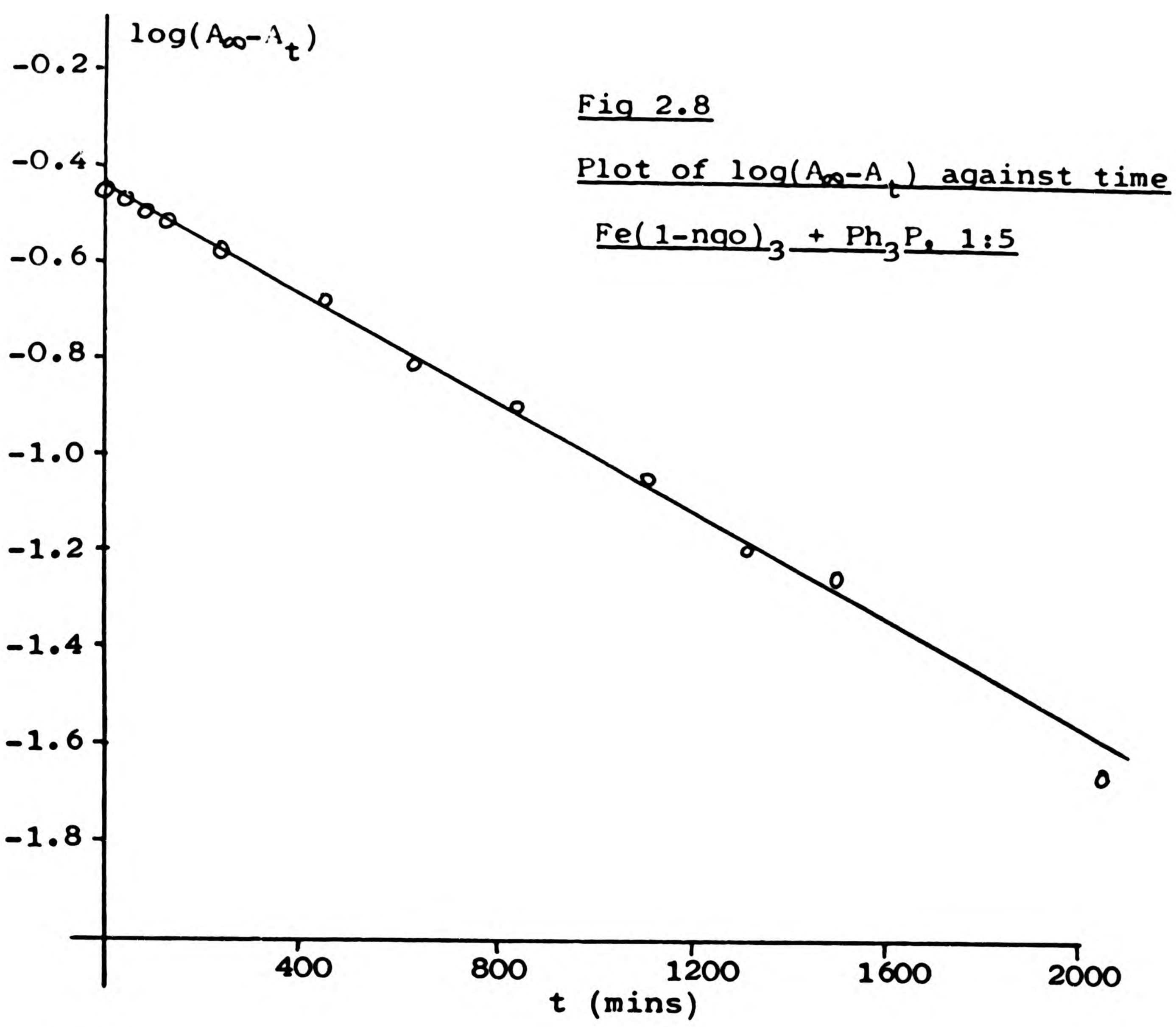


Fig 2.8

Plot of log(A_∞-A_t) against time

Fe(1-nqo)$_3$ + Ph$_3$P, 1:5

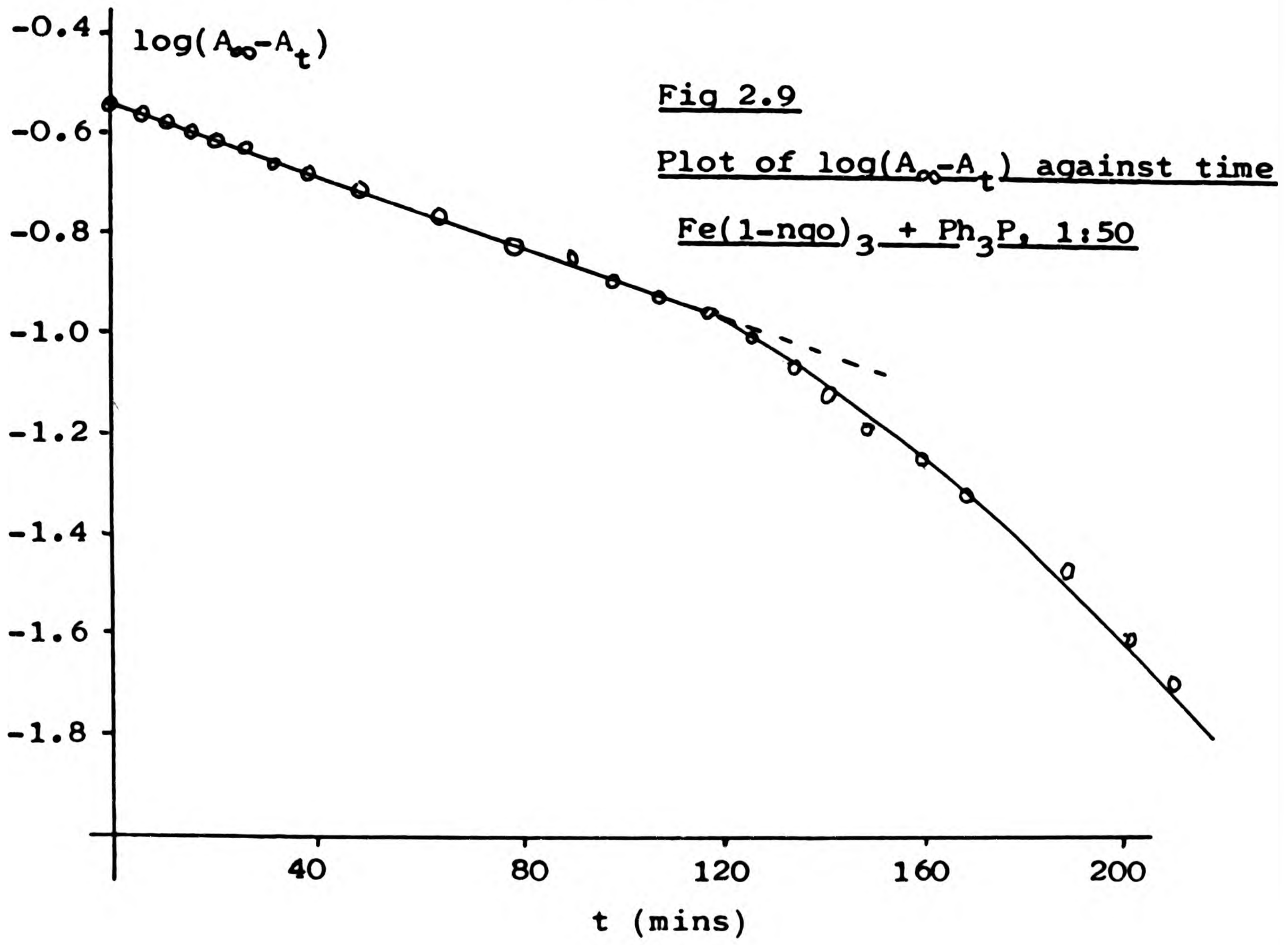


Fig 2.9

Plot of log(A_∞-A_t) against time

Fe(1-nqo)$_3$ + Ph$_3$P, 1:50

of $\log(A_\infty - A_t)$ against time gave rise to a graph with two distinct sections (Fig. 2.9), indicating that a further reaction with the phosphine was now occurring. A shifting in the position of the isosbestic points was also seen. In order to calculate the first order rate constants for the initial reaction, new values of A'_∞ were obtained by assuming that the first step in the reaction is the formation of $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$ and using the value of A_∞ obtained in the 5:1 reaction of phosphine to complex. Plots of $\log(A'_\infty - A_t)$ against time gave reasonable straight line graphs from which the first order rate constants were obtained (e.g. Fig. 2.10). These are given in Table 2.11.

Table 2.11

Initial conc. $Fe(1\text{-}nqo)_3/10^{-4}$ mol dm^{-3}	Initial conc. $Ph_3P/10^{-3}$ mol dm^{-3}	$k_{obs}/10^{-5}$ s^{-1}
5.56	3.28	2.12
5.52	5.56	3.34
5.51	28.00	18.42

A plot of k_{obs} versus initial concentration of phosphine gave a straight line which could be extrapolated back through zero (Fig. 2.11).

When a 100:1 ratio of phosphine to complex was used the final spectrum obtained differed from those of the previous reactions and corresponded to that of $Fe(1\text{-}nqo)_2(Ph_3P)_2$ (Fig. 2.12). T.l.c. examination

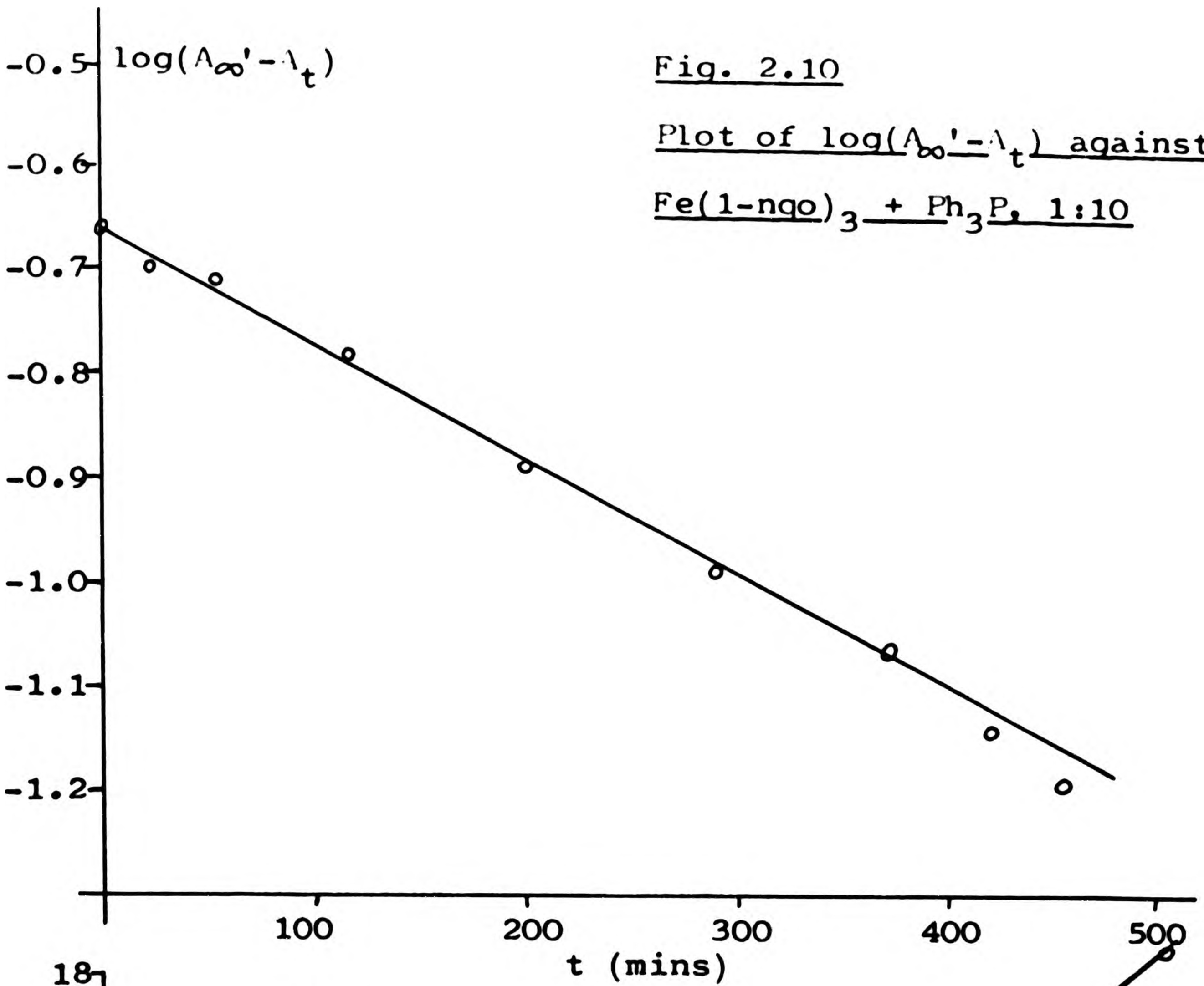


Fig. 2.10

Plot of $\log(\Lambda_\infty' - \Lambda_t)$ against time

$Fe(1\text{-nqo})_3 + Ph_3P$, 1:10

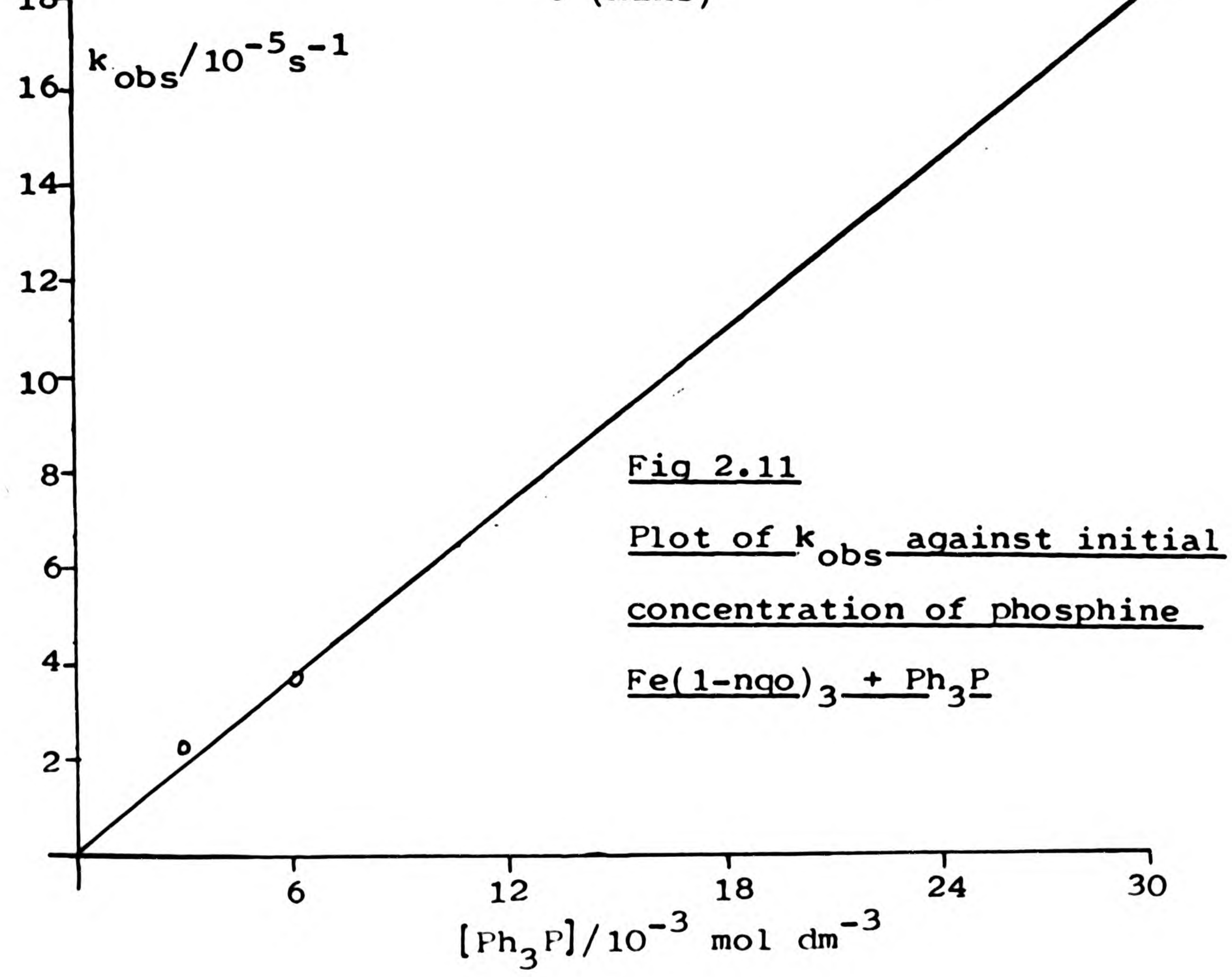


Fig 2.11

Plot of k_{obs} against initial concentration of phosphine

$Fe(1\text{-nqo})_3 + Ph_3P$

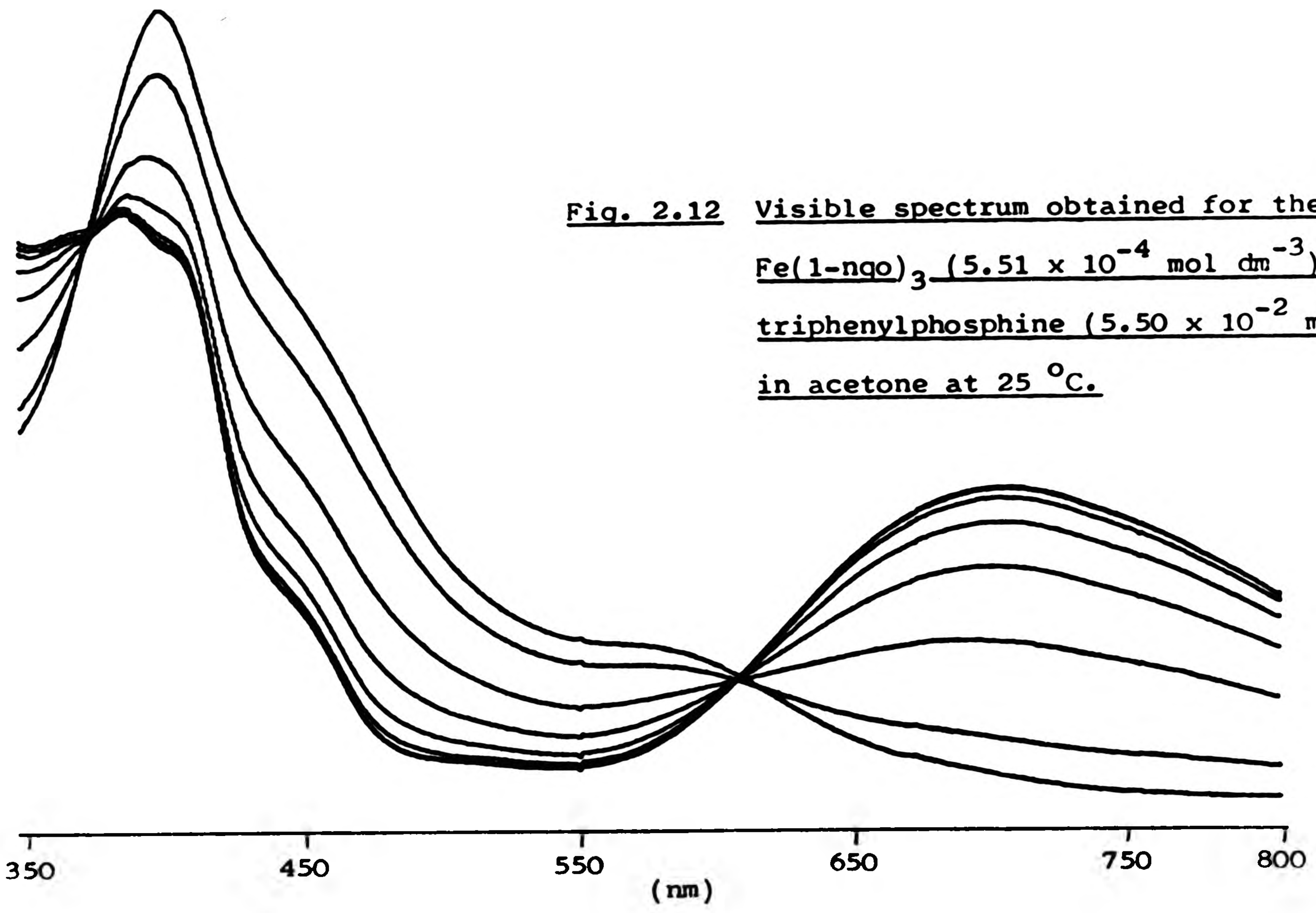


Fig. 2.12 Visible spectrum obtained for the reaction of $Fe(1\text{-}nqo)_3$ (5.51×10^{-4} mol dm^{-3}) and triphenylphosphine (5.50×10^{-2} mol dm^{-3}) in acetone at 25 °C.

of the kinetic solution confirmed the presence of this complex. A plot of $\log(A_\infty - A_t)$ against time for the absorbance at 735 nm gave a curve. Thus a plot of $(A_\infty - A_t)$ against time for the absorbance at 735 nm was drawn. Tangents to the curve were taken to give the rate at different times. Then log(rate) was plotted against $\log(A_\infty - A_t)$ to give a reasonably straight line graph with a gradient of 0.6. This indicates that the kinetics of the reaction must be complex. In view of the reactions of triphenylphosphine with $Fe(1\text{-}nqo)_3$ at lower concentrations, it seems likely that two reactions are occurring. Due to the high concentration of the phosphine, the second reaction occurs rapidly, such that no distinction between the first and second reactions can be seen.

2.6.2.5 The reaction of $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$ with triphenylphosphine.

In view of the results obtained from the reaction of $Fe(1\text{-}nqo)_3$ with triphenylphosphine at a high concentration, it was decided that a kinetic investigation of the reaction between the quinoneimine complex, $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$, and triphenylphosphine should be carried out. The reaction was monitored by recording the increase in absorbance at 660 nm and was considered complete after 2h. A solution of the phosphine in acetone was added to a solution of the quinoneimine complex in acetone such that the initial concentration of phosphine was 5.11×10^{-2} mol dm^{-3} and that of complex was 5.00×10^{-4} mol dm^{-3}. The spectrum obtained is shown in Fig. 2.13. A plot of $\log(A_\infty - A_t)$ against time for the increase in absorbance at 660 nm is shown in Fig. 2.14. This gives a straight line plot, indicating the reaction to be first order with respect to the concentration of the quinoneimine complex. T.l.c. examination of the solution showed it to contain $Fe(1\text{-}nqo)_2(Ph_3P)_2$, triphenylphosphine oxide and organic products similar to those obtained from the macroscale reaction of the quinoneimine complex with triphenylphosphine.

2.6.2.6 Kinetic conclusions.

The kinetic investigation of the reaction of $Fe(2\text{-}nqo)_3$ with triphenylphosphine showed the reaction to be first order with respect to the complex, at all concentrations of phosphine. It was also found that the rate of reaction levels off at a certain concentration of phosphine. This behaviour is not uncommon, but is normally only observed when large concentrations of reactant (in this case phosphine) compared to concentration of complex are present. This is because the rate equation used to calculate k_{obs} assumes that a large excess of phosphine is present, such that for all intents and purposes the concentration of phosphine remains constant throughout the reaction. However, in the reactions described here, the ratio of phosphine to complex is quite low, e.g. 3:1, and hence the reaction would not be expected to follow first order behaviour. Two possible explanations for this are:

a) The acetone used was wet and it was water initiating the reaction rather than triphenylphosphine. This

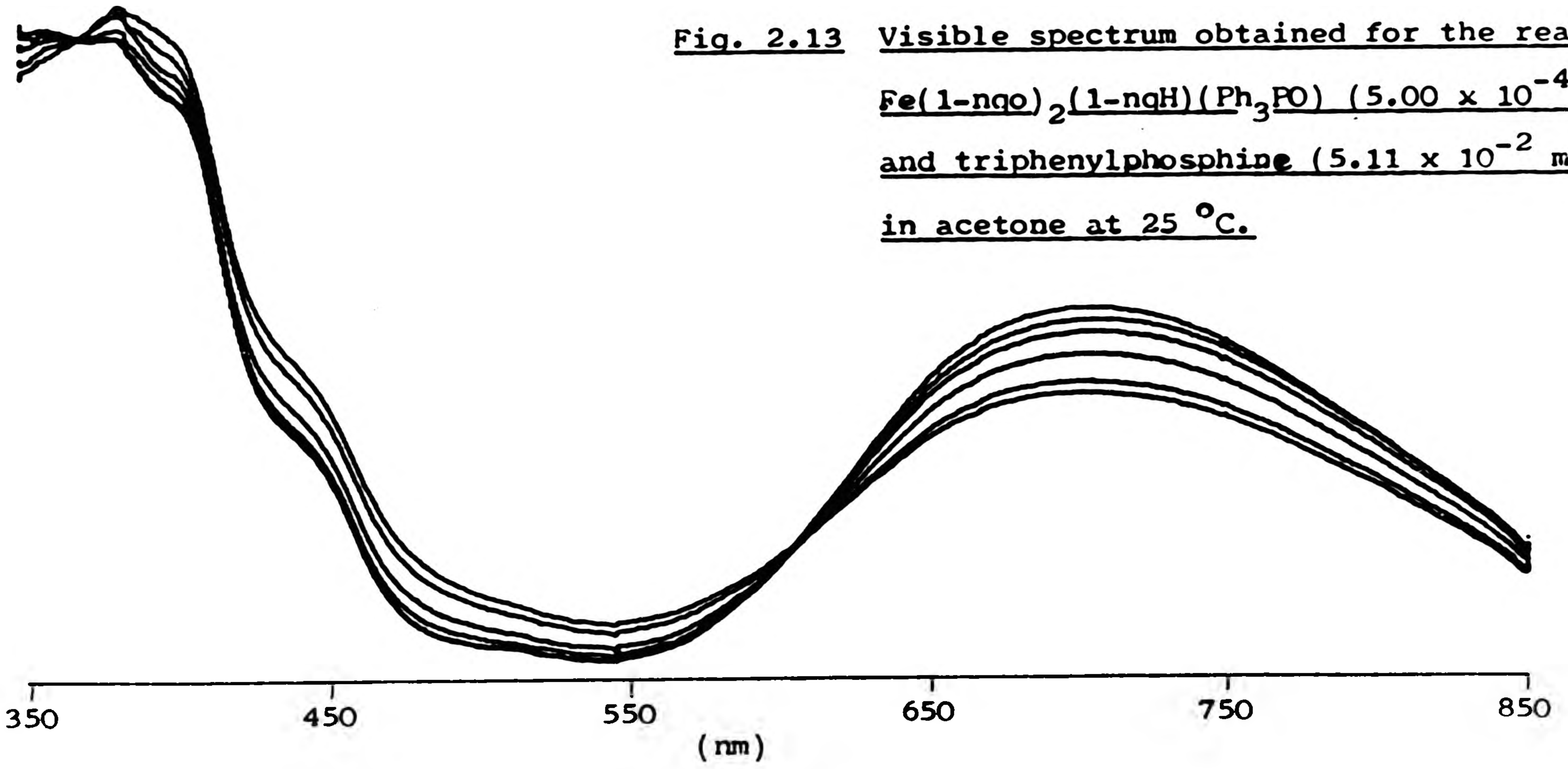


Fig. 2.13 Visible spectrum obtained for the reaction of $Fe(1\text{-nqo})_2(1\text{-nqH})(Ph_3PO)$ (5.00×10^{-4} mol dm^{-3}) and triphenylphosphine (5.11×10^{-2} mol dm^{-3}) in acetone at 25 °C.

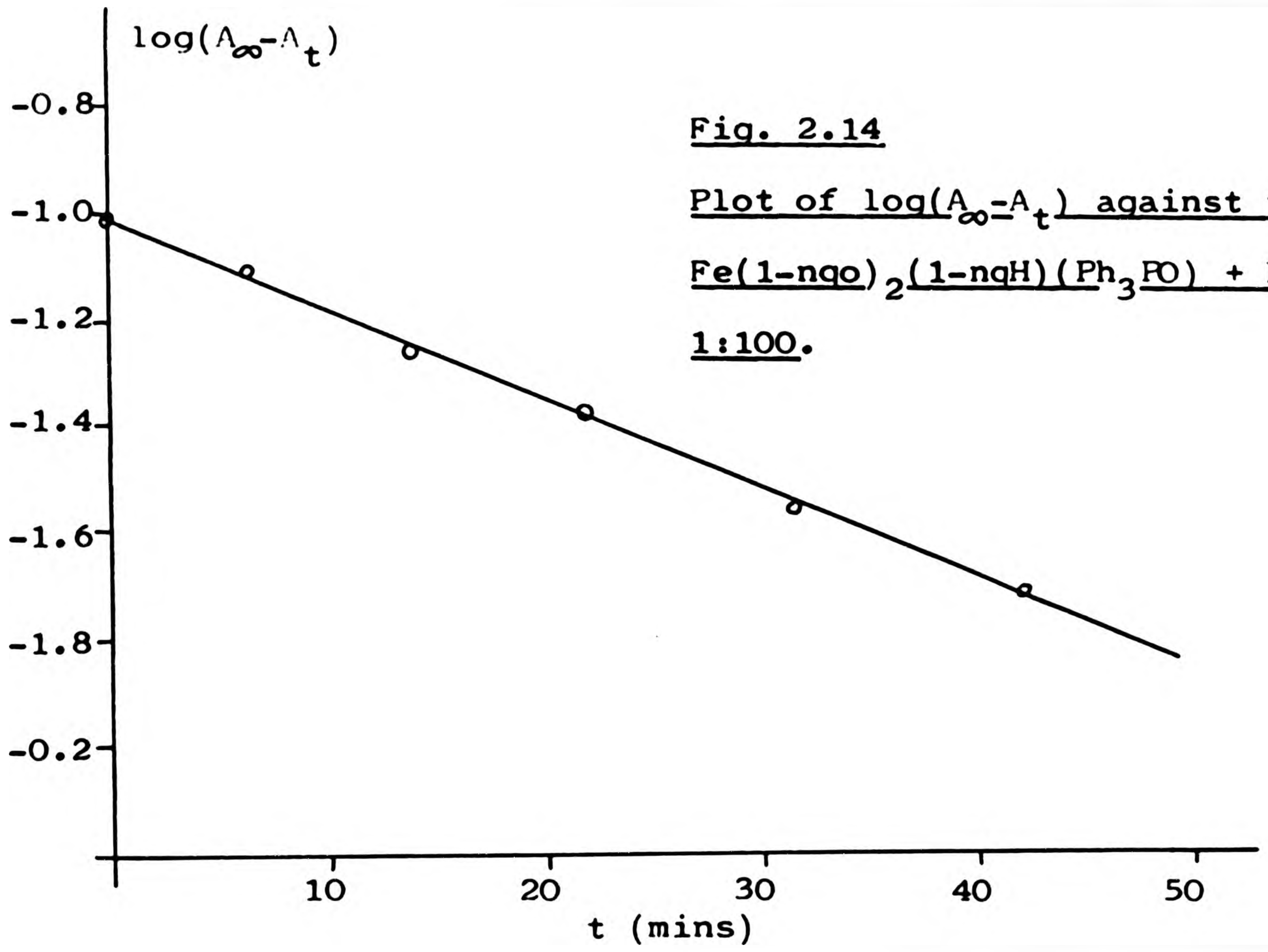


Fig. 2.14

Plot of $\log(A_\infty - A_t)$ against time

$Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO) + Ph_3P$,

1:100.

possibility was removed by carrying out a reaction in spectrosol acetone (dried further by refluxing with potassium permanganate) in glassware and reaction cells that had been kept as dry as possible before use. A seven fold excess of phosphine was used. This gave a a first order plot with a rate constant similar to that obtained in the equivalent reaction using undried acetone.

b) As the phosphine is involved in the rate determining step of the reaction, this implies that it is reacting with something other than $Fe(2\text{-}nqo)_3$, which is present in relatively small amounts such that the phosphine is in large excess. The concentration of this reactive species must be proportional to the concentration of $Fe(2\text{-}nqo)_3$, in order for the kinetics to be first order with respect to $Fe(2\text{-}nqo)_3$. Although it has not been established what the nature of the reactive species is, one possibility is that the solvent is involved such that;

$$Fe(2\text{-}nqo)_3 + S \underset{}{\overset{\text{rapid}}{\rightleftharpoons}} [Fe(2\text{-}nqo)_3.S]$$

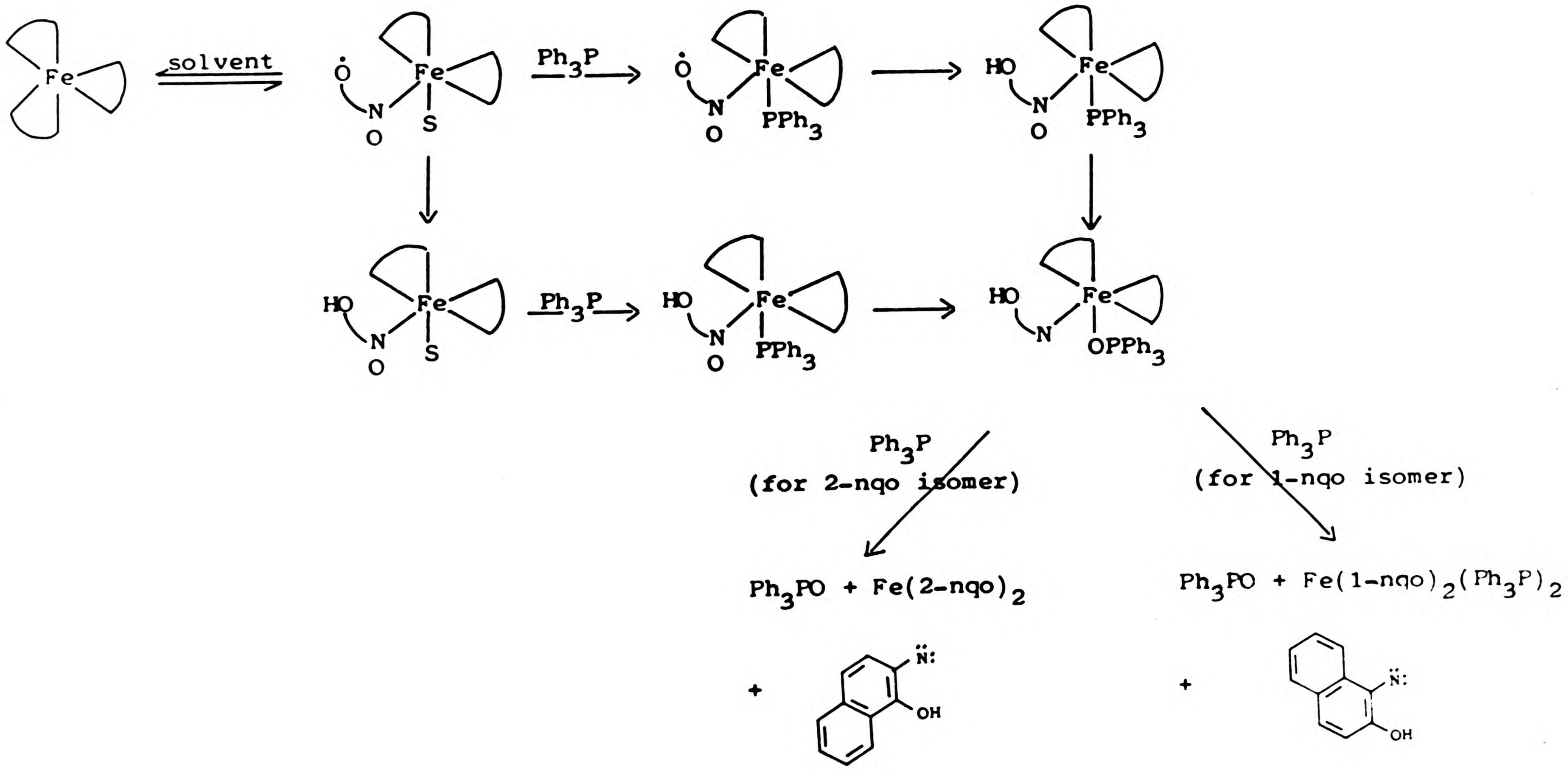
The species involving the solvent could then react with triphenylphosphine and the final product could be formed with a rate determining step dependent on the phosphine. If the amount of $[Fe(2\text{-}nqo)_3.S]$ at any time is small then the phosphine will be in large excess, thus accounting for the first order rate constants obtained.

The kinetic investigation of the reaction of $Fe(1\text{-}nqo)_3$ with triphenylphosphine showed the reaction to consist of two distinct stages. The first stage was shown to be first order with respect to $Fe(1\text{-}nqo)_3$ and gave rise to $Fe(1\text{-}nqo)_2(1\text{-}nqH)(Ph_3PO)$. Although the reaction could not be studied at concentrations as low as those used in the $Fe(2\text{-}nqo)_3/Ph_3P$ system (due to reaction time) it is probable that this stage is analogous to the reaction of $Fe(2\text{-}nqo)_3$ with triphenylphosphine. In the second stage the quinoneimine complex reacts further with the phosphine to give $Fe(1\text{-}nqo)_2(Ph_3P)_2$.

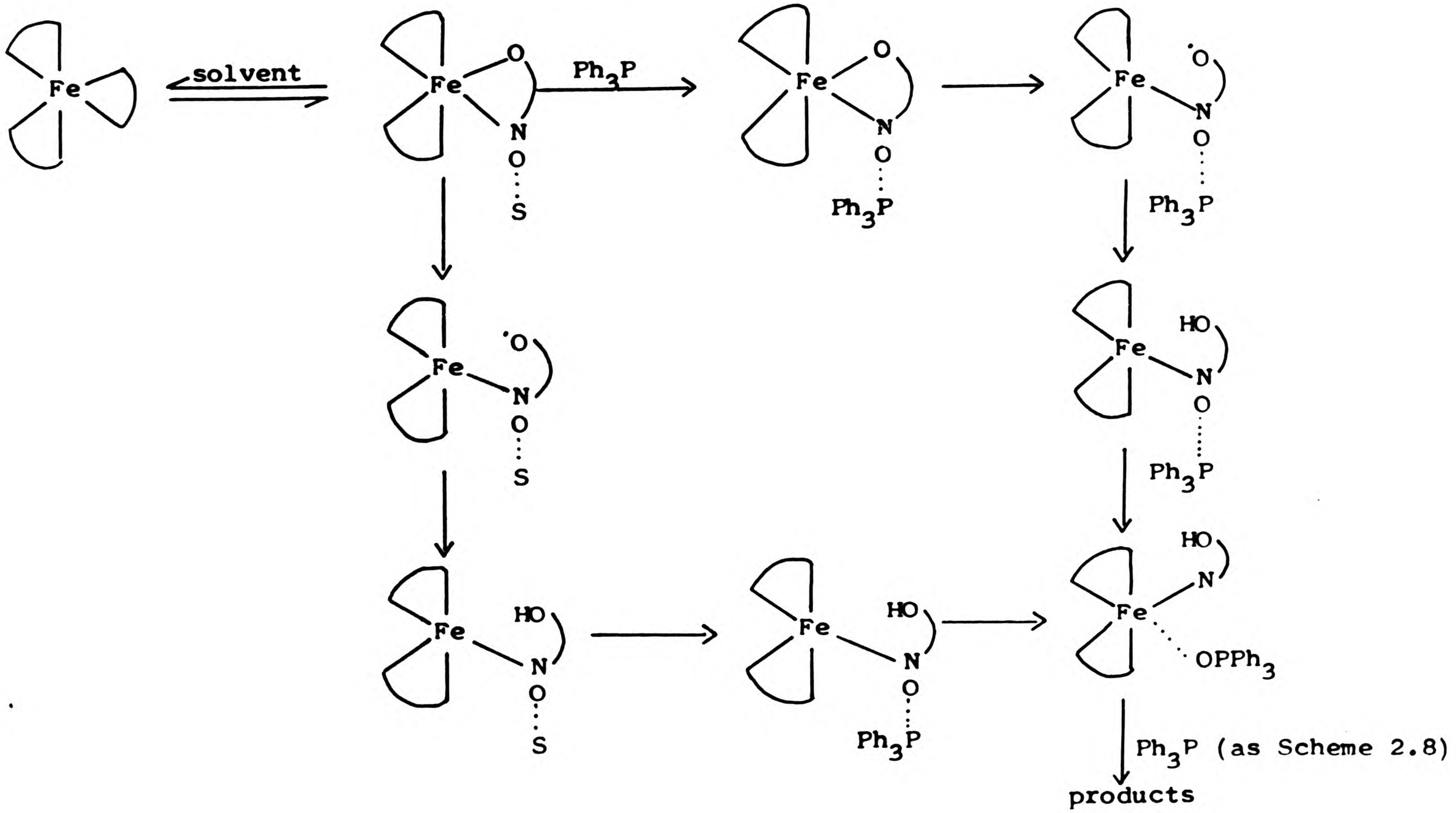
The reactive species has been described here as being of the type $[Fe(nqo)_3.S]$. This could take two possible forms. Either S could be associated with one of the nqo ligands, or alternatively one of the nqo ligands could become monodentate, with S coordinated to the metal.

Two possible mechanisms which are in accordance with these observations are given in Schemes 2.8 and 2.9.

Scheme 2.8


solvent
Fe
Ph$_3$P
PPh$_3$
OPPh$_3$
Ph$_3$P
(for 2-nqo isomer)
Ph$_3$P
(for 1-nqo isomer)
Ph$_3$PO + Fe(2-nqo)$_2$
Ph$_3$PO + Fe(1-nqo)$_2$(Ph$_3$P)$_2$
+
OH

Scheme 2.9



2.6.3 The effect of different solvents on the reaction of triphenylphosphine with $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$.

The reactions were carried out in two other solvents, as well as acetone. These were :

a) Trichlorotrifluoroethane

The reactions were carried out in this solvent because it does not contain hydrogen. Thus any hydrogen abstracting step involving the ligand radical will be blocked and the radical forced to react in a different fashion. Isolation of the reaction products should provide evidence for the involvement of hydrogen abstraction during the reaction. When the trischelates were stirred with triphenylphosphine in the hydrogen free solvent no reaction was observed, even when the reactions were attempted under reflux conditions.

b) Propan-2-ol

This solvent was used because it has strong hydrogen atom donating properties.[59] It would be expected that if hydrogen atom abstraction is the crucial step in the reactions, then it will be speeded up by the use of propan-2-ol. When the trischelates were stirred in propan-2-ol it was found that the reaction products were similar to those obtained when the reactions were carried out in acetone. However, the reactions were much slower in propan-2-ol.

2.6.3 The effect of different solvents on the reaction of triphenylphosphine with Fe(1-nqo)$_3$ or Fe(2-nqo)$_3$.

The reactions were carried out in two other solvents, as well as acetone. These were :

a) Trichlorotrifluoroethane

The reactions were carried out in this solvent because it does not contain hydrogen. Thus any hydrogen abstracting step involving the ligand radical will be blocked and the radical forced to react in a different fashion. Isolation of the reaction products should provide evidence for the involvement of hydrogen abstraction during the reaction. When the trischelates were stirred with triphenylphosphine in the hydrogen free solvent no reaction was observed, even when the reactions were attempted under reflux conditions.

b) Propan-2-ol

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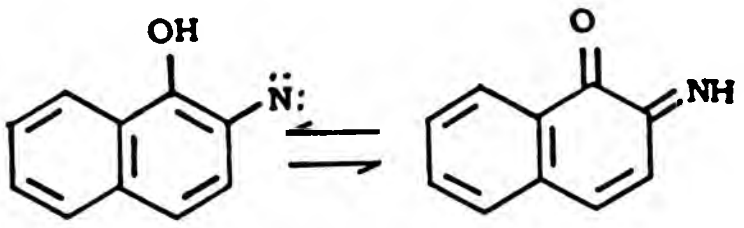
2.6.4 Mechanistic conclusion.

On the basis of the kinetic data two possible mechanistic proposals can be made. Both of these are dependent on the solvent interacting with the trischelate, Fe(nqo)$_3$, to produce a 'reactive species', which is capable of reacting with triphenylphosphine. In the mechanism outlined in Scheme 2.8 the solvent coordinates to the metal and initiates an internal redox reaction. In the mechanism outlined in Scheme 2.9 the solvent associates with one of the nqo ligands and the internal redox reaction is initiated later by either the solvent or triphenylphosphine, or by a mixture of both. Each mechanism then requires a solvent capable of donating a hydrogen atom to a ligand radical. Thus it would be expected that use of a strong hydrogen donating solvent would speed the reaction up. However, when propan-2-ol was used as a solvent the reactions were slowed down considerably. An explanation for this (particularly for the mechanism in Scheme 2.8) is that the amount of interaction between the solvent and the trischelate will depend on the Lewis base strength of the solvent and on the size of the solvent molecule. Acetone is both a stronger Lewis base and a smaller molecule than propan-2-ol and is thus able to more easily interact with the iron complex.

One of the organic products obtained from the decomposition of Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO), or the reaction of this complex with various reagents (Section 2.4), is

2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinonemonoimine. The formation of this has previously been ascribed to the reaction of 2-amino-1-naphthol with 2-nitroso-1-naphthol,[2] as it is known that such compounds can be formed by the attack of an amino compound on the 4-position of naphthoquinoid species.[60] However, if the mechanisms involving intramolecular deoxygenation are correct this is unlikely as the nitrene released upon decomposition of the quinone imine complex would show little tendency to abstract oxygen to form 2-nitroso-1-naphthol. However, the nitrene species, 2.26, is known to abstract hydrogen to form 2-amino-1-naphthol, which could then react with 2.26 to give the naphthoquinone monoimine.

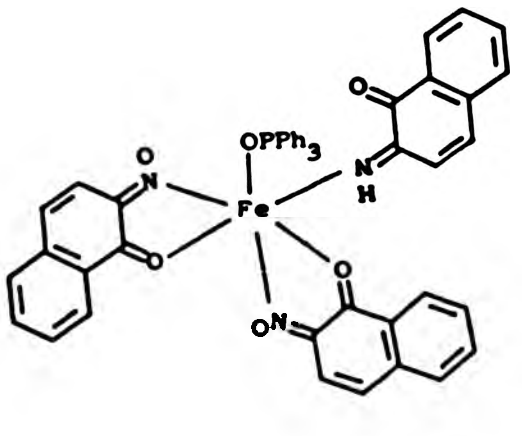


2.26a 2.26b

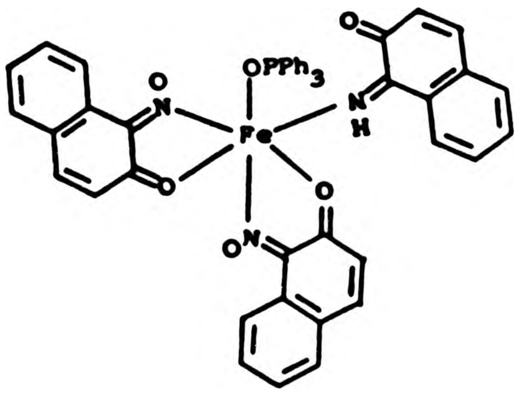
The other organic products formed from the decomposition and reactions of the quinoneimine complexes can all be rationalised in terms of nitrene intermediacy.

2.7 Conclusion.

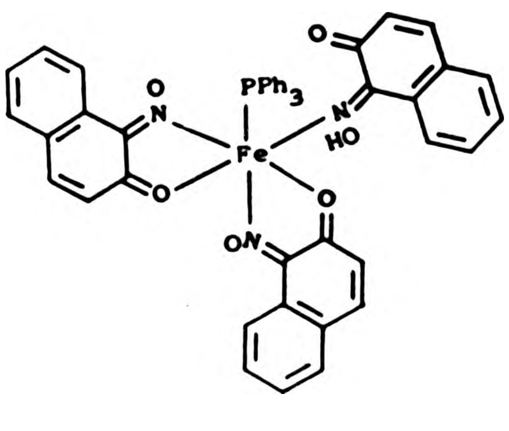
Both $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ react with triphenylphosphine to give rise to complexes of a novel type. The chemical and spectroscopic studies carried out indicate that the complex obtained from the 1-nitroso-system has structure 2.14 and that from the 2-nitroso-system structure 2.11. In the case of the 1-nitroso-system, the evidence for the complex having structure 2.14 is not as strong as that for the complex obtained from the 2-nitroso-system having structure 2.11. Some of the experimental results indicate that the 1-nitroso-system complex may instead have structure 2.15.



2.11



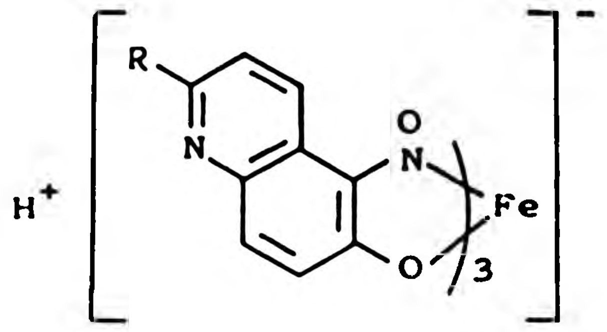
2.14



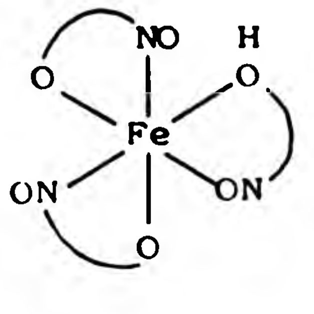
2.15

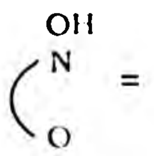
Both Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO) and Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO) are stable in the solid form but decompose readily in solution to the respective bischelate, triphenylphosphine oxide and organic compounds arising from a deoxygenated nqo ligand. The complexes react with pyridine to give the pyridine adduct of the bischelate and similar organic products to those obtained from the solvent decomposition. Similarly, Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO) reacts with triphenylphosphine to give the adduct Fe(1-nqo)$_2$(Ph$_3$P)$_2$. However, in the presence of triphenylphosphine, Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO) yields the bischelate, Fe(2-nqo)$_2$. Although it is not clear why there is this difference, it may be due to steric factors. Other differences between the two systems were also observed. The reaction between Fe(1-nqo)$_3$ and the phosphine is much slower than that of Fe(2-nqo)$_3$ with triphenylphosphine. Also, Fe(1-nqo)$_2$(1-nqH)(Ph$_3$PO) is not decomposed by hydrogen sulphide, whereas Fe(2-nqo)$_2$(2-nqH)(Ph$_3$PO) is. These differences could suggest that the two complexes have different structures. However, the Mössbauer spectra of the complexes are very similar and their i.r. spectra indicate that they are of a similar type and that both contain triphenylphosphine oxide as a ligand, rather than triphenylphosphine. Thus, on balance, it seems more likely that the complex obtained from the 1-nitroso-system has structure 2.14 and not 2.15.

Recently, iron(II) complexes with structures similar to those proposed have been reported. El'tsov et al have patented a new dye for polyamide fibres, which has been formulated as being of the type $H^{+}[FeL_3]^{-}$ (2.27),[61] on the basis that the complex is low spin, iron(II). This type of structure is extremely unlikely and alternatively it is better formulated as FeL_2LH. In this form it can be seen that the dye has a similar structure to those proposed for the complexes isolated in this study. Other complexes with this type of structure have been described and have also been assigned structures of the type $H^{+}[FeL_3]^{-}$, on the basis that the complexes are iron(II) and diamagnetic.[62-65] Again, these complexes are best formulated as containing an LH type ligand, to give a structure of type 2.28



2.27





= 7-nitroso-6-hydroxybenzothiazole,
5-nitroso-6-hydroxyquinoline,
violuric acid, monomethyl violuric acid
and dimethyl violuric acid.

2.28

2.8 References.

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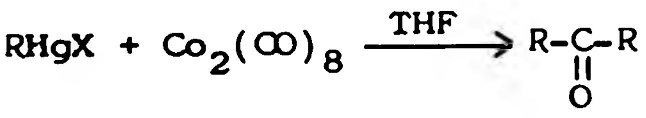
CHAPTER 3

3. The reaction of selected quinone monoximes with iron pentacarbonyl and the interaction of quinone monooximic and related complexes with carbon monoxide and/or nitric oxide.

3.1 Introduction.

Reactions of carbon monoxide and/or nitric oxide with metal compounds are important because of their synthetic, catalytic and physiological implications.

Compounds containing coordinated carbon monoxide are of use in organic synthesis. The majority of these synthetic applications either involve the use of metal carbonyls,[1-4] e.g. Reaction 3.1,[1] or require the formation of an intermediate organometallic complex in situ, from carbon monoxide and a metal compound,[5-15] e.g. Reaction 3.2.[10]



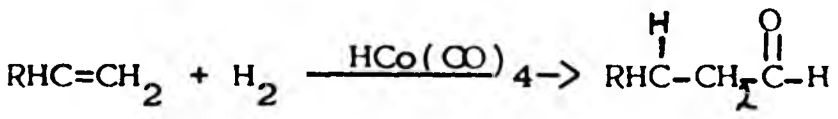
$$RHgX + Co_2(CO)_8 \xrightarrow{THF} R\text{-}\underset{\underset{O}{\|}}{C}\text{-}R$$

Reaction 3.1

$$RCl + R'OH \xrightarrow[CO,\ (PPh_3)_2PdBr_2]{100\ ^{o}C} RCOOR'$$

Reaction 3.2

Carbon monoxide complexes have also been widely used as catalysts in organic synthesis. For example, the OXO reaction uses a cobalt carbonyl to convert an alkene into an aldehyde (Reaction 3.3).[16,17] The mechanism for this reaction probably involves an intermediate complex between the alkene and the cobalt carbonyl which is subsequently hydrogenated and then reacts with carbon monoxide.[18]



$$RHC{=}CH_2 + H_2 \xrightarrow{HCo(CO)_4} RH\overset{H}{C}{-}CH_2{-}\overset{O}{\overset{\|}{C}}{-}H$$

Reaction 3.3

Carbon monoxide and nitric oxide will readily react with a variety of metal complexes, such as bis(dithioacetylacetonato)iron(II), $Fe(C_5H_7S_2)_2$,[19] to form adducts. Some of these are useful model compounds for a number of biological systems. Both carbon monoxide and nitric oxide have an adverse physiological effect and particular emphasis has been placed on the interaction of carbon monoxide with iron complexes in an effort to synthesise model compounds for hæmoglobin.[20-35]

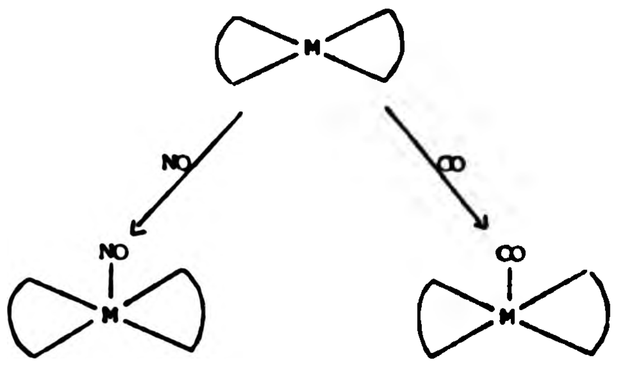
These physiological effects are of particular significance with regard to the aim of this thesis, i.e. the removal of carbon monoxide and nitric oxide from tobacco smoke. Normal cigarette filters are not capable of appreciably affecting the levels of the oxides. However, a number of filters have been designed which utilise the reactions of metal compounds with carbon monoxide and/or nitric oxide. These are discussed in Chapter 4, but it is worth noting at this stage that none of these filters has been particularly successful.

The work described in the following sections of this chapter was undertaken with the aim of assessing aspects of the chemistry of metal complexes which could be successfully used in the removal of carbon monoxide and nitric oxide from tobacco smoke.

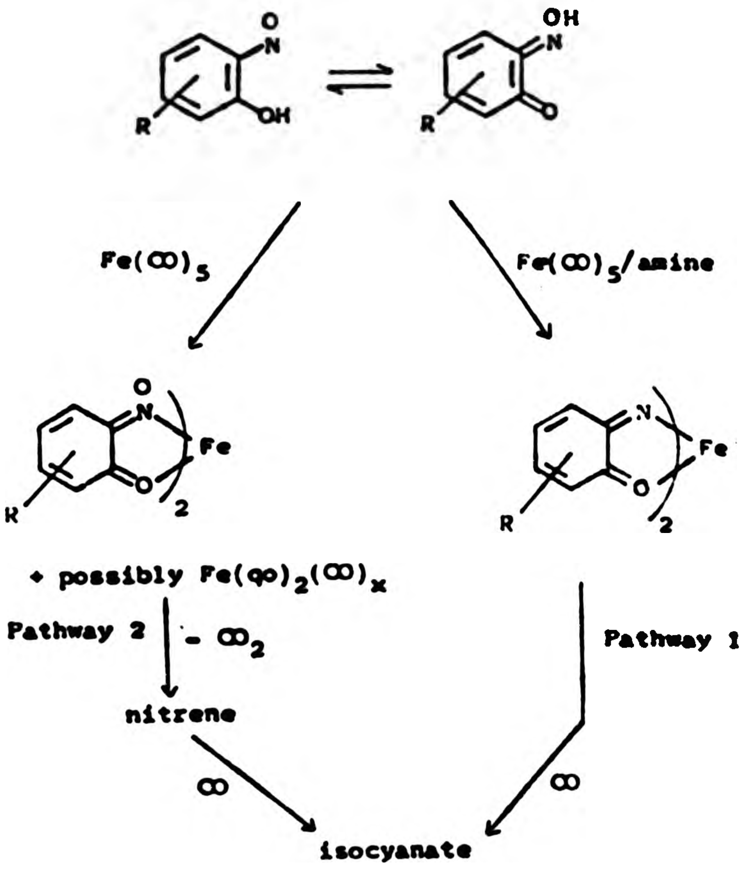
As stated previously, a number of complexes are known to react with carbon monoxide and nitric oxide to form adducts (Scheme 3.1). In the case of complexes derived from quinone monooximes, in addition to the possibility of adduct formation, there are other features which can be of value in the removal of carbon monoxide. These features are indicated in Scheme 3.2. There is evidence to suggest that deoxygenating agents, such as aniline,[36,37] lead to complexes containing nitrene ligands. There is the possibility that this type of ligand could react with carbon monoxide to form isocyanate-type ligands (Pathway 1, in Scheme 3.2). Also, it has been established that iron pentacarbonyl will react with quinone monooximes to give complexes of the type $Fe(qo)_2$ and possibly $Fe(qo)_2(CO)_x$.[36,38,39] Deoxygenation of the qo ligands in these complexes would also lead to nitrene ligands, which could react further with carbon monoxide to give isocyanate type ligands (Pathway 2, in Scheme 3.2).

The examples above all utilise an iron(II) complex in the reactions with carbon monoxide/nitric oxide. However, there is also the possibility that complexes of the type FeL_3 can be used. These complexes are capable of undergoing an internal redox reaction in the presence of a Lewis base to give a reduced metal species and a ligand radical (Scheme 3.3). The reduced metal species can react further with carbon monoxide or nitric oxide to give products such as those outlined in Schemes 3.1 and 3.2. The ligand radical can react further with nitric oxide, which itself has a radical nature, to give other products.

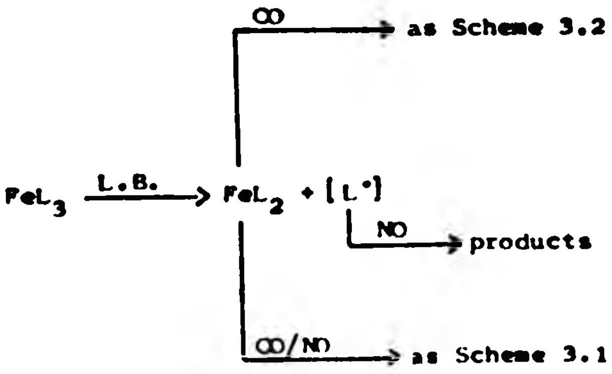
Scheme 3.1



Scheme 3.2



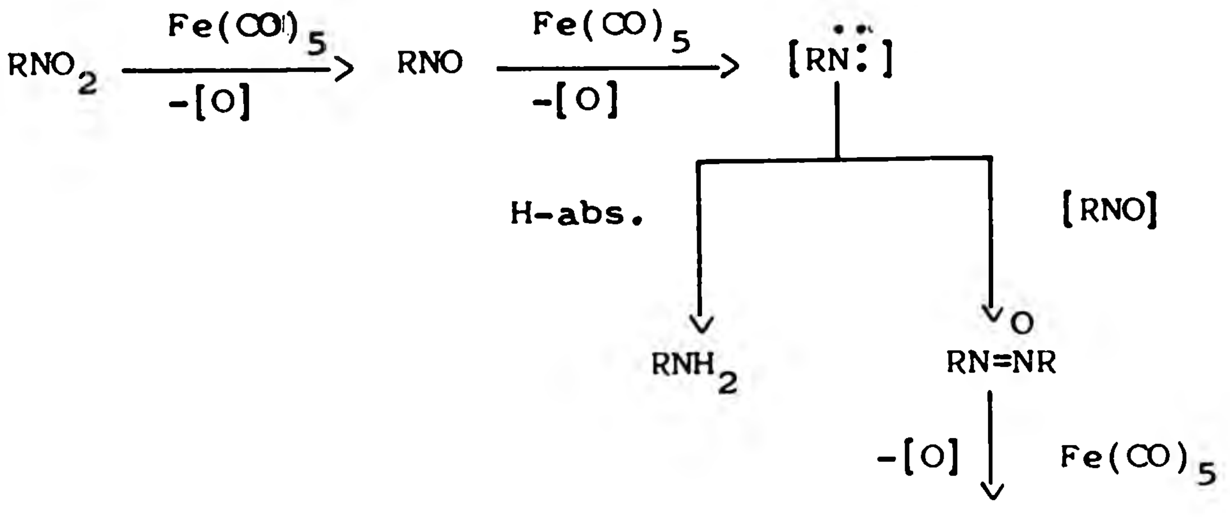
Scheme 3.3



3.2. The interaction of iron pentacarbonyl with the monooximes of 1,2-naphthoquinone.

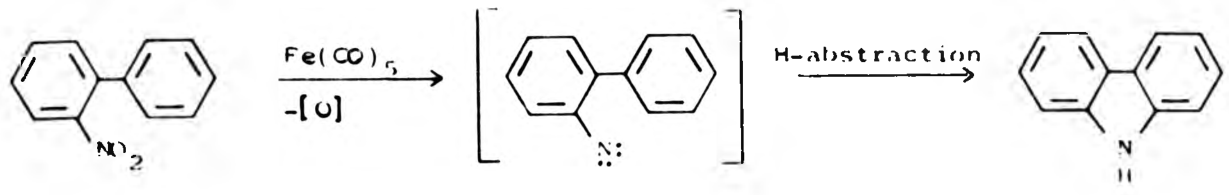
3.2.1. A survey of the reactions of iron pentacarbonyl with chelating ligands and organic compounds containing N-O bonds.

Metal carbonyls will react with organic compounds containing N-O bonds (e.g. N-oxides, nitrones, azoxy, nitro, nitroso and oximino compounds).[40-55] In the majority of cases, where chelation does not occur, deoxygenation of the N-O group occurs, leading to a nitrene intermediate , the formation of carbon dioxide and stable oxygen free products. Thus nitro- and nitroso-compounds react with iron pentacarbonyl to give amines, azo, azoxy or heterocyclic compounds (Scheme 3.4).[41,52-54]



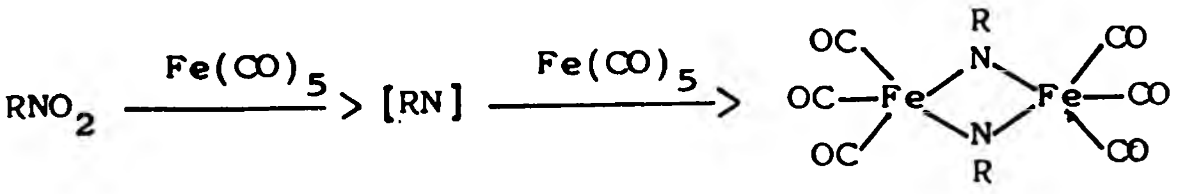
Scheme 3.4

Nitrene intermediacy has also been proposed in the synthesis of carbazoles using iron pentacarbonyl (Reaction 3.4).[51]



Reaction 3.4

Evidence for the nitrene intermediate is given by the trapping of nitrene species as ligands in the metal containing products (e.g. Reaction 3.5[44]).



Reaction 3.5

Recent studies on the reactions of 1,2-naphthoquinone-1-oxime, 1,2-naphthoquinone-2-oxime and 5-methoxy-1,2-quinone-2-oxime have shown that each reaction gives a variety of organic products which have been accounted for in terms of nitrene intermediacy. In each case the metal containing product is the iron(II) chelate of the quinone monooxime (Reaction 3.6).[36,38,39]

$$Fe(CO)_5 + qoH \longrightarrow Fe(qo)_2 + ([qH] \longrightarrow \text{Organic products})$$

Reaction 3.6

Hence it would seem that in these reactions complexation and deoxygenation compete with each other. The complexation is not unexpected as the reactions of metal carbonyls with a variety of chelating ligands have been widely studied and frequently give rise to metal complexes. In the case of iron pentacarbonyl this generally leads to iron(II) complexes.[38,39,56-65] In some cases the bischelate is isolated. Thus, acetylacetone reacts to give bis(acetylacetonato)iron(II) (Reaction 3.7).[57]

$$\text{acacH} + \text{Fe(CO)}_5 \longrightarrow \text{Fe(acac)}_2$$

Reaction 3.7

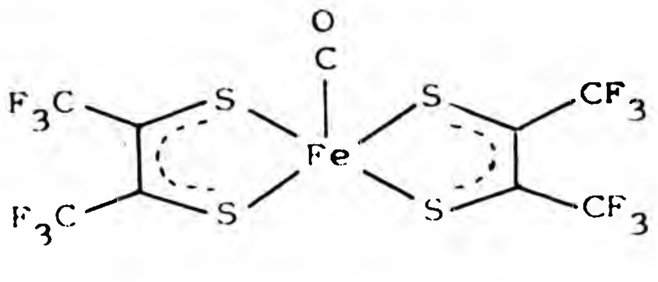
In other cases however, complexes retaining carbonyl moieties are obtained. Bis(perfluoromethyl)dithietene reacts with iron pentacarbonyl to give a mixture of complexes (Reaction 3.8),[62-64] one of which contains carbonyl ligands. It has been further established that the other complex formed in this reaction, $\{\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}_2$, is capable of reacting with a stream of carbon monoxide to give the carbonyl complex 3.1.[65]

$$\text{Fe(CO)}_5 + [\text{S}_2\text{C}_2(\text{CF}_3)_2]_2 \longrightarrow \{\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}_2$$

$$n=1,2 \qquad \text{and/or } [\text{Fe(CO)}_3]_n\text{S}_2\text{C}_2(\text{CF}_3)_2$$

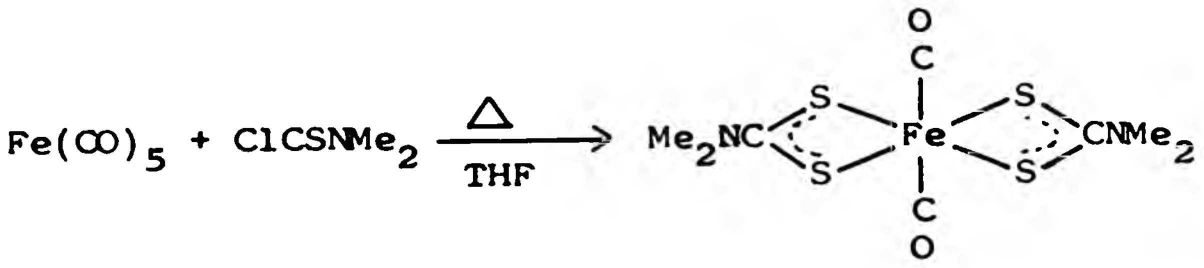
Reaction 3.8

Hence the carbonyl complexes in Reaction 3.8 could arise either by (i) incomplete loss of carbonyl ligands from iron pentacarbonyl during the reaction, or (ii) reaction of $\{\text{Fe}[\text{S}_2\text{C}_2(\text{CF}_3)_2]_2\}_2$ with the carbon monoxide liberated during the reaction.



3.1

In a similar reaction dimethylthiocarbimoyl reacts with iron pentacarbonyl to give a complex which contains two carbonyl ligands (Reaction 3.9).[66]

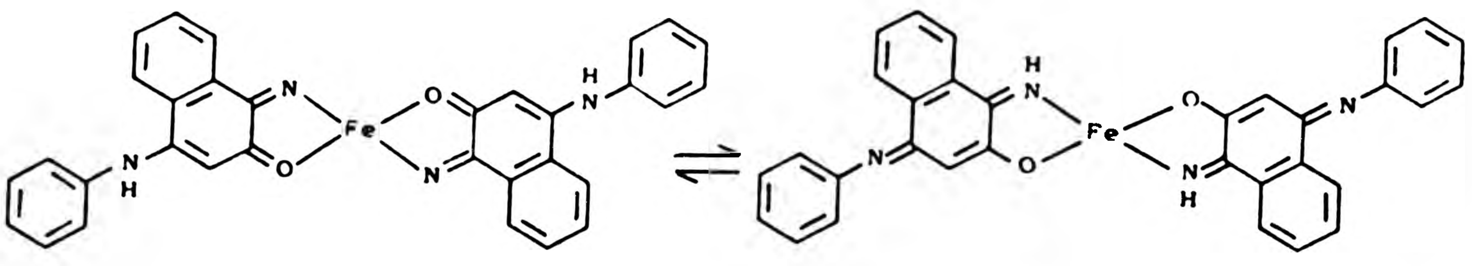


Reaction 3.9

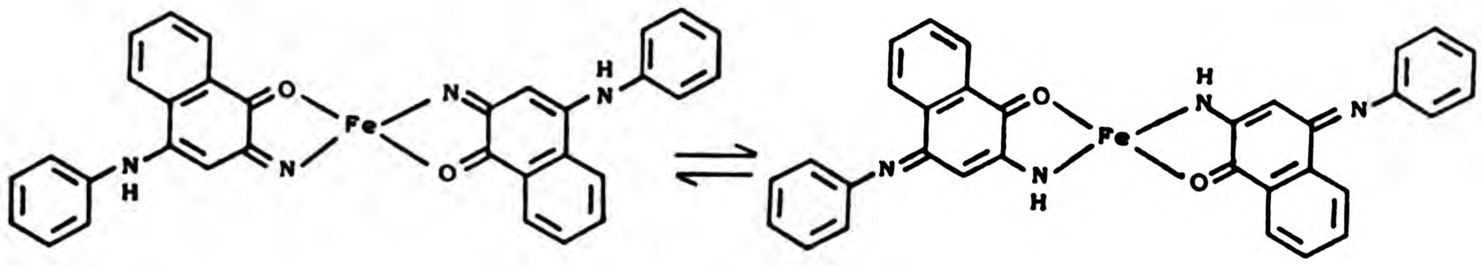
So in the reactions of iron pentacarbonyl with quinone monooximes it is possible that carbonyl adducts of the bischelates were formed, but were not isolated.

When the reactions of 1,2-naphthoquinone-1-oxime and 1,2-naphthoquinone-2-oxime with iron pentacarbonyl are carried out in the presence of aniline the $Fe(nqo)_2$-type complexes are obtained, together with two complexes which have been tentatively formulated as bis(4-phenylamino-1-imino-1,2-naphthoquinone)iron(II) (3.2)($Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2$) and bis(4-phenylamino-2-imino-1,2-naphthoquinone)iron(II) (3.3)($Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2$).[36]

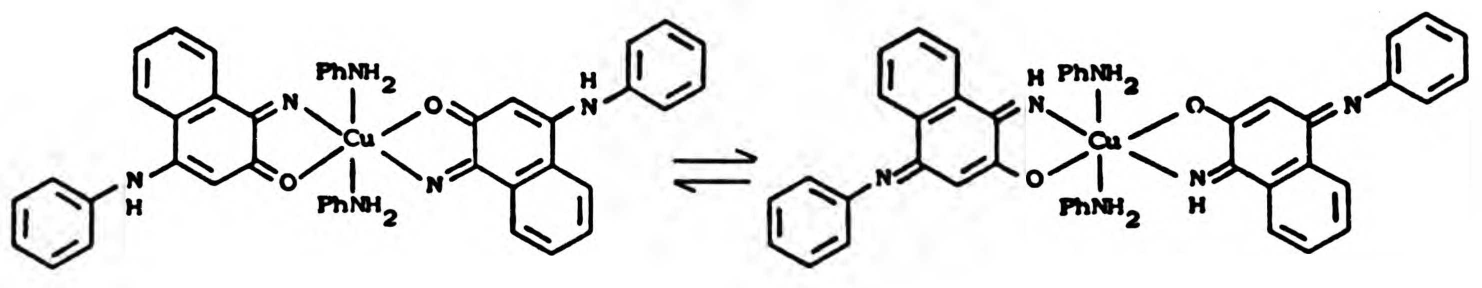
A similar complex (3.4) was previously obtained by the action of aniline on bis(1,2-naphthoquinone-1-oximato) copper(II).[37]



3.2a 3.2b

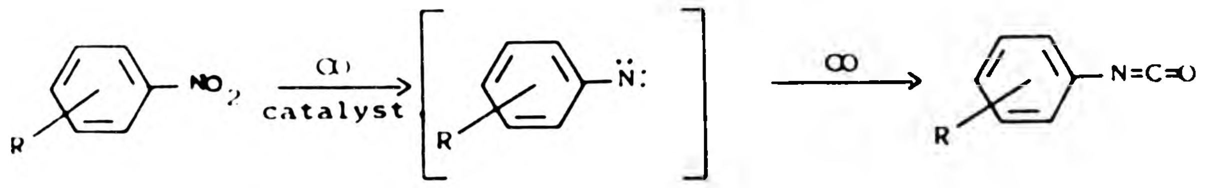


3.3a 3.3b



3.4a 3.4b

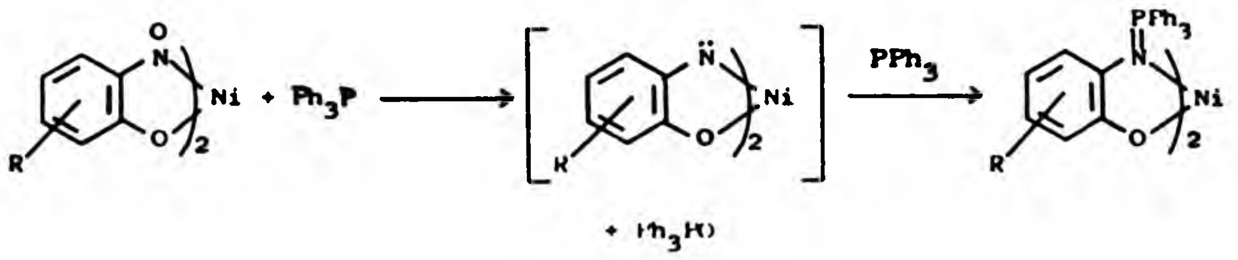
The complexes 3.2-3.4 may be of use in the trapping of carbon monoxide, either by reaction with the nitrogen of the chelated imine/nitrene groups or by forming adducts with the complexes. In the Reaction 3.10, a nitro compound when reacted with carbon monoxide (at high temperature and low pressure in the presence of a noble metal/Lewis acid catalyst such as a palladium salt, or oxide, with ferric chloride as co-catalyst) gives rise to an isocyanate.[67,68]



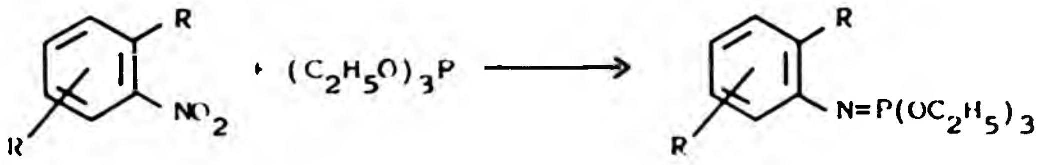
R = o-CH_3, p-CH_3, m-CF_3, m-Cl

Reaction 3.10

Also, a number of reactions are known in which triarylphosphines, which are also deoxygenating agents, deoxygenate nitro or nitroso compounds and then interact further with the nitrene formed (e.g. Reactions 3.11[69] and 3.12[70]).



Reaction 3.11



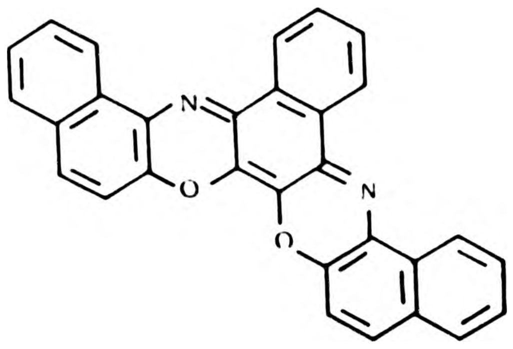
Reaction 3.12

3.2.2 The reaction of 1,2-naphthoquinone-1-oxime with iron pentacarbonyl.

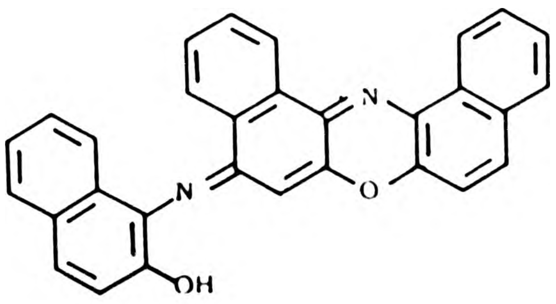
In this study, when 1,2-naphthoquinone-1-oxime (3 mol equiv.) was reacted with iron pentacarbonyl (1 mol equiv.) in tetrahydrofuran a complex mixture of products resulted.

In a previous study the only iron-containing complex isolated was Fe(1-nqo)$_2$.[36] It was thought however, that a carbonyl adduct, Fe(1-nqo)$_2$(CO)$_x$, could also be formed in the reaction. The solution cell i.r. of the reaction mixture showed stretches assignable to carbonyl groups at 2033 cm^{-1} and 2013 cm^{-1}. However, these peaks correspond to those due to iron pentacarbonyl. T.l.c. examination of the solution on silica plates, followed by development with iodine, confirmed the presence of iron pentacarbonyl. As there were no other peaks in the i.r. spectrum assignable to carbonyl stretches it seems unlikely that any carbonyl complex other than iron pentacarbonyl was present.

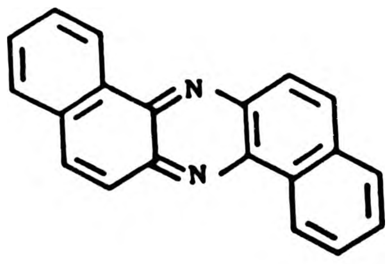
Filtration of the reaction mixture yielded Fe(1-nqo)$_2$. Separation of the organic species present in the filtrate, using column chromatography, gave unreacted 1,2-naphthoquinone-1-oxime as the main component. Other compounds identified in small yield were the dioxazine 3.5, the oxazine 3.6, the phenazine 3.7 together with traces of 1-amino-2-naphthol, the phenoxazine 3.8 and 1-nitro-2-naphthol.



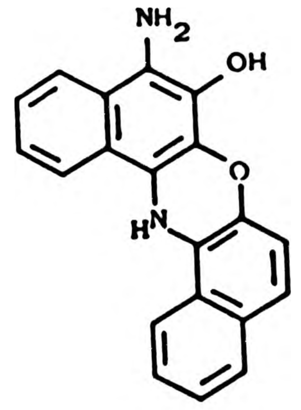
3.5



3.6



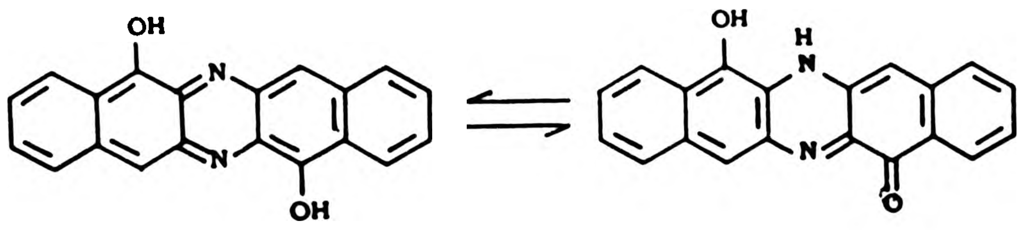
3.7



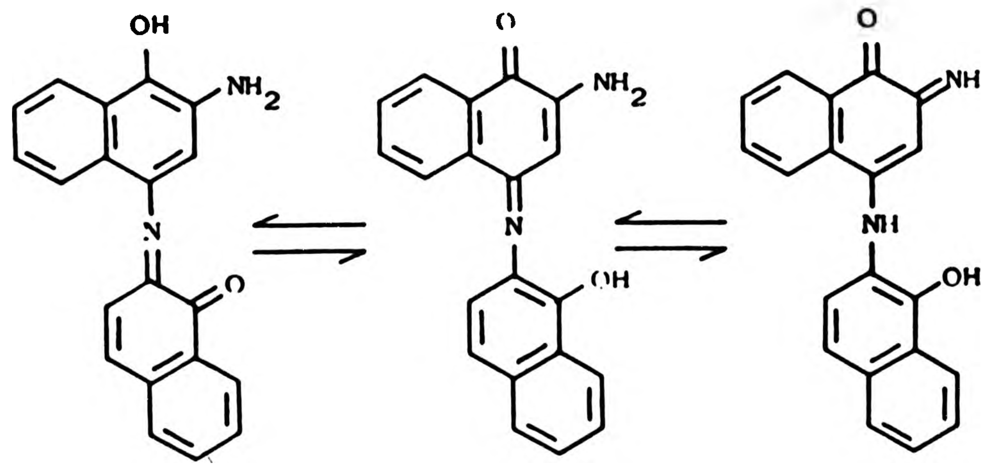
3.8

3.2.3 The reaction of 1,2-naphthoquinone-2-oxime with iron pentacarbonyl.

1,2-Naphthoquinone-2-oxime (3 mol equiv.) reacted with iron pentacarbonyl (1 mol equiv.) in tetrahydrofuran in a similar fashion to 1,2-naphthoquinone-1-oxime. Solution cell i.r. of the reaction mixture showed no carbonyl stretches assignable to anything other than iron pentacarbonyl; the presence of iron pentacarbonyl was confirmed by t.l.c. Filtration of the reaction mixture yielded $Fe(2\text{-}nqo)_2$. Separation of the organic species using column chromatography, gave unreacted 1,2-naphthoquinone-2-oxime as the main component. Other compounds identified in small yields were dibenzo[b,i]phenazine-5,12-diol (3.9) and the monoimine 3.10, with a trace of 2-nitro-1-naphthol.



3.9a 3.9b

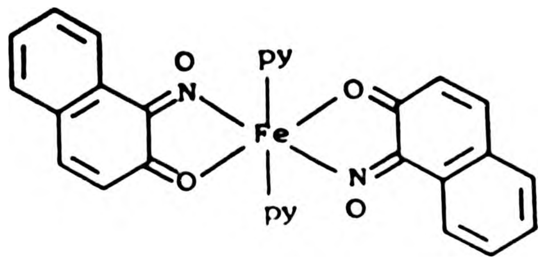


3.10a 3.10b 3.10c

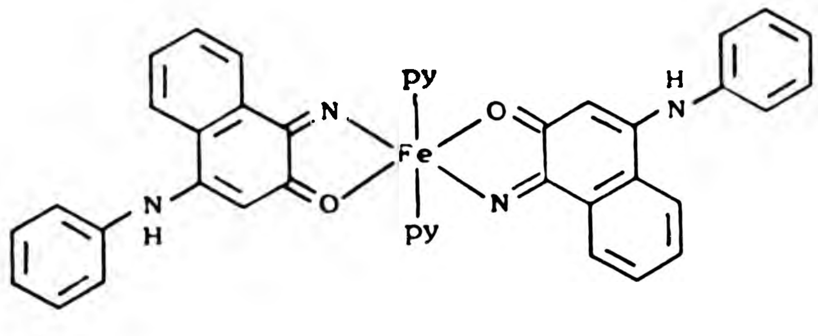
3.2.4 The reaction of 1,2-naphthoquinone-1-oxime with iron pentacarbonyl in the presence of aniline.

The reaction of 1,2-naphthoquinone-1-oxime with iron pentacarbonyl and aniline in tetrahydrofuran gave rise to a diamagnetic iron(II) containing solid and a number of organic products. The iron(II) containing solid had a well defined i.r. spectrum and was soluble in acetone. T.l.c. examination of the solid on cellulose indicated that the solid was a mixture. On silica the solid had an $R_f = 0$ in all solvents, except pyridine and appeared to become darker in colour when spotted onto silica t.l.c. plates, perhaps indicating decomposition. The i.r. spectrum of the solid coated onto silica was ill-defined and of little use.

Treatment of the iron(II) containing solid with pyridine followed by chromatographic separation afforded two iron containing products. One of these was identified as bis(1,2-naphthoquinone-1-oximato)di(pyridine)iron(II)(3.11), by comparison with an authentic sample. The other complex was characterised as bis(4-phenylamino-1-imino-1,2-naphthoquinone)di(pyridine)iron(II) (3.12). This complex was isolated and tentatively formulated in a previous study.[36]

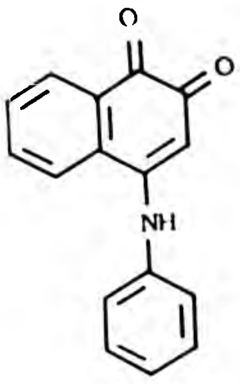


3.11



3.12

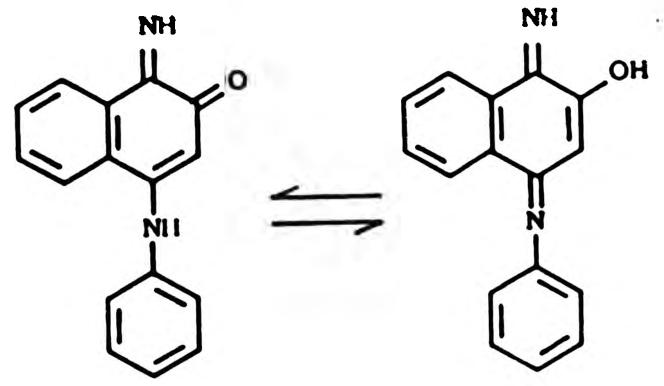
The techniques used to characterise 3.12 were treatment with aqueous hydrochloric acid, hydrogen sulphide and elemental analysis. Further information on the structure was obtained from the i.r. and Mössbauer spectra and magnetic susceptibility measurements. Pyrolysis of 3.12 at 150 °C/0.3 mmHg resulted in the loss of pyridine, which was trapped and identified by its i.r. spectrum. The measured weight loss was 20.6% as compared with the theoretical loss of 20.3%. Treatment of the iron-containing compound remaining after pyrolysis, with aqueous hydrochloric acid, followed by neutralisation and extraction, gave (N)-4-phenylamino-1,2-naphthoquinone (3.13).



3.13

The i.r. spectrum of 3.13 showed a sharp band at 3308 cm^{-1} and a band at 1690 cm^{-1} attributable to a ν N-H group and a ν C=O group, respectively. Elemental analysis was in agreement with the proposed structure and further proof was obtained by comparison with an authentic sample.[37]

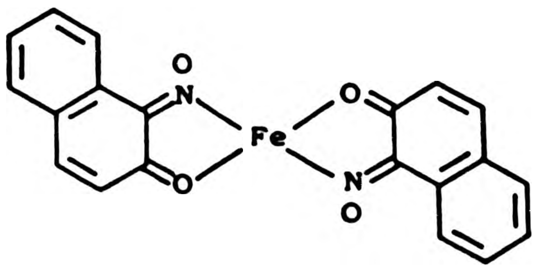
Treatment of the iron compound 3.12 with hydrogen sulphide also yielded 3.13. That the quinone 3.13 was obtained from the reactions of the imine complex with aqueous hydrochloric acid and hydrogen sulphide, rather than the free imine ligand is not unexpected as quinone imines[71] and imines in general[72] are known to be highly susceptible to hydrolysis.



3.14a **3.14b**

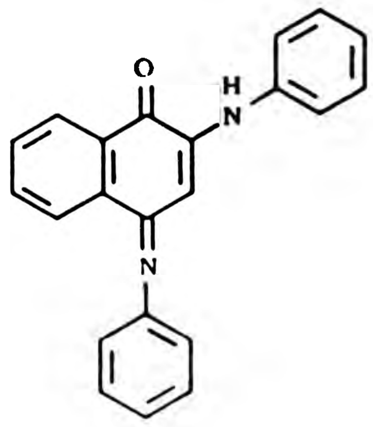
Before treatment with pyridine, the original iron(II) containing solid was found to be diamagnetic and soluble in acetone. This indicates that the solid was not a mixture containing $Fe(1\text{-}nqo)_2$ (3.15), as this complex is known to be paramagnetic.

As the reaction was carried out in the presence of aniline it would seem likely that the solid could be a mixture of the aniline adducts of 3.2 and 3.15. As the major component of the solid is derived from 3.15, with a relatively small proportion derived from 3.2, it would be unexpected for a strong ν N-H stretch to be present in the i.r. spectrum. If such a stretch were seen it could be indicative of the presence of aniline as a ligand. However, there is no firm indication of a ν N-H stretch in the i.r. spectrum. Other possibilities are that either the solvent, tetrahydrofuran, or water (produced during the course of the reaction) are coordinated to the metal in each complex.



3.15

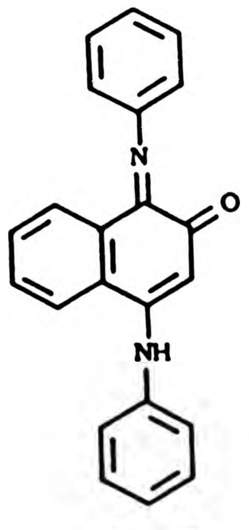
The major organic product arising from the reaction of 1,2-naphthoquinone-1-oxime with iron pentacarbonyl in the presence of aniline was (N)4-phenylimino-(N)2-phenylamino-1,4-naphthoquinone (3.16).



3.16

This was characterised on the basis of elemental analysis and spectral methods. The i.r. spectrum showed a sharp band at 3360 cm^{-1} and a band at 1660 cm^{-1} attributable to a $\rangle$N-H group and a $\rangle$C=O group respectively. The ^{13}C n.m.r. showed the correct number of signals for 3.16, including one at 181.8 ppm, which is assignable to the carbonyl carbon. The mass spectrum indicated a parent ion at m/e 324. This formulation was confirmed by comparison with an authentic sample.

Initially there was some doubt as to whether 3.16 had the assigned structure as it was thought more likely that the isomer 3.17 would have been obtained.



3.17

However, the ^{13}C n.m.r. spectrum is identical with that of the authentic sample of 3.16 and with that of the product obtained from the reaction of 1,2-naphthoquinone-2-oxime with iron pentacarbonyl and aniline (Figure 3.1). It is extremely unlikely that 3.16 and 3.17 would have chemical shift values which are the same to the second decimal place. A shift of approximately 1 ppm would be expected for the carbonyl carbon and as it was not observed structure 3.17 was ruled out.

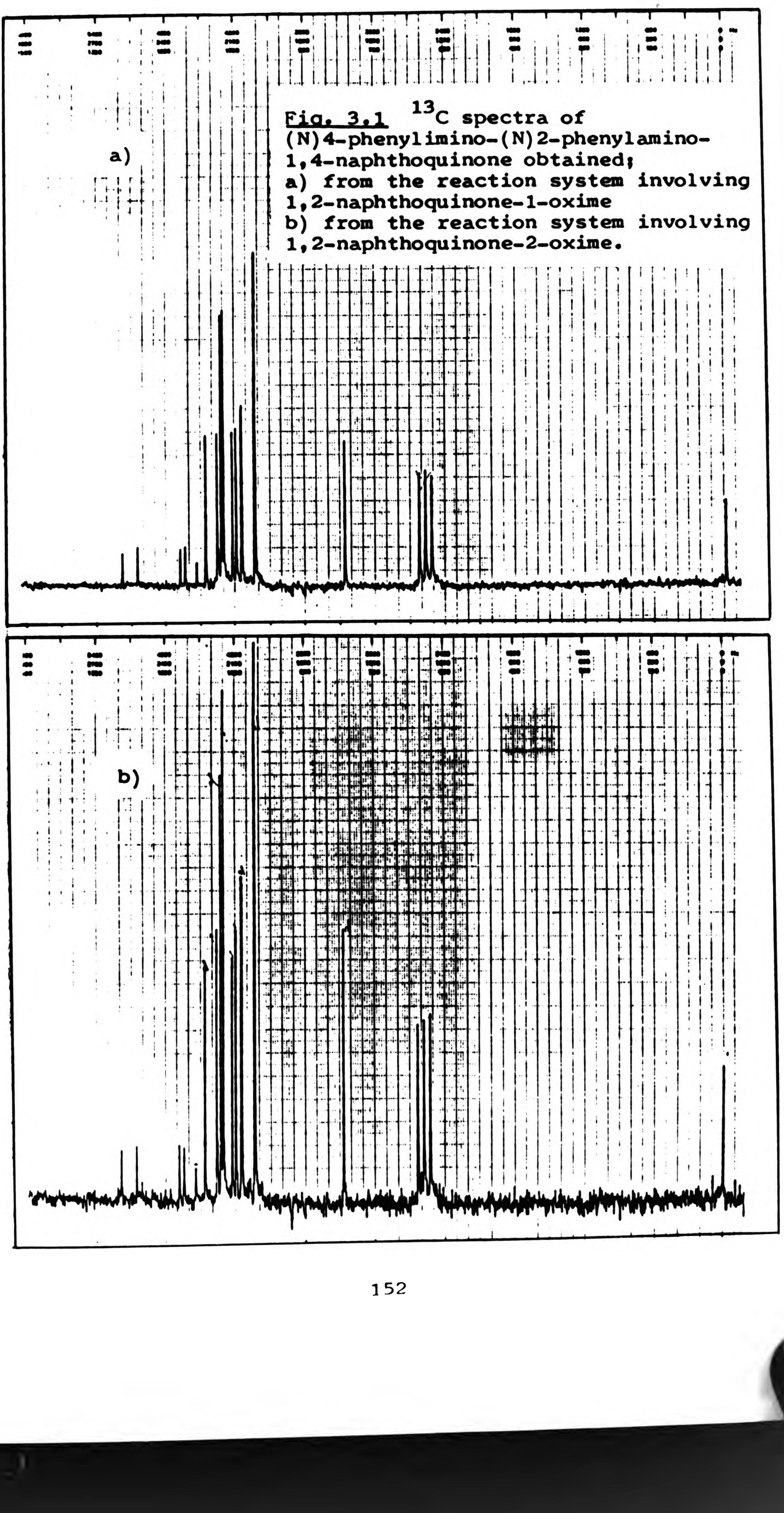
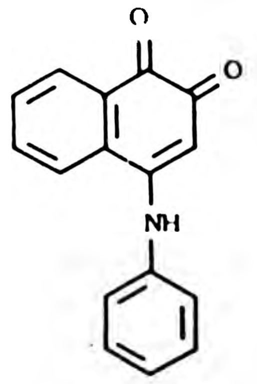


Fig. 3.1 ^{13}C spectra of (N)4-phenylimino-(N)2-phenylamino-1,4-naphthoquinone obtained;
a) from the reaction system involving 1,2-naphthoquinone-1-oxime
b) from the reaction system involving 1,2-naphthoquinone-2-oxime.

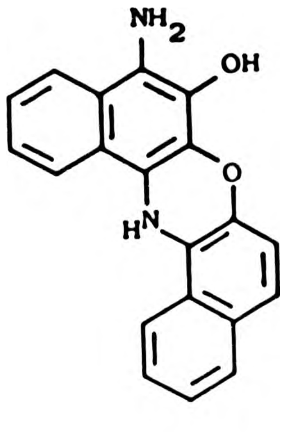
As 3.16 was obtained from both the reaction system involving 1,2-naphthoquinone-1-oxime and that involving 1,2-naphthoquinone-2-oxime (cf Sec. 3.2.5) it is likely that it arises by a similar route in both reactions. One such possible route to 3.16 would be the reaction of 3.13 with aniline.



3.13

To check this hypothesis the reaction of 3.13 with aniline was carried out in tetrahydrofuran with the result that 3.16 was obtained in high yield.

Other products obtained from the reaction of 1,2-naphthoquinone-1-oxime with iron pentacarbonyl and aniline were (N)4-phenylamino-1,2-naphthoquinone (identified as described earlier) and the phenoxazine 3.8. Both of these products were obtained in reasonable yield.



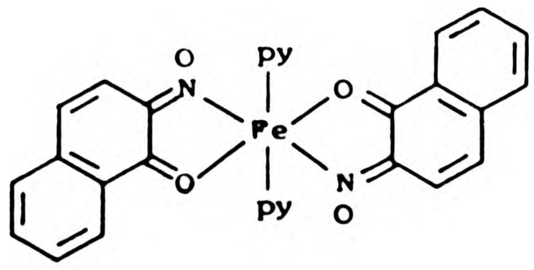
3.8

Compound 3.8 was characterised by elemental analysis and spectral methods. The i.r. spectrum showed a broad band at 3400 cm^{-1} attributable to the hydrogen bonded OH group and a test for an amine proved positive. The formulation was confirmed by comparison with an authentic sample.[73] Traces of (N)1-phenylnaphthylamine and (N)1-phenylamino-2-naphthol were also obtained and identified by comparative t.l.c. with authentic samples.

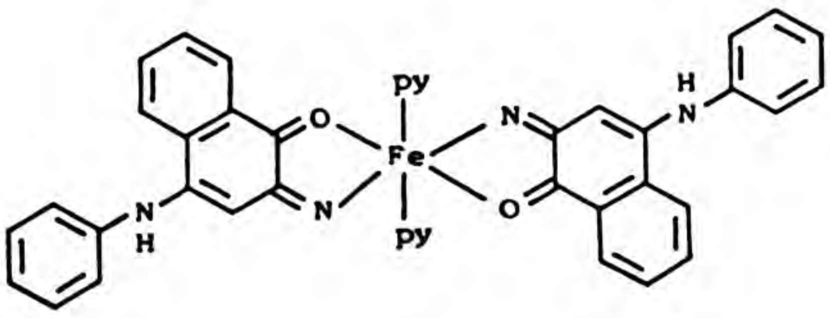
3.2.5. The reaction of 1,2-naphthoquinone-2-oxime with iron pentacarbonyl in the presence of aniline.

The reaction of 1,2-naphthoquinone-2-oxime with iron pentacarbonyl in the presence of aniline gave rise to a diamagnetic iron(II) containing solid and a number of organic products. The iron(II) containing solid had a well defined i.r. spectrum and was soluble in acetone. As in the case of the analogous reaction involving the 1-oxime, t.l.c. examination of the solid on cellulose indicated that it was a mixture. On silica the solid had an $R_f = 0$ in all solvents and a change in colour indicated decomposition.

Treatment of the iron(II) containing solid with pyridine followed by chromatographic separation afforded two iron-containing products and a further yield of organic products. One of the iron-containing products was identified as bis(1,2-naphthoquinone-2-oximato)di(pyridine)-iron(II) (3.18), by comparison with an authentic sample. The other iron complex was characterised as bis(4-phenylamino-2-imino-1,2-naphthoquinone)di(pyridine)-iron(II) (3.19).



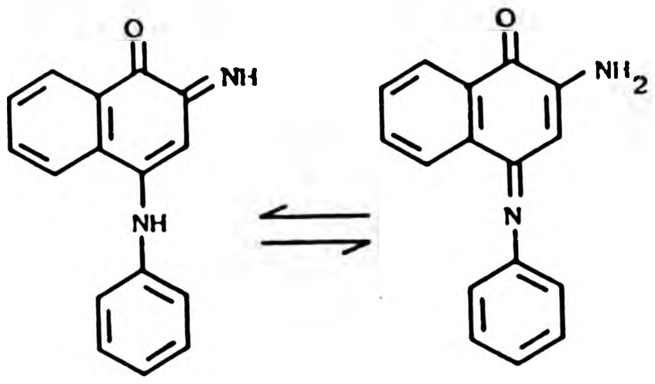
3.18



3.19

Pyrolysis of 3.19 at 150 °C/0.3 mmHg resulted in the loss of pyridine, which was trapped and identified by its i.r. spectrum. The measured weight loss was 20.8% as compared with the theoretical loss of 20.3%. Treatment of the iron-containing compound remaining after pyrolysis with aqueous hydrochloric acid, followed by neutralisation and extraction, gave (N)4-phenylimino-2-amino-1,4-naphthoquinone (3.20). This was characterised by elemental analysis and spectral methods. The i.r. spectrum showed a strong band at 1660 cm^{-1}, attributable to the carbonyl group and sharp bands at 3380 cm^{-1} and 3490 cm^{-1}

indicative of a primary amine. The ^{13}C n.m.r. spectrum showed the correct number of signals for 3.20, including one at 181.7 ppm, which is assignable to the carbonyl carbon. The mass spectrum indicated a parent ion at m/e 248. The formulation was confirmed by comparison with an authentic sample.[36] Treatment of the iron complex with hydrogen sulphide also yielded 3.20.



3.20a 3.20b

As in the 1,2-naphthoquinone-1-oxime system, it is likely that in the original iron(II) containing solid a mixture of adducts of some form is present as Fe(2-nqo)$_2$ is insoluble in acetone and paramagnetic. Again, there is no significant stretch in the i.r. spectrum indicative of ν N-H, thus aniline is eliminated.

Separation of the organic species using column chromatography gave (N)4-phenylimino-(N)2-phenylamino-1,4-naphthoquinone (3.16) and (N)4-phenylimino-2-amino-1,4-naphthoquinone (3.20) as the major products. Other products isolated in measurable amounts were dibenzo[b,i]phenazine-5,12-diol (3.9) and N(4)-phenylamino-1,2-naphthoquinone (3.13). These compounds were identified using comparative t.l.c. with authentic samples,[36,37] elemental analyses, i.r. and n.m.r. spectra and mass spectrometry. Traces of 2-naphthol and 2-nitro-1-naphthol were identified using comparative t.l.c.

\s stated in Section 3.2.4, 3.16 probably arose as a result of interaction between 3.13 and aniline. However, it is also possible that in the system involving 1,2-naphthoquinone-2-oxime it arose from a species such as 3.20.

3.2.6 Structural determination of the complexes obtained from the reaction of iron pentacarbonyl with the monooximes of 1,2-naphthoquinone in the presence of aniline.

In order to gain information on the structures of the complexes Fe(4-PhNH-1-imnq)$_2$ (3.2) and Fe(4-PhNH-2-imnq)$_2$ (3.3) magnetic moment studies were carried out and the Mössbauer spectra recorded. Magnetic moments of the complexes were obtained at room temperature and then over the temperature range 298-115 K. The Mössbauer spectra of 3.2 and 3.3 (Fig. 3.2) were recorded along with those of Fe(1-nqo)$_2$, Fe(2-nqo)$_2$, Fe(1-nqo)$_2$.2py and Fe(2-nqo)$_2$.2py. The Mössbauer parameters obtained for these complexes, together with their room temperature magnetic moments, are given in Table 3.1.

It can be seen that the imine complexes, 3.2 and 3.3, and the bischelates have two pairs of peaks in their Mössbauer spectra, whereas the pyridine adducts of the

Fig. 3.2 Mössbauer spectra of Fe(4-PhNH-1-imnq)$_2$ (3.2) and Fe(4-PhNH-2-imnq)$_2$ (3.3) relative to iron foil.

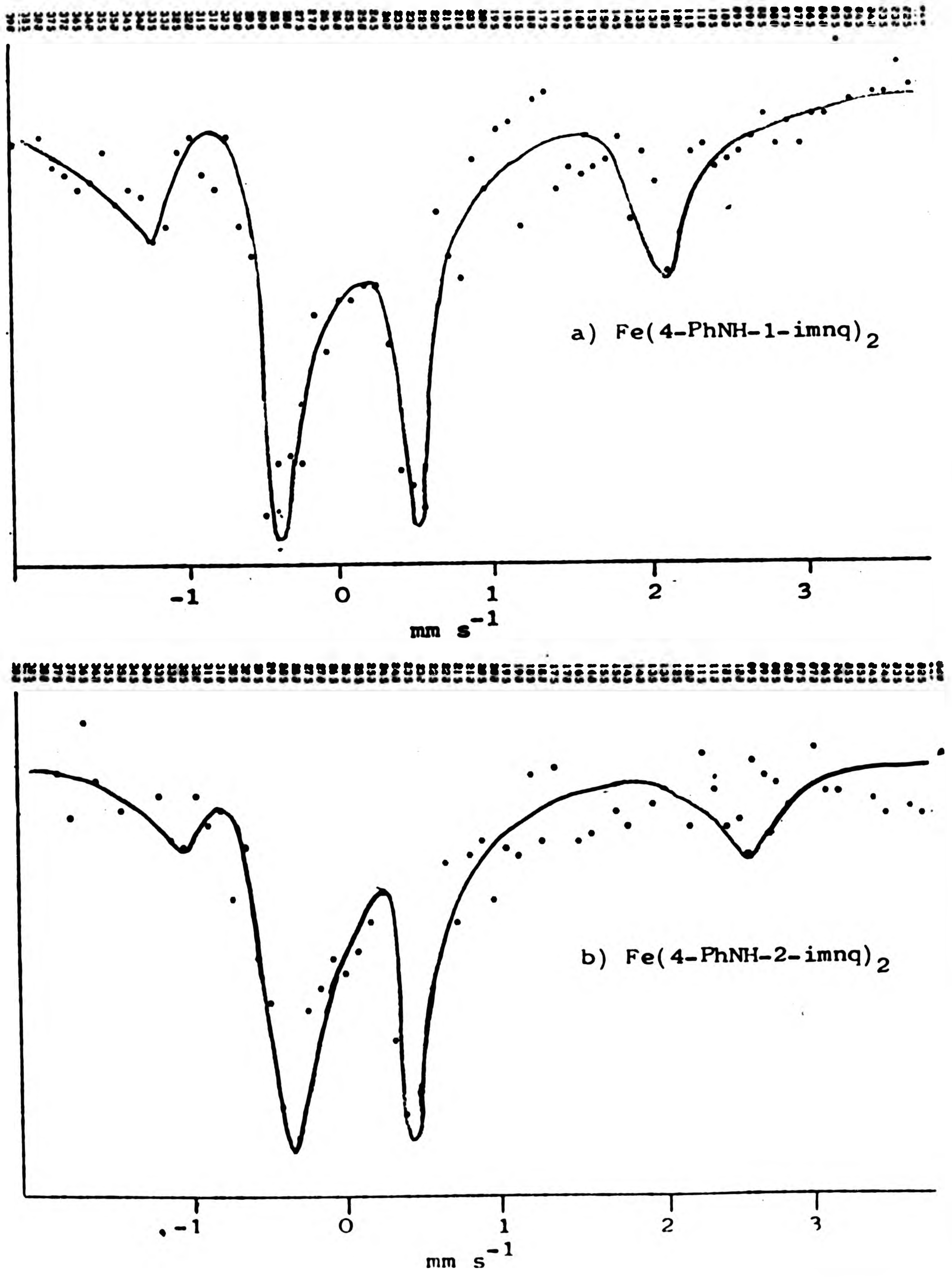
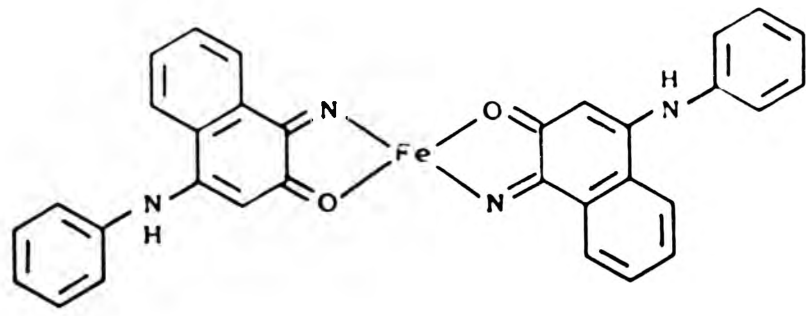


Table 3.1 **Mössbauer parameters and room temperature magnetic moments of iron(II) complexes derived from the monooximes of 1,2-naphthoquinone.**

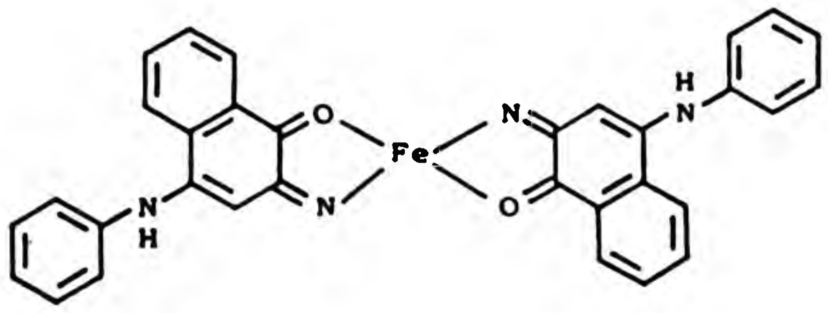
Complex	Δ/mm s^{-1}	δ(Fe)/mm s^{-1}	μ_{eff}/B.M.
Fe(1-nqo)$_2$·2py	0.92	0.19	0.50
Fe(2-nqo)$_2$·2py	0.88	0.20	0.60
Fe(1-nqo)$_2$	0.79 4.00	0.08 1.22	3.08
Fe(2-nqo)$_2$	0.71 3.99	0.05 1.22	3.04
Fe(4-PhNH-1-imnq)$_2$ (3.2)	0.88 3.27	0.12 0.47	3.12
Fe(4-PhNH-2-imnq)$_2$ (3.3)	0.77 3.40	0.08 0.92	3.13

All spectra were recorded at room temperature. No significant differences were observed when recording spectra at liquid nitrogen temperatures (77 K).

bischelates and other iron(II) complexes (such as the examples given in Table 3.2) have only one set of peaks.



3.2



3.3

The outer set of peaks have parameters typical for a high spin iron(II) species, whilst the inner set have values that can be attributed to either a low spin iron(II) species, or a low spin iron(III) species.

Also, Fe(4-PhNH-1-imnq)$_2$, Fe(4-PhNH-2-imnq)$_2$, Fe(1-nqo)$_2$ and Fe(2-nqo)$_2$ have a room temperature magnetic moment that is intermediate between that for a high spin complex (4.9-5.3 B.M.) and a low spin complex (≈0 B.M.).[74] Hence, it was decided to carry out a study of the effect of temperature on the magnetic moments of the complexes.

Table 3.2 Magnetic properties and Mössbauer parameters of some iron(II) complexes.

Compound	T/K	Δ /mms^{-1}	δ(Fe)/mms^{-1}	μ/B.M.	Ref.
$Fe(phen)_2Cl_2$	R.T.	3.28	1.06	5.27	75
$Fe(phen)_2(NCS)_2$	R.T.	3.09	1.04	5.22	75
$Fe(bipy)_2(NCS)_2$	R.T.	2.18	1.06	L.S.	76
$Fe(dipyam)_2(NCS)_2$	R.T.	1.66 2.62	1.07 1.03	5.48	77
$Fe(isoquin)_2Cl_2$	295	3.18	1.03	5.30	78
$Fe(sal)_2$	78	2.53	1.30	$\approx$ 0	79
$Fe(salox)_2$	78	2.51	1.17	$\approx$0	79
$Fe(phen)_2(CN)_2$	R.T.	0.58	0.18	$\approx$ 0	80
$K_2[Fe(bipy)(CN)_4]$	300	0.64	0.03	$\approx$0	80
$Fe(dtoH)_2$	300	2.02	0.07	$\approx$0	81

dtoH = diacetylsemicarbazoneoxime
salH = salicylaldehyde
dipyam = di-2-pyridylamine
phen = 1,10-phenanthroline

isoquin = isoquinoline
saloxH = salicylaldoxime
bipy = 2,2'-bipyridine

The magnetic properties of complexes 3.2 and 3.3 were investigated over the temperature range 298-115 K. It was found that μ_{eff} does not change appreciably over the temperature range for either of the complexes. A plot of $1/\chi_A$ versus temperature gave a negative intercept on the temperature axis, with a Weiss constant of -12 for $Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2$ and -10 for $Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2$, indicating ferromagnetism and association (Table 3.3.). However, values of θ obtained by extrapolation may contain a degree of inaccuracy and as the values of θ obtained for the quinoneimine complexes are very small, they should be treated with caution.

There are three possible explanations for the overall magnetic properties of the imine complexes, 3.2 and 3.3.

(1) Spin crossover between two states. For this to occur it must be assumed that an iron(II) species is present in an octahedral environment.

(2) A mixture of two or more species could be present.

(3) Association between units of the complex such that an oligomer is formed containing different types of iron centres.

These explanations are discussed below.

(1) $^5T_2$ - $^1A_1$ crossover between two spin states.

Octahedral iron(II) complexes usually adopt either the $^5T_2$ high spin (S=2, weak ligand field) configuration with four unpaired electrons, or the $^1A_1$ low spin

Table 3.3. Variable temperature magnetic moment data for the complexes obtained from the reaction of $Fe(CO)_5$ with 1-nqoH or 2-nqoH in the presence of aniline.

$Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2$

T/K	298	272	249	219	190	162	134	115
$10^6\chi_A$	4079	4411	4756	5373	6153	7123	8555	9968
$1/10^6\chi_A$	245.2	226.7	210.3	186.1	162.6	140.4	116.9	100.3
μ_{eff}/B.M.	3.12	3.10	3.08	3.07	3.06	3.04	3.03	3.03

θ/K = -12

$Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2$

T/K	298	272	249	219	190	162	134	115
$10^6\chi_A$	4105	4440	4819	5409	6194	7217	8725	10100
$1/10^6\chi_A$	243.6	225.2	207.5	184.9	161.4	138.6	114.6	99.0
μ_{eff}/B.M.	3.13	3.11	3.10	3.08	3.07	3.06	3.06	3.05

θ/K = -10

(S=0, strong ligand field) diamagnetic configuration. If the energies of the two possible states are very similar, then both forms should be capable of coexistence. Ligand field spin crossover has been observed for several complexes by using magnetic and Mössbauer spectroscopic techniques.[82-91] This normally occurs quite suddenly over a small temperature range, although there have been cases reported where the situation is more complex. For example, tris(2-aminomethylpyridine)iron(II) chloride exists in the $^5T_2$ state at room temperature (as shown by the magnetic moment and Mössbauer spectrum), the $^1A_1$ state at 4.2 K and both states in coexistence at 77 K, with no detectable interconversion within the observation time scale.[84]

As the imine type complexes do not show any appreciable differences in their magnetic moments or Mössbauer spectra over the temperature range used it is extremely unlikely that a $^5T_2$-$^1A_1$ crossover situation exists.

(2) <u>A mixture of two or more species/Oligomeric association</u>.

If the complexes are comprised of a mixture of high and low spin species, in appropriate amounts, then average magnetic moments would be obtained, corresponding to those which have been experimentally determined for complexes 3.2 and 3.3. This would also account for the Mössbauer spectra, which can be interpreted as containing a high spin iron(II) species, together with either a low spin iron(II) species or a low spin iron(III) species. It is unlikely that a low spin iron(III) species is present as the complexes can be converted into low spin, diamagnetic (hence iron(II)) pyridine adducts and then pyrolysed back to complexes of type FeL_2 which have magnetic moments of approximately 3 B.M. This also rules out the possibility that mixtures of complexes are present, as it is extremely unlikely that mixtures of complexes would react with pyridine to give the same product.

These properties are also observed for the complexes $Fe(1\text{-}nqo)_2$ and $Fe(2\text{-}nqo)_2$ (refer to Ch.2, section 2) and have been rationalised in terms of association. Square-planar monomeric units of $Fe(nqo)_2$ combine through the phenolic oxygen to form an oligomer. In this oligomer the 6-coordinate iron centres are diamagnetic. The terminal units at the ends of the chains are 5-coordinate and high spin. The outer quadrupole splitting observed in the Mössbauer spectrum is in agreement with values found for 5-coordinate high spin iron(II). The magnetic moments of $Fe(1\text{-}nqo)_2$ and $Fe(2\text{-}nqo)_2$ are approximately 3 B.M. These are in agreement with the polymeric theory as high spin iron(II) complexes have magnetic moments in the range 5.2-5.6 B.M. Low spin iron(II) will be either diamagnetic or have a small amount of residual paramagnetism in the range 0-0.8 B.M.

As the Mössbauer spectra and magnetic moments of the imine type complexes resemble those of the $Fe(nqo)_2$ complexes so closely, it seems reasonable to assume that the complexes have the same type of associated, oligomeric structure. In addition to their magnetic behaviour and Mössbauer spectra, both complexes are insoluble in a wide range of solvents, except pyridine, and do not move on silica, alumina or cellulose t.l.c. plates in a range of solvents. If the complexes have an oligomeric structure this would be expected. The complexes will dissolve in pyridine because of the breaking of the oligomeric units by pyridine to give rise to the pyridine adducts.

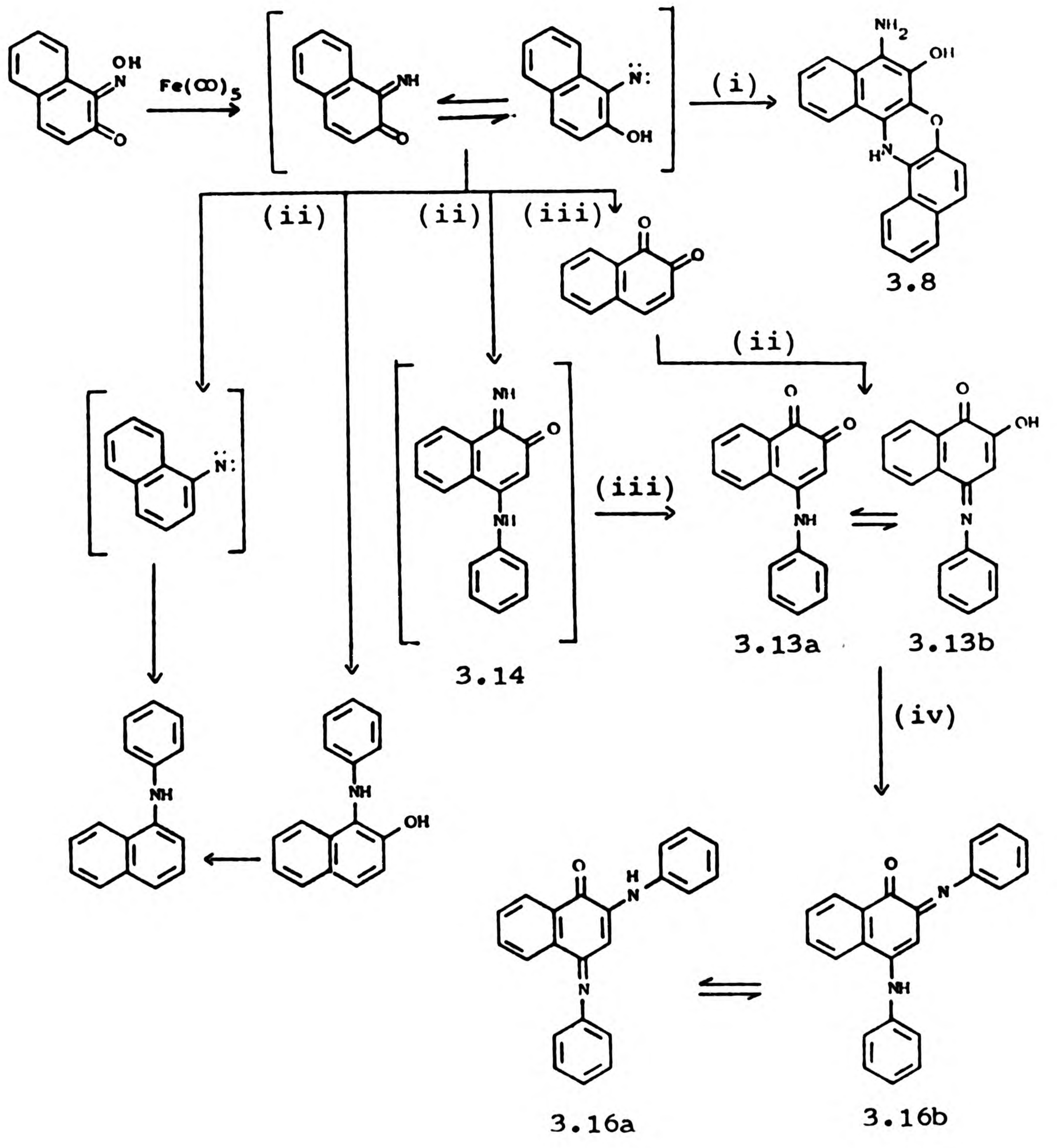
Knowing the magnetic moments of the complexes, compared to those for high spin iron(II) complexes, it should be possible to estimate the average chain length within the oligomers. However, the magnetic moment study shows that there may be interaction of the iron centres within the polymer. Thus any calculation of chain length would be suspect.

3.2.7 Overall conclusion for the reactions between iron pentacarbonyl and the monooximes of 1,2-naphthoquinone, with or without the presence of aniline.

The reactions outlined in Section 3.2 of this Chapter have shown that complexation takes place between iron pentacarbonyl and 1,2-naphthoquinone-1-oxime or 1,2-naphthoquinone-2-oxime to give complexes of the type $Fe(nqo)_2$. Some of the organic products obtained in these reactions are accountable in terms of deoxygenation and nitrene intermediacy (by similar mechanisms to those described elsewhere in this thesis). When aniline is introduced into the systems deoxygenation of the iron complex ligands occurs to quinoneimine/nitrene ligands. The organic products from the reactions involving aniline can be rationalised in terms of deoxygenation and nitrene intermediacy, together with condensation or coupling with aniline (e.g. Scheme 3.5).

However, in all of these reactions, there were no carbon monoxide adducts or isocyanate ligand complexes isolated.

Scheme 3.5



(i) coupling
(ii) aniline
(iii) hydrolysis
(iv) condensation with aniline

3.3 The interaction of carbon monoxide with selected metal complexes.

Initially, the complexes used in this study were:

$Fe(1\text{-}nqo)_2 \cdot 2py$
$Fe(2\text{-}nqo)_2 \cdot 2py$
$Fe(1\text{-}nqo)_2$
$Fe(2\text{-}nqo)_2$
$Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2 \cdot 2py$ (3.12)
$Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2 \cdot 2py$ (3.19)
$Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2$ (3.2)
$Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2$ (3.3)

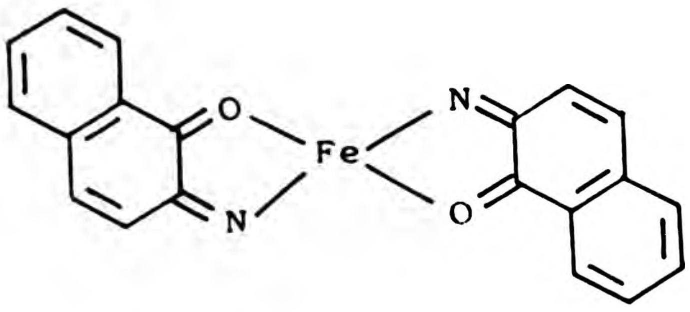
Carbon monoxide was bubbled through a solution, or suspension, of the complex in toluene and then on through a cold trap containing baryta water, for fifteen hours. At the end of this period the solvent was removed by evaporation under nitrogen and the solid remaining examined by t.l.c. In addition, elemental analyses of the complexes previous to reaction and of the reaction products were obtained.

It was thought that for the pyridine adducts, substitution of pyridine for carbon monoxide could occur, to give carbon monoxide adducts. In addition, for the imino type complexes 3.2 and 3.3 and their pyridine derivatives 3.12 and 3.19, there was the possibility that interaction of the quinone imine/nitrene ligands with carbon monoxide would lead to complexes containing isocyanate type ligands. However, at the end of the fifteen hour period the only complex that showed any sign of reaction was $Fe(2\text{-}nqo)_2 \cdot 2py$. T.l.c. examination showed that the main component of the reaction mixture was green $Fe(2\text{-}nqo)_2$, with a small amount of another green substance and traces of other compounds.

All of the complexes used in this study were iron(II) bischelates and hence unable to undergo reduction. In addition, all are coordinatively saturated, either because they are pyridine adducts or have oligomeric structures. Thus, it was decided to use complexes of type ML_3, which are capable of undergoing an internal redox reaction in the presence of a Lewis base (such as carbon monoxide) to give a reduced metal species and a ligand radical (refer to Scheme 3.3). The nascent complex formed in such a reaction, ML_2, will not be coordinatively saturated and hence can react further with the Lewis base. The complexes selected were $Fe(1\text{-}nqo)_3$, $Fe(2\text{-}nqo)_3$ and $Co(1\text{-}nqo)_3$. The latter does not normally undergo redox reactions as a reduction from low spin cobalt(III)(d^6) to cobalt(II)(d^7) is not favoured. Thus it was not expected that the cobalt complex would react (because of its lack of redox behaviour and also because it is coordinatively saturated) but it was included as a comparison against the iron complexes.

The reactions were carried out under the same conditions used for the iron(II) complexes. For the cobalt complex there was no sign of any reaction. For the $Fe(1\text{-}nqo)_3$ system, t.l.c. examination showed that some reaction had occurred, but the major component was still unreacted trischelate. For the $Fe(2\text{-}nqo)_3$ system however, t.l.c. examination showed a mixture of products, including a green component which moved on a silica plate after addition of pyridine. T.l.c. examination showed that the green compound was not the pyridine adduct of the bischelate Fe(2-nqo)$_2$. Also, t.l.c. comparison showed that this green compound was the same as the unidentified green component observed in the reaction of carbon monoxide with Fe(2-nqo)$_2$.2py. Analysis of the final reaction mixture compared to the starting complex indicated that the carbon to nitrogen ratio had been increased. However, this could have been due to solvent residue in the reaction mixture. In addition to these observations, a precipitate of Ba(CO$_3$)$_2$ was obtained from the baryta water, implying that carbon monoxide had been oxidised to carbon dioxide.

The reaction of Fe(2-nqo)$_3$ with carbon monoxide was then repeated on a larger scale, to clarify the reaction products. Filtration of the reaction mixture after fifteen hours gave a black solid. Repeated washing of this solid left a green solid. Elemental analysis of the solid showed that it is an iron complex with a carbon to nitrogen ratio of 10:1. The analysis of the complex is in agreement with it being bis(1,2-naphthoquinone-2-iminato)iron(II) (3.21).



3.21

That carbon monoxide has not been incorporated at all is supported by the i.r. spectrum. This has common features with the spectrum of $Fe(2\text{-nqo})_2$ and does not contain any carbonyl stretches assignable to a coordinated carbon monoxide ligand, or an isocyanate group.

Treatment of 3.21 with pyridine followed by t.l.c. examination showed that the complex is identical to that observed in the small scale reactions of $Fe(2\text{-nqo})_3$ and $Fe(2\text{-nqo})_2.2py$ with carbon monoxide.

Treatment of 3.21 with acid gave a number of products. The major ones were identified as the phenazine 3.9 and the monoimine 3.10. The formation of these compounds can be rationalised in terms of deoxygenation and nitrene intermediacy, as discussed previously in this thesis. This is in contrast with the hydrolysis of $Fe(2\text{-nqo})_2$, which gives 1,2-naphthoquinone-2-oxime as the major organic product.

Separation of the organic products obtained from the filtrate of the reaction between $Fe(2\text{-nqo})_3$ and carbon monoxide also gave the phenazine 3.9 and the monoimine 3.10 as the major products, with traces of 2-nitro-1-naphthol and other, unidentified, products.

Thus, the organic products isolated from this reaction system, together with the products isolated from the hydrolysis of 3.21, support the suggested formulation and structure of the complex.

From this study of the interaction of carbon monoxide with selected metal complexes it can be seen that for a reaction to take place with carbon monoxide, it is advisable to use a system in which an internal redox reaction can occur. Also, it should be noted that different products can be obtained where a redox reaction is involved. In the reaction of iron pentacarbonyl with 1,2-naphthoquinone-2-oxime a complex containing quinone imine/nitrene ligands is not isolated, thus the redox reaction of carbon monoxide with Fe(2-nqo)$_3$ has useful synthetic potential.

After investigating the interaction of the various complexes with carbon monoxide, the trischelates Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ were successfully utilised in the selective filtration of tobacco smoke. These studies are described in Chapter 4.

3.4 The interaction of nitric oxide with selected metal complexes.

The complexes used for this study were Fe(1-nqo)$_2$.2py, Fe(2-nqo)$_2$.2py, Fe(1-nqo)$_3$, Fe(2-nqo)$_3$ and Co(1-nqo)$_3$. Nitric oxide was bubbled through a solution or suspension of the complex in toluene and then on through a cold trap for three hours. At the end of this period the solvent was removed by evaporation under nitrogen and the solid remaining examined by t.l.c. In addition, elemental analyses of the complexes previous to reaction and of the reaction product were obtained. These reactions are summarised in Table 3.4. All complexes, except Co(1-nqo)$_3$, reacted to give multicomponent mixtures in which it appears that the metal complex is completely broken down. In none of the iron complex systems was there any indication that the iron(II) bischelates were present. Small amounts of green compounds were observed in the t.l.c. examinations, but these move on a silica plate (unlike the bischelates of the 1,2-naphthoquinone monooximes). Also, they were not present in quantities great enough to account for all of the iron being present in the form of an adduct of an iron(II) bischelate. Additionally, none of the components seen in the t.l.c. examinations were identifiable as products found in other reactions of the starting complexes with Lewis bases, i.e. phenazines, 1,2-naphthoquinones monooximes e.t.c. Thus it is clear that in the reactions of the complexes with nitric oxide something more drastic than straightforward reduction and adduct formation is occurring.

Comparison of the carbon to nitrogen ratios of the reaction product with those of the complexes previous to reaction indicate that in each reaction nitric oxide has been incorporated into the reaction products. A further observation noted in all of the reactions with the iron complexes, was the trapping of the intensively blue dinitrogen trioxide. As this was not observed in the Co(1-nqo)$_3$ system it is unlikely that O_2 or N_2O_4 were present as impurities in the nitric oxide supply. As a further check, nitric oxide was bubbled through toluene and also through a suspension of Fe(acac)$_3$ in toluene, for three hours, as it is known that this complex will not react with nitric oxide, but reacts readily with nitrogen dioxide.[92] Neither system showed the formation of dinitrogen trioxide and the Fe(acac)$_3$ system showed no indication that a reaction had occurred. As it is extremely unlikely that O_2 was involved in the formation of dinitrogen trioxide this means that nitrogen dioxide is produced during the reactions. This would explain why such drastic reactions occur, as in a previous study of the reactions of nitrogen dioxide with complexes such as Fe(acac)$_3$ and Fe(Et$_2$NCSS)$_3$ in toluene, complete destruction of the complex occurred with the formation of $Fe(NO_3)_3$.[92] In the present study it is possible that this was also formed, or possibly $Fe(NO_3)_2$.

Table 3.4 Interaction of nitric oxide with selected metal complexes.

Complex	Initial C:N ratio*	Final C:N ratio	Results of t.l.c. study
Fe(1-nqo)$_2$•2py	7.6:1	5.3:1	Multicomponent mixture with at least 9 components, none of which could be identified.
Fe(1-nqo)$_3$	10:1	5.9:1	Same components as those seen in the reaction of Fe(1-nqo)$_2$•2py
Fe(2-nqo)$_2$•2py	7.3:1	5.6:1	Multicomponent mixture with at least 8 components, none of which could be identified.
Fe(2-nqo)$_3$	9.7:1	6.1:1	Same components as those seen in the reaction of Fe(2-nqo)$_2$•2py
Co(1-nqo)$_3$	10:1	10:1	No reaction

*As estimated by analysis of the samples used

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CHAPTER 4

4. The interaction of selected metal complexes with Lewis bases present in tobacco smoke.

4.1 Introduction.

Tobacco smoke is a complex mixture of compounds forming an aerosol. It is a two phase system consisting of a particulate phase suspended in a vapour phase.[1] The vapour phase is composed mainly of gases such as nitrogen, carbon dioxide and carbon monoxide, with lesser amounts of nitric oxide, nitrous oxide and hydrogen cyanide. Also present are volatile organic substances such as aldehydes, ketones, hydrocarbons and a small proportion of substances of a free radical nature. The particulate phase, 'tar', contains the majority of the non gaseous organic compounds such as nicotine, phenols and high boiling hydrocarbons. Fresh tobacco smoke is composed of particles ranging in size from 0.1 to 1.0 microns.[2]

The majority of the compounds found in tobacco smoke are known to have detrimental health effects. For example, many of the nitrogen bases found in cigarette smoke, such as nicotine and pyridine, are poisonous and may cause lung cancer. Other components found in the tar lead to heart disease, whilst gases such as carbon monoxide and nitric oxide interfere with the uptake of oxygen by hæmoglobin and lead to respiratory problems. Thus filtration of tobacco smoke is necessary in order to reduce the health risk.

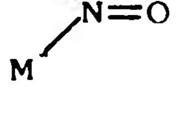
Cigarette filters made from fibrous material, normally cellulose based, are used to reduce the particulate phase by mechanical filtration.[3] When a liquid medium is incorporated into these filters it is also possible to remove certain smoke constituents of 'intermediate' volatility, such as furans, phenols and other polar compounds.[2] Also, various absorbents, such as charcoal or alumina, can be imbedded into filters to remove toxic, volatile substances from tobacco smoke.[3] However, these absorbents are not particularly selective and can result in an undesirable effect on the taste of the smoke. In general, both the absorbent and fibrous type of filters are best regarded as non-selective, especially towards permanent gases.

Over the past twenty five years research has been concentrated on the development of selective tobacco smoke filters.[4-25] The majority of this work has centred on the removal of certain vapour phase constituents, particularly hydrogen cyanide, hydrogen sulphide, acetaldehyde, nitric oxide and carbon monoxide. Hydrogen cyanide has been successfully removed by filters containing absorbents such as zinc oxide, iron(III) oxide and copper(I) oxide.[10,11] and also by metal complexes of polydentate amines, e.g. ethylene diamine.[7-12] In addition a number of filtration materials have been patented which remove both hydrogen cyanide and hydrogen sulphide[7,12-14] and also acetaldehyde.[15] The majority of these filters make use of zinc acetate or other, similar, metal salts.

A number of filter additives have been used in an attempt to selectively filter carbon monoxide and nitric oxide. Before discussing these it is necessary first to outline the chemical properties of the oxides and the possible types of reaction that can occur with them.

Generally, carbon monoxide and nitric oxide are fairly inert in their behaviour towards acids and bases. Also, carbon monoxide is resistant to oxidation under ambient conditions and has exceedingly weak Lewis base properties towards compounds of non-transition metals. However, both carbon monoxide and nitric oxide are capable of reacting with a variety of transition metal compounds. The nitric oxide molecule contains one more electron than the carbon monoxide molecule and because of this can react with a wider spectrum of transition metal compounds and also some non-transition metal compounds.

The ability of carbon monoxide and nitric oxide to form bonds with transition metal atoms/ions is attributed to the fact that in addition to a weak dative bond, e.g. $O{\equiv}C\overset{\cdot}{\underset{\cdot}{\rightarrow}}M$, there exists 'backbonding' by the donation of electrons in metal orbitals to the antibonding π^* orbitals of the oxides. This type of bonding is synergic, i.e. the effects of σ bond formation strengthen the π-bonding and vice versa. Carbon monoxide effectively acts as a two electron donor and nitric oxide as a three electron donor. In this type of bonding nitric oxide and carbon monoxide are acting as π-acceptor ligands. Nitric oxide can also act as a one electron donor ligand to give complexes with bent MNO groups (4.1).

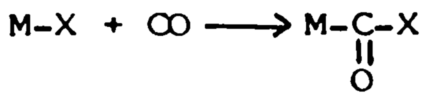


4.1

Dioxygen is also a π-acceptor ligand and bonds in a similar fashion as the examples above to hæmoglobin.

Because of this carbon monoxide and nitric oxide are capable of replacing dioxygen in the blood supply of animals.

Carbon monoxide is also capable of reacting with transition metal compounds via an insertion reaction (Reaction 4.1).



$$M{-}X + CO \longrightarrow M{-}\underset{\displaystyle \overset{\|}{O}}{C}{-}X$$

$(X = -CR_3, -H, -OH, -NR_2)$

Reaction 4.1

These types of reaction usually require high pressure conditions, but there are some examples which operate at atmospheric pressure, e.g. the reaction of methylpentacarbonyl manganese(I) with carbon monoxide (Reaction 4.2).[26]

$$CH_3Mn(CO)_5 + CO \longrightarrow CH_3COMn(CO)_5$$

Reaction 4.2

However, substrates used in these reactions and the products of such reactions are often air-sensitive and thermally unstable. Hence, they are unsuitable for use in tobacco smoke filtration.

Transition metal compounds can also be used for the catalytic oxidation of carbon monoxide and nitric oxide. As stated previously, carbon monoxide is resistant towards oxidation under ambient conditions. Nitric oxide though reacts instantly with oxygen (Reaction 4.3).

$$2NO + O_2 \longrightarrow 2NO_2$$

Reaction 4.3

However, tobacco smoke is oxygen deficient, thus Reaction 4.3 cannot operate. Therefore, for oxidation of nitric oxide and carbon monoxide in tobacco smoke to be effective a catalyst is required. One such catalyst is an iridium complex, $[Ir(PPh_3)_2(NO)_2]PF_6$, which catalyses the reaction of carbon monoxide and nitric oxide. (Reaction 4.4).[27,28]

$$2NO + CO \longrightarrow N_2O + CO_2$$

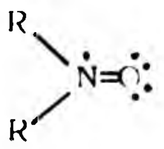
Reaction 4.4

There are also a few reactions which occur between nitric oxide and certain organic compounds that are of interest. Nitrosobenzene in chloroform solution is known to absorb nitric oxide to give benzenediazonium nitrate (Reaction 4.5).[29]

$$PhNO + 2NO \longrightarrow PhN_2^+[NO_3^-]$$

Reaction 4.5

There is another type of compound that nitric oxide, but not carbon monoxide, can react with, due to its electronic configuration. Nitric oxide has an unpaired electron and thus should be capable of reacting with radicals, such as the nitroxide radical 4.2, to yield stable, relatively harmless compounds (Reaction 4.6).



$(= Y^\bullet)$

4.2

$$Y^{\bullet} + NO^{\bullet} \longrightarrow YNO$$

Reaction 4.6

Thus in summary, both carbon monoxide and nitric oxide are capable of reacting with transition metal compounds to form adducts and can be catalytically oxidised by certain compounds. In addition, because of its electronic nature, nitric oxide can react selectively with relatively stable radicals or certain organic compounds.

These reactions have been utilised in attempts to prepare cigarette filters which selectively remove carbon monoxide and nitric oxide. The majority of the literature on these filters is in the form of patents. Because of this the amount of information on the active ingredient being used is restricted. There is also little discussion about reaction products and usually no attempt at a mechanistic evaluation. Consequently, it is often difficult to get a clear picture of what is occurring. However, the different types of filter can be grouped and these will be outlined here.

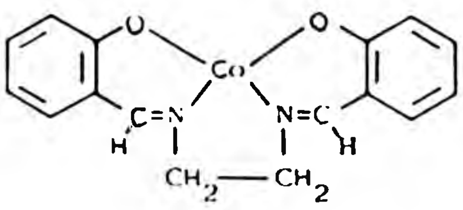
A number of metal compounds have been used which have sucessfully selectively removed the oxides.[6-9,16-18,24,25] However, the majority of these compounds are unsuitable for commercial use in cigarette filters due to toxicity or cost. Most of the compounds used to remove carbon monoxide were oxidation catalysts such as manganese dioxide[16,17] or hopcalite, a mixed copper oxide/manganese dioxide catalyst,[17] or catalysts referred to in the cigarette industry as redox catalysts.[18] These redox catalysts make use of two components.

The first is a palladium, or other noble metal, compound which acts as a catalyst in the oxidation of carbon monoxide and is reversibly reduced in the process. The second component is a substance such as a copper salt, which acts as an oxidising agent to reoxidise the first component back to a catalytically active state and is reversibly reduced in the process. Reoxidation of the second component then occurs, but only in the presence of moisture.

In all of these systems carbon monoxide is oxidised to carbon dioxide. In Chapter 3 a number of complexes were described which react with carbon monoxide to form adducts. Attempts to use such complexes in cigarette filters have failed.[16-18,30,31] These included the phthalocyanine chelates of iron, cobalt and nickel and the chelates formed from the Schiff base of salicylaldehyde and ethylenediamine with cobalt (salcomine), manganese, copper, chromium, iron and nickel.

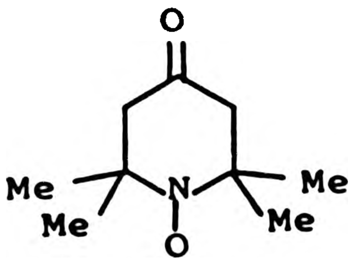
Similarly, nitric oxide reacts reversibly with a number of Schiff base complexes[32-34] and with the phthalocyanine complexes of iron and cobalt[35,36] to form adducts.

A number of complexes of this type have been used with varying amounts of success to remove nitrogen oxides from tobacco smoke.[6,9] In particular, it was found that salcomine (4.3) would remove upto 48% of the oxides NO and NO_2 from cigarette smoke (dependent on the support used). However, it was not determined if the removal was more selective for one oxide than the other, although the amount of NO_2 present in tobacco smoke compared to that of NO is very small.[6]



4.3

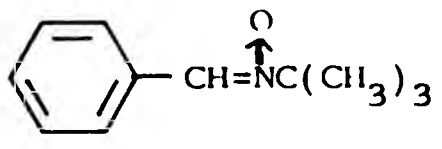
Another method of removing nitric oxide has involved the use of free radical compounds.[19-22] Nitric oxide itself has an odd electron character and can thus be 'trapped' by a similar species. One such substance is 4-oxo-2,2,6,6-tetramethylpiperidino-oxy (4.4), a stable, non-volatile free radical nitroxide.[19]



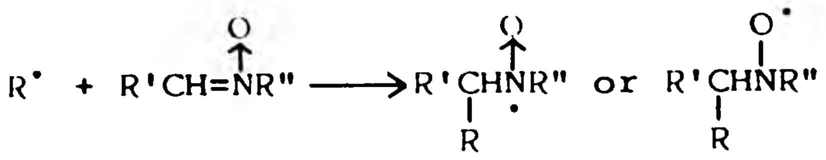
4.4

It has been claimed that this compound loaded onto a carbon base and placed in a triple cavity cellulose acetate filter is capable of removing up to 72% of nitric oxide. As with the salcomine complex, efficiency of removal is dependent upon the support used. Thus the drawback of this filter is that it has to be used on a carbon base, which is non-selective and removes a variety of the components of tobacco smoke.

Another study uses nitrones such as N-benzylidine-tert-butylamine N-oxide (4.5) for the removal of nitric oxide.[20] It is thought that these compounds react with free radicals in tobacco smoke (including nitric oxide) to yield a stable nitroxide radical (Reaction 4.7)



4.5

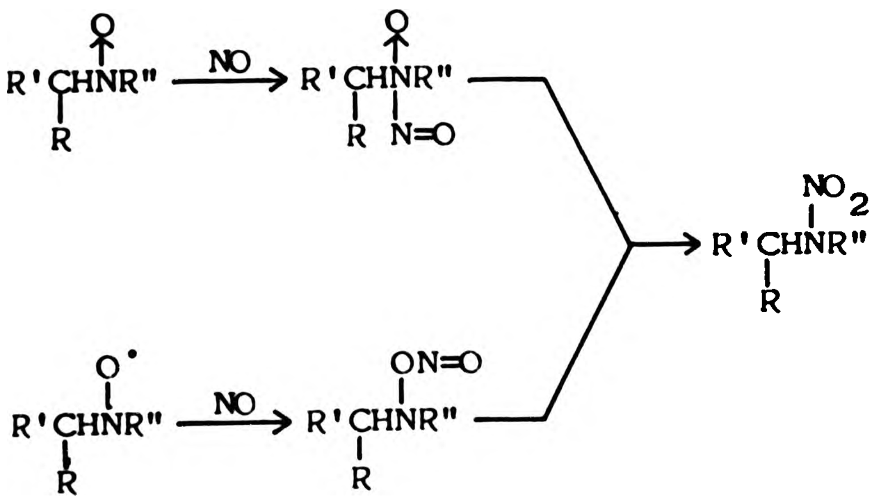


$$R^{\bullet} + R'CH=\overset{\overset{O}{\uparrow}}{N}R'' \longrightarrow R'\underset{R}{C}H\overset{\overset{O}{\uparrow}}{\underset{\bullet}{N}}R'' \text{ or } R'\underset{R}{C}H\overset{O^{\bullet}}{N}R''$$

Reaction 4.7

The nitroxide radicals may then react with nitric oxide by one of the following mechanisms (Scheme 4.1)[37]:

Scheme 4.1



However, the amounts of nitric oxide removed by these compounds are not as high as those removed when nitroxides are placed directly onto a filter.

More recently, filters in which nitrosobenzene (15 mg.) has been absorbed onto carbon coated with iron (1 mg.) have removed upto 61% nitric oxide.[23] It is obvious that here the inventors were attempting to utilise the reaction outlined earlier (Reaction 4.5) between nitric oxide and nitrosobenzene to give benzenediazonium nitrate.[29] It is not clear what role the iron plays in this filter, but it is possible that under the conditions which exist in the filter, when tobacco smoke is being drawn through, an iron complex of some sort is formed with the nitrosobenzene. It would be this complex that reacts with the nitric oxide rather than the nitrosobenzene. Alternatively, the iron could be there in the role of a catalyst. It is unlikely that the nitrosobenzene would be an effective filter additive on its own as, under normal conditions, the reaction with nitric oxide will only occur in solution.

Both nitric oxide and carbon monoxide are Lewis bases and as such would be expected to react with a variety of metal complexes to form adducts. As described here, a number of attempts to use complexes in this fashion have been carried out. In general though, attempts to remove these Lewis bases by adduct formation have been unsuccessful. It is found that complexes which react with the bases in solution at ambient temperature and pressure are inactive or have a negligible effect when placed in cigarette filters. In a previous study it was indicated that there was significant interaction between carbon monoxide and the complexes $Fe(1\text{-}nqo)_2.2py$, $Fe(2\text{-}nqo)_2.2py$ and $Fe(5\text{-}MeOqo)_2.2py$ when in solution.[38] However, when placed in cigarette filters and used in smoking tests, analysis suggested that only a small portion of compound had reacted and that the reaction was very slow. The possible reaction occurring here is shown in Reaction 4.8.

$$Fe(qo)_2.2py \xrightarrow[-py]{+CO} Fe(qo)_2(py)(CO)$$

Reaction 4.8

There is also the possibility that some interaction between carbon monoxide and the ligands was occurring, as this was indicated during the solution studies. These reactions are most likely slowed down because the pyridine is blocking the site at which carbon monoxide attacks. It would not be possible though to use the bischelates, $Fe(qo)_2$, as these compounds are oligomeric and thus are also coordinatively saturated. This type of complex is known to be very unreactive towards Lewis bases, with the exception of pyridine (refer to Ch.2).

In the above studies it was also indicated that the iron(III) trischelates, $Fe(qo)_3$, might be active in cigarette filters. This was unexpected as these complexes are also coordinatively saturated. However, with these complexes there is the possibility of an internal redox reaction occurring (Reaction 4.9).

$$Fe(qo)_3 \longrightarrow Fe(qo)_2 + qo^{\bullet}$$

Reaction 4.9

This could be promoted by one or more of the Lewis bases present in tobacco smoke and would lead to the formation in situ of the $Fe(qo)_2$ complex. This would be in a monomeric rather than oligomeric form and thus more reactive. Hence, by promoting an internal redox reaction using the bases in tobacco smoke, the reactivity of the complexes towards carbon monoxide and possibly nitric oxide, should be enhanced.

Before carrying out any studies on the effect of tobacco smoke on selected metal complexes a range of preliminary reactions were carried out. These involved the reactions of a number of copper and iron complexes with a selection of Lewis bases found in tobacco smoke. Triphenylphosphine, which like carbon monoxide is a π-acceptor ligand, was also used. These are summarised in Table 4.1.

As a result of carrying out these reactions it was possible to classify them into two main groups:

(i) Reactions in which the oxidation state of the metal remains unchanged (adduct formation), e.g. Reaction 4.10.

$$\mathrm{Cu(1\text{-}nqo)_2 + nic \longrightarrow Cu(1\text{-}nqo)_2.nic}$$

Reaction 4.10

(ii) Reactions in which the oxidation state of the metal is lowered (Lewis base promoted internal redox reaction), e.g. Reaction 4.11.

$$\begin{tikzcd} \mathrm{Fe(1\text{-}nqo)_3 + py} \arrow[r] & \mathrm{Fe(1\text{-}nqo)_2.2py} + [\mathrm{1\text{-}nqo^{\bullet}}] \arrow[d, "\text{H-abstraction from solvent}"] \\ & \mathrm{1\text{-}nqoH} \end{tikzcd}$$

Reaction 4.11

The results obtained suggest that for both iron and copper complexes the occurrence of redox behaviour is dependent on, or favoured by, Lewis bases which can stabilise low oxidation states, e.g. triphenylphosphine. The nature of the initial chelating ligand is also important. Redox

Table 4.1 Interaction of a variety of iron(III) and copper(II) complexes with selected Lewis bases.

Complex	Lewis base	Metal product	Organic products
Cu(1-nqo)$_2$	nicotine	Cu(1-nqo)$_2$•nic	none
Cu(2-nqo)$_2$	nicotine	Cu(2-nqo)$_2$•nic	none
Cu(dtc)$_2$[a]	pyridine	no reaction	
Fe(dtc)$_3$[a]	pyridine	Fe(III) product	(Et$_2$NCSS)$_2$ + b
Cu(dtc)$_2$[a]	methyl cyanide	not established	(Et$_2$NCSS)$_2$ + b
Fe(dtc)$_3$[a]	methyl cyanide	Fe(III) product	(Et$_2$NCSS)$_2$ + c
Cu(dtc)$_2$[a]	aniline	not established	(Et$_2$NCSS)$_2$ + c
Fe(acac)$_3$	pyridine	no reaction	
Fe(bha)$_3$[d]	pyridine	no reaction	
Fe(1-nqo)$_3$	pyridine	Fe(1-nqo)$_2$•2py	1-nqoH + b
Fe(2-nqo)$_3$	pyridine	Fe(2-nqo)$_2$•2py	2-nqoH + b
Fe(1-nqo)$_3$	nicotine	Fe(II) product which decomposes to Fe(1-nqo)$_2$	upon decomposition of iron(II) product 1-nqoH is obtained.
Fe(2-nqo)$_3$	nicotine	Fe(II) product which decomposes to Fe(2-nqo)$_2$	upon decomposition of iron(II) product 2-nqoH is obtained.
Fe(1-nqo)$_3$	pyrrole	Fe(II) product	1-nqoH + c
Fe(2-nqo)$_3$	pyrrole	Fe(II) product	2-nqoH + c

Table 4.1 cont.

Complex	Lewis base	Metal product	Organic products
Fe(1-nqo)$_3$	Ph$_3$P	Fe(II) complex[e]	Ph$_3$PO + c
Fe(2-nqo)$_2$	Ph$_3$P	Fe(II) complex[e]	Ph$_3$PO + c
Cu(dtc)$_2$[a]	Ph$_3$P	Cu(Et$_2$NCSS)(Ph$_3$P)$_2$	Ph$_3$PS + c
Fe(dtc)$_3$[a]	Ph$_3$P	not established	Ph$_3$PS + c
Cu(acac)$_2$	Ph$_3$P	Cu(acac)(Ph$_3$P)$_2$	not established
Fe(acac)$_3$	Ph$_3$P	no reaction	
Cu(bha)$_2$[d]	Ph$_3$P	Cu(I) product	not established
Fe(bha)$_3$[d]	Ph$_3$P	no reaction	

[a] dtcH = diethyldithiocarbamic acid

[b] traces of other products

[c] considerable quantities of various unidentified products

[d] bhaH = benzohydroxamic acid

[e] these reactions are presented in detail in Chapter 2

behaviour is favoured by those ligands with a strong ligand field, e.g. $\mathrm{Fe(1\text{-}nqo)_3}$ is readily reduced to iron(II) complexes, but $\mathrm{Fe(acac)_3}$ (in which a high spin iron(III) species is present) is not reduced.

It can be seen from Table 4.1 that reactions of type (ii) result in a variety of organic products. In these reactions a ligand radical is formed which may react further in three ways:

a) Abstract hydrogen to give the protonated ligand ($[\mathrm{L}^{\bullet}] \xrightarrow{[\mathrm{H}^{\bullet}]} \mathrm{LH}$), e.g. in the reaction of $\mathrm{Fe(2\text{-}nqo)_3}$ with pyridine the major organic product obtained is 2-nitroso-1-naphthol (Reaction 4.12). In this reaction, the hydrogen is most likely abstracted from solvent molecules.

$$\begin{tikzcd}
\mathrm{Fe(2\text{-}nqo)_3 + py} \arrow[r] & \mathrm{Fe(2\text{-}nqo)_2{\cdot}2py + [2\text{-}nqo^{\bullet}]} \arrow[d, "\text{H-abstraction}"] \\
 & \mathrm{2\text{-}nqoH}
\end{tikzcd}$$

Reaction 4.12

b) Dimerise to give L-L ($2[\mathrm{L}^{\bullet}] \longrightarrow \mathrm{L\text{-}L}$), e.g. in the reaction of $\mathrm{Fe(Et_2NCSS)_3}$ with pyridine diethylthiuram disulphide is obtained (Reaction 4.13). This 'dimerisation' reaction has been discussed in greater detail in Chapter 1 and probably involves the formation of LH, which because it is unstable reacts further to give L-L.

$$\begin{tikzcd}
\mathrm{Fe(Et_2NCSS)_3 + py} \arrow[r] & \mathrm{[Fe(Et_2NCSS)_2{\cdot}py_x]} \arrow[d] & \mathrm{+\ [Et_2NCSS^{\bullet}]} \arrow[d] \\
 & \text{iron(III) product} & \mathrm{(Et_2NCSS)_2}
\end{tikzcd}$$

Reaction 4.13

c) React with the Lewis base to give a mixture of organic products, e.g. in the reaction of $Cu(Et_2NCSS)_2$ with triphenylphosphine the triphenylphosphine adduct of the copper(I) complex is obtained together with a variety of organic products, including triphenylphosphine sulphide (Reaction 4.14). The majority of these products arise as a result of interaction between triphenylphosphine and the ligand and/or ligand radical.

$$Cu(Et_2NCSS)_2 + Ph_3P \longrightarrow Cu(Et_2NCSS)(Ph_3P)_2 + Ph_3PS + \text{organic products}$$

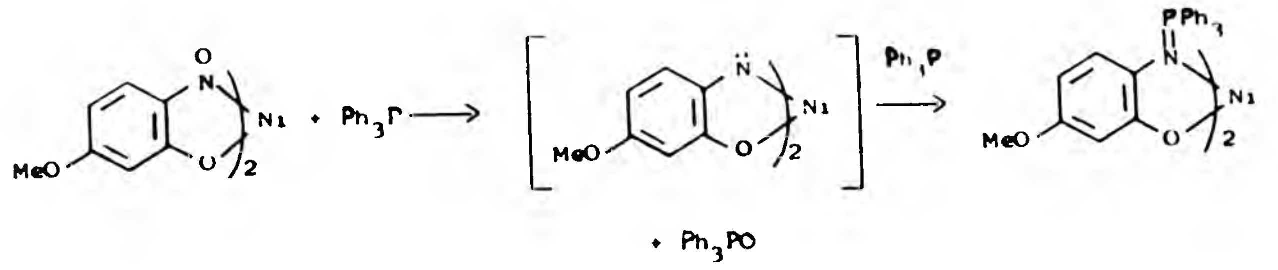
Reaction 4.14

If complexes which are capable of undergoing Lewis base promoted internal redox reactions were to be used in cigarette filters they should prove to be more effective than complexes used previously for a number of reasons:

(i) Speed of reaction should be faster.

(ii) Once reaction has occurred, the released ligand radical can react further with free radicals, or Lewis bases, in the tobacco smoke.

(iii) If a complex such as $Fe(1\text{-}nqo)_3$ were to be used then further interaction could occur with the ligands surrounding the reduced metal species. In the reaction of $Ni(5\text{-}MeOqo)_2$ with triphenylphosphine the phosphine deoxygenates the qo ligands and then interacts further with the quinoneimine/nitrene ligands produced (Reaction 4.15).[39]



Reaction 4.15

Due to the similarity between triphenylphosphine and carbon monoxide as ligands, this type of reaction should be possible with carbon monoxide leading to carbon dioxide and a complex containing ligands derived from qo ligands and carbon monoxide. This complex could then react further with carbon monoxide (or another Lewis base) to form an adduct.

On the basis of the experiments carried out and listed in Table 4.1 it was decided to examine the complexes Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ in the filtration of tobacco smoke. These complexes were investigated at the research laboratories of Filtrona Ltd. Their effects on both the vapour phase and the particulate phase of tobacco smoke were studied using gas chromatographic, infrared and chemiluminescence techniques. A number of attempts had to be made before suitable filters for the experiments could be prepared, as there were difficulties in loading the complex onto suitable supports. However, these difficulties were overcome and the results are presented in section 4.2.

4.2 A study of the filtration of tobacco smoke using the complexes $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$.

4.2.1 Experimental technique.

During the course of this study the iron complexes were used in conjunction with a number of filters supplied by Filtrona Ltd. Two basic types of filter were used:

(i) A solid filter impregnated with metal complex.

(ii) A triple cavity filter in which metal complex coated onto a support had been placed (Figure 4.1).

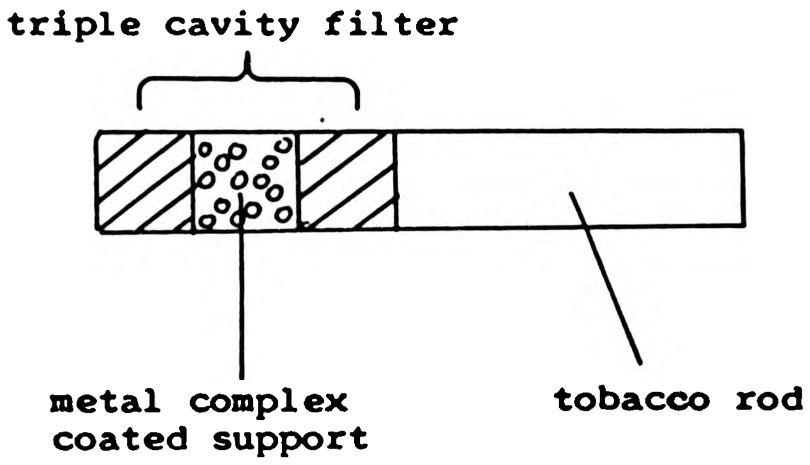


Figure 4.1

A variety of Filtrona supports and several types of filter were used. The tobacco rods were smoked under standard conditions to a length of 9 mm (one puff per minute lasting two seconds and drawing through 35 cm^3 tobacco smoke/air). The vapour phase was collected in a suitable bag and used a) to determine the concentrations of volatile organic substances using g.l.c. techniques and b) to determine the carbon monoxide concentration using a non-dispersive infra-red (NDIR) carbon monoxide analyser. The particulate phase was collected on a Cambridge filter pad (a specially designed pad composed of glass fibre that is able to retain 99% of the particulate phase) and then dissolved in acetone and analysed using g.l.c. techniques.

In a separate set of experiments a smoking machine was connected directly to a nitric oxide analyser to enable nitric oxide concentrations to be determined directly.

4.2.2 Results of the analysis of the particulate phase after smoking tests.

For these experiments filter types 1 and 2 were used with approximately 16 mg of iron complex in each filter. Eight cigarettes were used in each smoking experiment. The tar collected was dissolved in a known volume of acetone and passed through a g.l.c. column. The chromatogram obtained from this preliminary separation was too complex for proper analysis (Figure 4.2). Hence, selected fractions of the particulate phase were "trapped" as they passed through the column and were then sent through a secondary column. The results from this were analysed by computer to give relative amounts of selected components of tobacco smoke (Figure 4.3). In all, four major fractions were trapped and separated in this fashion. The results from these tests were compared with those obtained from blank "smokings", in which filters containing no complex were used. The average percentage losses between the blank filters and the filters plus complex, for selected Lewis bases, are summarised in Table 4.2.

After smoking through the filters it was noticed that both $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ had changed colour, $Fe(1\text{-}nqo)_3$ from brown to green and $Fe(2\text{-}nqo)_3$ from purple to green, indicating that reduction of iron(III) to iron(II) had taken place.

Figure 4.2 Example of the primary g.l.c. chromatogram obtained for the particulate phase of tobacco smoke after smoking through selected filters.

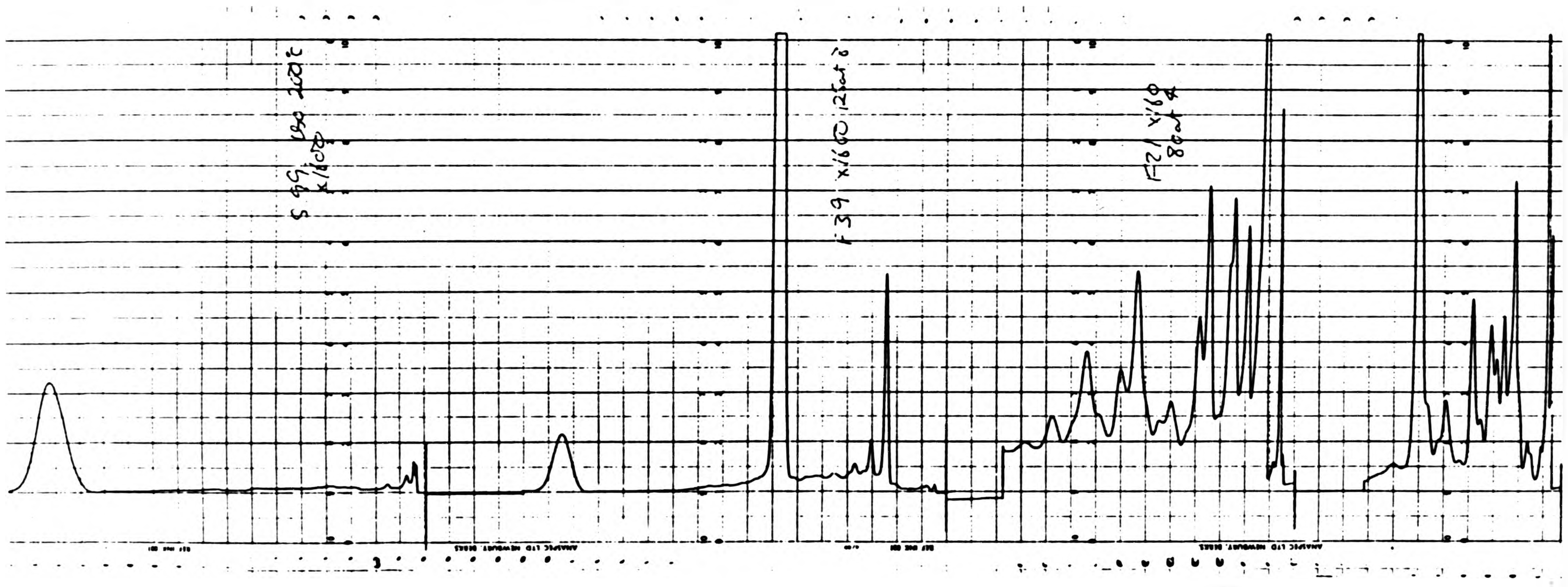


Figure 4.3 Examples of the secondary, computer produced, chromatograms obtained after the trapping of selected fractions of the particulate phase of tobacco smoke.

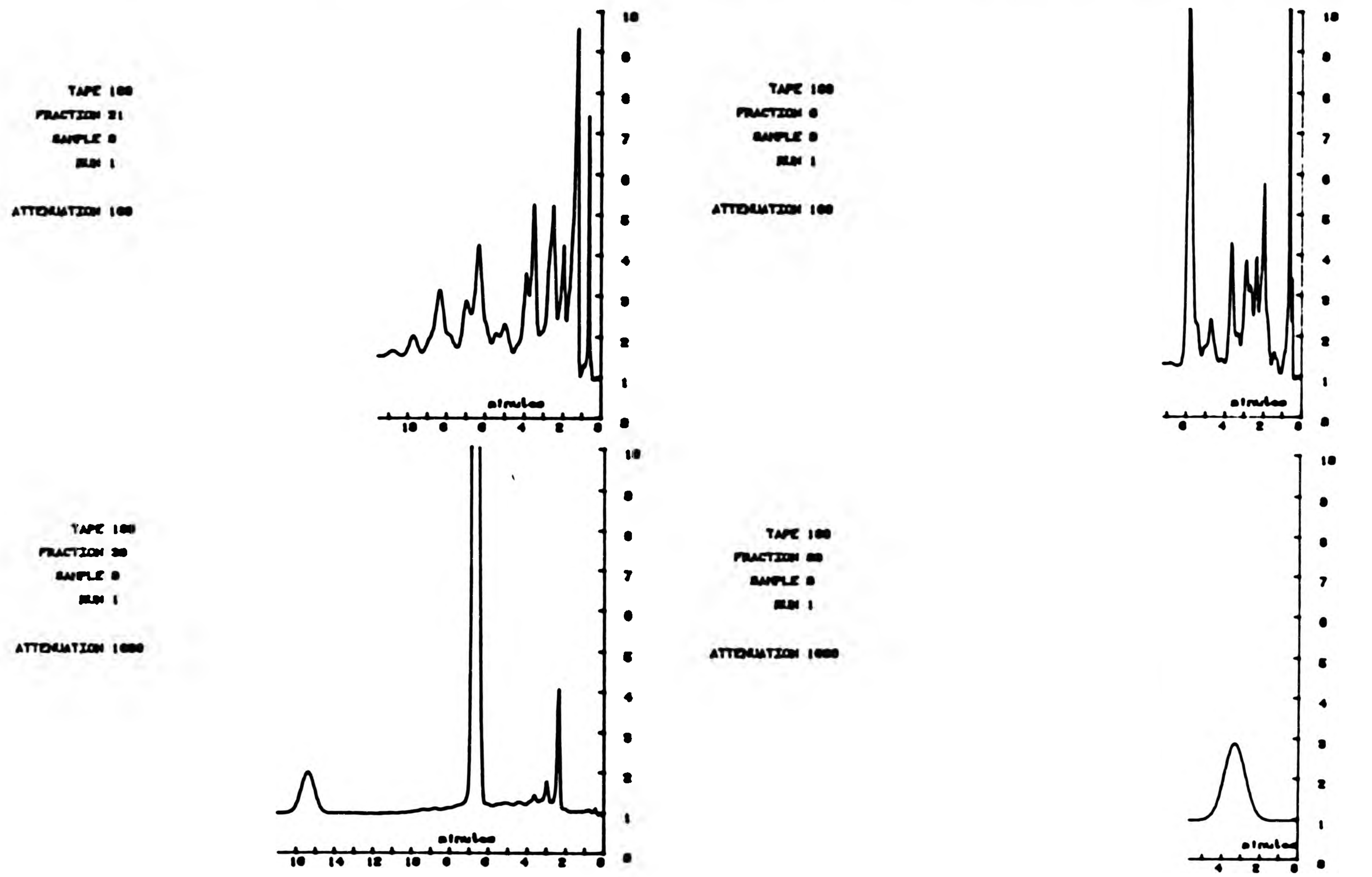


Table 4.2 Results of the smoking tests carried out on the semi-volatile components of tobacco smoke.

Constituent Removed	Complex used			
	$Fe(1\text{-}nqo)_3$ Constit. red^{tn} (%)		$Fe(2\text{-}nqo)_3$ Constit. red^{tn} (%)	
	Filter 1	Filter 2	Filter 1	Filter 2
Pyridine	minor	minor	8	11
o-Xylene	10	minor	15	9
Dipentene	10	minor	11	minor
Pyrrole	21	15	18	15
Furfural	19	17	20	17
2-Acetylfuran	16	10	minor	minor
3-Vinylpyridine	15	13	20	12
Indene	17	13	13	9
Phenol	19	18	4	3
o-Cresol	30	17	8	9
Nicotine	22	16	15	19
Phytadiene	17	9	11	14

4.2.3 The effect of $Fe(qo)_3$ filters on the volatile, organic components of tobacco smoke.

The volatile phase of tobacco smoke is not as complex as the particulate phase and needs to be passed through a g.l.c. column only once.

. Again, filter types 1 and 2 were used. Comparison of the chromatograms obtained after smoking through filters containing the complex compared with blank filters showed there to be no significant differences.

4.2.4 The effect of $Fe(qo)_3$ filters on the carbon monoxide concentration in the volatile phase of tobacco smoke.

All seven filter types were examined with regard to carbon monoxide uptake. In each case approximately 16 mg of complex was present in the filter. The amount of carbon monoxide present in a sample was given by an NDIR carbon monoxide analyser.

Positive results (i.e. a reduction in carbon monoxide levels) were obtained using five filter types with $Fe(2\text{-}nqo)_3$ and four filter types with $Fe(1\text{-}nqo)_3$. However, the experiments were complicated in some cases by the decomposition of the iron complexes on certain supports, indicated by a change in colour from purple/brown to green. In certain cases this problem was overcome by different methods of adsorption. However, for the smoking tests, both "decomposed" and "normal" complex on support was used. A number of smoking tests were carried out for each type of filter in order that a statistical analysis of the results could be obtained, as the results of smoking vary from sample to sample. For each smoking of filters plus complex, an equivalent number of "blank" smokings were carried out. The results of these tests are given in Tables 4.3 and 4.4.

Table 4.3 shows the percentage difference in carbon monoxide levels between blank and complex coated filters after one standard smoking. It can be seen that the majority of filter types lead to a reduction of 8-9% in the levels of carbon monoxide. For one filter (type 3 with $Fe(2\text{-}nqo)_3$ adsorbed) only a small difference between blank and filter was observed. Upon examining the filter after smoking it was found that the complex was still purple, indicating that $Fe(2\text{-}nqo)_3$ was still present and that no reaction had occurred with most of the complex. With the majority of the filters, coated with both $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$, after smoking the filters were a greenish colour. When washed with acetone some purple $Fe(2\text{-}nqo)_3$ or brown $Fe(1\text{-}nqo)_3$ was removed, indicating that reaction was not complete. Because of this it was decided to carry out repetitive smoking of filters. Selected filters containing $Fe(1\text{-}nqo)_3$ or $Fe(2\text{-}nqo)_3$ in both "normal" and "decomposed" forms were smoked through three times, in order to see if the filters were reusable. The results from these tests were variable but did show that the filters retain some degree of activity after the first smoking. These results are summarised in Table 4.4.

Statistical evaluation of the results to ascertain the validity of the figures (due to variation between smokings) showed that statistically there is a greater than 99% chance that the results are meaningful.

Table 4.3 **The effect of Fe(1-nqo)$_3$ and Fe(2-nqo)$_3$ on the levels of carbon monoxide in tobacco smoke**

Filter type	Complex	CO yield*						Average CO yield*	Wt. difference between blank and complex filters/mg	% Difference between blank and complex.
		1	2	3	4	5	6			
1	Fe(1-nqo)$_3$	16.0	16.3	16.2	16.5	16.3		16.3	negligible	
	Fe(2-nqo)$_3$	14.4	14.8	15.0	15.0	15.1	--	14.9	1.5	9.4
	Blank	16.1	16.3	16.9	16.4	16.2	--	16.4		
3	Fe(2-nqo)$_3$	15.7	16.0	-	-	-	--	15.85	0.3	1.9
	Blank	16.1	16.2	-	-	-	--	16.15		
	+Fe(2-nqo)$_3^d$	15.1	15.1	14.6	14.7	15.0	15.1	14.9	1.5	9.1
	+Fe(1-nqo)$_3^d$	15.0	14.8	14.0	14.6	15.0	15.2	14.8	1.6	9.1
	Blank	16.6	16.5	17.0	16.4	16.2	15.8	16.4		
4	Fe(2-nqo)$_3$	15.4	15.5	15.4	-	-	-	15.4	1.1	6.7
	Blank	16.7	16.3	16.5	-	-	-	16.5		
5	Fe(2-nqo)$_3$	No significant results obtained								
7	Fe(2-nqo)$_3$	15.2	14.7	14.9	15.0	-	-	14.9	1.2	7.4
	Fe(1-nqo)$_3$	15.3	14.9	14.7	15.3	-	-	15.0	1.1	6.8
	Blank	16.1	15.8	15.8	16.6	-	-	16.1		

* CO/mg obtained per smoking per tobacco rod; each smoking corrected for atmospheric temperature and pressure.

+ Fe(1-nqo)$_3^d$ and Fe(2-nqo)$_3^d$ = decomposed complexes

Table 4.4 The effect of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ on the levels of carbon monoxide in tobacco smoke after repetitive smoking of filters.

Filter type	Complex	1st smoking of filters		2nd smoking of filters		3rd smoking of filters	
		Average CO yield*	% Difference between blank and complex.	Average CO yield*	% Difference between blank and complex.	Average CO yield*	% Difference between blank and complex.
1	$Fe(2\text{-}nqo)_3$	14.8	8.6	15.8	2.8	15.9	2.4
	$Fe(1\text{-}nqo)_3$	16.1	0.6	15.9	2.4	16.2	0.6
	Blank	16.2		16.3		16.3	
4	$Fe(2\text{-}nqo)_3$	15.4	6.1	15.5	3.7	15.2	5.6
	Blank	16.4		16.1		16.1	
	+$Fe(2\text{-}nqo)_3^d$	14.6	10.4	15.2	6.1	16.0	2.1
	+$Fe(1\text{-}nqo)_3^d$	15.0	7.7	15.2	6.7	15.7	4.0
	Blank	16.2		16.3		16.3	
7	$Fe(2\text{-}nqo)_3$	15.2	6.7	14.7	11.4	14.9	8.3
	$Fe(1\text{-}nqo)_3$	15.3	6.1	16.1	3.3	16.3	-
	Blank	16.3		16.6		16.2	

* CO/mg obtained per smoking per tobacco rod; each smoking corrected for atmospheric temperature and pressure.

\+ $Fe(1\text{-}nqo)_3^d$ and $Fe(2\text{-}nqo)_3^d$ = decomposed complexes.

4.2.5 The effect of $Fe(qo)_3$ filters on the nitric oxide concentration in the volatile phase of tobacco smoke.

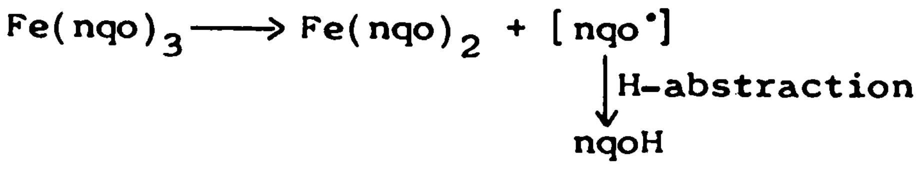
For the purpose of monitoring any reaction between nitric oxide and the complexes $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$, smoking tests were carried out using a smoking machine connected to an automatic nitric oxide analyser.

Neither of the complexes were found to react significantly with nitric oxide. In all tests, the variation in nitric oxide concentration between smokings was considerable. Hence, in order to carry out a proper statistical analysis many more smoking tests would need to be carried out.

4.3 Conclusion

As a result of these studies it has been shown that both $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ are capable of removing a number of constituents from the semi-volatile components of tobacco smoke. Both complexes (either in the normal, trischelate, form or, more interestingly, in the green "decomposed" form) can also remove carbon monoxide. Although the exact nature of the "decomposed" complexes were not determined there are a number of possibilities, the most likely of which all involve the reduction of iron(III) to iron(II). This is because in general iron(II) complexes of quinoneoximes are green whereas the iron(III) complexes are brown/purple. Possible types of complex that could have been formed include:

(i) The appropriate bischelate. Formation of this would involve the formation of a ligand radical which would abstract hydrogen to give the appropriate quinoneoxime



$$\mathrm{Fe(nqo)_3} \longrightarrow \mathrm{Fe(nqo)_2} + \underset{\mathrm{nqoH}}{\underset{\big\downarrow \text{H-abstraction}}{[\mathrm{nqo}^{\bullet}]}}$$

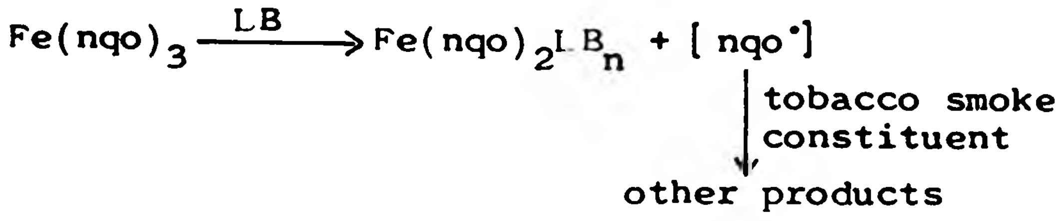
Reaction 4.16

However, there was no indication that either 1,2-naphthoquinone-1-oxime or 1,2-naphthoquinone-2-oxime was formed. In addition, the iron(II) bischelates of these oximes form oligomeric complexes which are generally unreactive toward Lewis bases (refer to Ch.2). As the "decomposed" complexes were as reactive toward carbon monoxide as the trischelates the complexes are unlikely to have this form. However, it is possible that when the complexes are coated onto the filter support they remain in individual units rather than form oligomers, thus leaving them in a more reactive form.

(ii) An iron(II) complex which still retains three coordinated quinone oximato type ligands, one of which has abstracted hydrogen to become a neutral ligand. Complexes of this type have been discussed in Ch.2. If this type of complex were present it would account for the non observance of the quinoneoxime and would also be reactive towards Lewis base constituents of tobacco smoke.

When filters impregnated with the trischelates were smoked through the final colour of the filters (green) implies that internal redox reactions occur for both complexes, such that $\mathrm{Fe}^{III} \longrightarrow \mathrm{Fe}^{II}$. The amounts of

Lewis base constituents removed indicates that the reactions occurring are complex and probably involve further interaction of the released ligand radical with constituents of tobacco smoke (Reaction 4.17).



$$\begin{tikzcd} \mathrm{Fe(nqo)_3} \arrow[r, "\mathrm{LB}"] & \mathrm{Fe(nqo)_2LB_n} + [\,\mathrm{nqo}^{\bullet}] \arrow[d, "\text{tobacco smoke constituent}"] \\ & \text{other products} \end{tikzcd}$$

Reaction 4.17

Overall, the complexes $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$, or related complexes, are suitable for utilisation in the selective filtration of tobacco smoke. In respect of this, a patent application has been made[40] and the discovery is now being exploited further with other companies.

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CHAPTER 5

5. Experimental

5.1 General

The reagents and solvents used were generally of 'AnalaR' grade and were used without further purification.

The kinetic experiments were carried out using 'Spectrosol' acetone, which was used as supplied.

Iron pentacarbonyl was distilled under vacuum at room temperature immediately prior to use.

Silica gel adsorbent used in the chromatography columns was of 70-230 mesh and supplied by B.D.H. Chemicals Ltd. Pre-coated silica gel and cellulose plates of 0.25 mm. thickness were used for thin layer chromatography purposes. Large preparative plates were made up at The Polytechnic of North London.

5.2 Analytical techniques

Carbon, hydrogen and nitrogen analyses were carried out by the microanalytical services of The Polytechnic of North London.

Metal analyses were carried out by atomic absorbtion spectroscopy on a Pye Unicam SP9 machine at The Polytechnic of North London. Wet oxidation was achieved by heating a small amount (ca. 0.1g) of the material in concentrated nitric acid (10 cm^3), plus a few drops of 100 volume hydrogen peroxide.

Phosphorus was determined gravimetrically, after wet digestion of the sample (ca. 0.5g) with concentrated nitric and sulphuric acids, as magnesium pyrophosphate.

5.3 Physical techniques

Infrared spectroscopy

Infrared spectra over the region 600-4000 cm^{-1} were recorded on a Pye Unicam SP4-200 microdisc spectrophotometer. The spectra were recorded as KBr discs.

Electronic spectra

Ultra violet and visible spectra in the region 200-900 nm were recorded on a Varian DMS 90 programmable spectrophotometer.

Nuclear magnetic resonance spectroscopy

Nuclear magnetic resonance (n.m.r.) spectra were obtained using a Perkin Elmer R12B 60MHz spectrometer (^1H), Bruker WP80 80MHz Fourrier Transform spectrometer (^1H and ^{13}C) at The Polytechnic of North London. Tetramethylsilane was used as the standard reference.

Mass spectrometry

Routine mass spectra were recorded using a Hitachi-Perkin Elmer RMS4 single focusing instrument.

^{57}Fe Mössbauer spectra

Mössbauer spectra were obtained by kind permission of Dr. M.Campbell at Thames Polytechnic.

Magnetic susceptibility measurements

Room temperature magnetic moments were determined using a Gouy balance with a permanent magnet of 0.36T flux density, at The Polytechnic of North London.

Variable temperature measurements were determined on a Newport Instruments' Gouy balance by kind permission of Durham University. The temperature recording device was calibrated using $CuSO_4.5H_2O$ and the sample tubes calibrated using mercury tetrathiocyanocobaltate(II). Diamagnetic corrections used in the calculations were obtained from values given in Earnshaw[1].

5.4 Reactions

PREPARATION OF THE IRON TRIS CHELATE COMPLEXES DERIVED FROM THE MONOOXIMES OF 1,2-NAPHTHOQUINONE.

Preparation and purification of tris(1,2-naphthoquinone-1-oximato)iron(III).

Iron(III) chloride hexahydrate (3.3g, 11.0 mmol) in water (20 cm^3) was added to a solution of 1,2-naphthoquinone-1-oxime (6.4g, 37.1 mmol) in ethanol (100 cm^3). The mixture was stirred at room temperature for 1 h. Impure tris(1,2-naphthoquinone-1-oximato)iron(III) (5.2g) was filtered off, washed with water (4 x 100 cm^3), ethanol (4 x 50 cm^3) and dried at 40 °C/0.1 mm Hg. The complex was purified by chromatographing on silica gel. Rapid elution with light petrol (b.p. 30-40 °C) followed by chloroform gave unreacted 1,2-naphthoquinone-1-oxime (0.1g, 0.6 mmol) followed by tris(1,2-naphthoquinone-1-oximato)iron(III) (4.03g, 64%)(Found: C,62.8; H,3.0; Fe,9.8; N,7.4. Calc. for $C_{30}H_{18}FeN_3O_6$: C,62.9; H,3.1; Fe,9.8; N,7.3%). Ethyl acetate eluted bis(1,2-naphthoquinone-1-oximato)iron(II) (1.0g, 23%)(identified by t.l.c. and i.r.)

Preparation and purification of tris(1,2-naphthoquinone-2-oximato)iron(III).

Iron(III) chloride hexahydrate (3.3g, 11.0 mmol) in water (20 cm^3) was added to a solution of 1,2-naphthoquinone-2-oxime (6.4g, 37.1 mmol) in ethanol (100 cm^3). The mixture was stirred at room temperature for 1 h. Impure tris(1,2-naphthoquinone-2-oximato)iron(III)(5.6g) was filtered off, washed with water (4 x 100 cm^3), ethanol (4 x 50 cm^3) and dried at 40 °C/0.1 mm Hg. The complex was purified by chromatographing on silica gel. Rapid elution with light petrol (b.p. 30-40 °C) followed by chloroform gave unreacted 1,2-naphthoquinone-2-oxime (0.15g, 0.9 mmol) followed by tris(1,2-naphthoquinone-2-oximato)iron(III) (3.52g, 56%)(Found: C, 63.0; H,3.1; Fe,9.7; N,7.2. Calc. for $C_{30}H_{18}FeN_3O_6$: C,62.9; H,3.1; Fe,9.8; N,7.3%). Ethyl acetate eluted bis(1,2-naphthoquinone-2-oximato)iron(II) (1.6g, 37%)(identified by t.l.c. and i.r.).

INTERACTION OF THE IRON TRIS CHELATE COMPLEXES DERIVED FROM THE MONOOXIMES OF 1.2-NAPHTHOQUINONE WITH TRIPHENYLPHOSPHINE.

Preliminary experiments

A number of preliminary experiments were carried out to decide which reaction conditions would be employed.

Triphenylphosphine was added to a stirred solution of the iron complex in acetone. The reactions were monitored by t.l.c. After a selected time period the solvent was removed either by evaporation under nitrogen or reduced pressure. The solid remaining was stirred in light petrol (b.p. 30-40 °C)(3 x 200 cm^3) and the resulting mixture filtered. The residue was dried at 30 °C/0.1 mm Hg, weighed and examined by t.l.c. Removal of the light petrol at 40 °C/0.3 mm Hg gave a solid whose weight was recorded. These experiments are outlined in Table 5.1.

When 1:1 experiments were carried out a considerable amount of decomposition of the iron complex formed occurred. There was little difference between 1:3 and 1:5 reactions, as long as the reactions were carried out in the shortest possible time. Thus, all further reactions were carried out in a 1:3 mole ratio of complex to triphenylphosphine.

Table 5.1 **Preliminary experiments of the interaction of $Fe(1\text{-}nqo)_3$ and $Fe(2\text{-}nqo)_3$ with Ph_3P at room temperature.**

Iron complex (1 mol equiv)	Wt./g	Ph_3P Wt./g	mol equiv.	Reaction conditions Solvent	Time	Pet. ether extract Wt./g	Residue Wt./g
$Fe(2\text{-}nqo)_3$	2.79	1.33	1.0	acetone[a]	20h	0.31	3.76
$Fe(2\text{-}nqo)_3$	2.98	4.20	3.1	acetone[b]	45min	3.27	3.90
$Fe(2\text{-}nqo)_3$	3.00	4.20	3.0	acetone[a]	30min	2.96	4.24
$Fe(2\text{-}nqo)_3$	2.85	6.53	5.0	acetone[a]	20min	5.40	3.97
$Fe(1\text{-}nqo)_3$	2.83	1.33	1.0	acetone[a]	7 days	0.41	3.74
$Fe(1\text{-}nqo)_3$	2.84	4.01	3.1	acetone[a]	20h	2.38	4.47
$Fe(1\text{-}nqo)_3$	2.88	4.07	3.1	acetone[a]	5h	2.90	4.04

[a] acetone removed at 25 °C/0.3 mm Hg

[b] acetone removed by evaporation under nitrogen

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with triphenylphosphine.

Triphenylphosphine (8.40 g, 32.1 mmol) was added to a stirred solution of tris(1,2-naphthoquinone-1-oximato)iron(III) (6.0 g, 10.5 mmol) in acetone (200 cm^3). The mixture was stirred for 5 h at room temperature and the the solvent removed at 30 °C/0.3 mm Hg to leave a dark green solid 1A (14.4 g). 13.4 g of this solid was stirred in light petrol (b.p. 30-40 °C) (3 x 200 cm^3) and the resulting mixture filtered to give a dark green solid 1B (7.57 g)(Found: Fe,7.15; P,3.6%). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a pale yellow solid 1C (5.73 g).

In another experiment triphenylphosphine (4.22 g, 16.1 mmol) was interacted with tris(1,2-naphthoquinone-1-oximato)iron(III) (3.00 g, 5.25 mmol) under the same conditions as those used for the foregoing experiment. After stirring with light petrol (b.p. 30-40 °C) (3 x 100 cm^3), the mixture was filtered to give a green solid 1B' (4.15 g)(Found: Fe,7.1; P,3.5%). This solid was shown by i.r ahd t.l.c. to contain the same components as solid 1B . Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a pale yellow solid 1C' (3.05 g), shown by i.r. and t.l.c. to contain the same components as solid 1C.

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with triphenylphosphine.

Triphenylphosphine (8.40 g, 32.1 mmol) was added to a stirred solution of tris(1,2-naphthoquinone-1-oximato)iron(III) (6.0 g, 10.5 mmol) in acetone (200 cm^3). The mixture was stirred for 5 h at room temperature and the the solvent removed at 30 °C/0.3 mm Hg to leave a dark green solid 1A (14.4 g). 13.4 g of this solid was stirred in light petrol (b.p. 30-40 °C) (3 x 200 cm^3) and the resulting mixture filtered to give a dark green solid 1B (7.57 g)(Found: Fe,7.15; P,3.6%). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a pale yellow solid 1C (5.73 g).

In another experiment triphenylphosphine (4.22 g, 16.1 mmol) was interacted with tris(1,2-naphthoquinone-1-oximato)iron(III) (3.00 g, 5.25 mmol) under the same conditions as those used for the foregoing experiment. After stirring with light petrol (b.p. 30-40 °C) (3 x 100 cm^3), the mixture was filtered to give a green solid 1B' (4.15 g)(Found: Fe,7.1; P,3.5%). This solid was shown by i.r ahd t.l.c. to contain the same components as solid 1B . Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a pale yellow solid 1C' (3.05 g), shown by i.r. and t.l.c. to contain the same components as solid 1C.

Chromatographic behaviour of solid 1B.

A portion of solid 1B (4.5g) was dissolved in acetone (40 cm^3) and silica (12.0g) was added with stirring. The solvent was removed by passing nitrogen over the solution and the impregnated silica was placed on a 15 x 4 cm silica chromatography column and eluted as shown in Table 5.2.

Interaction of solid 1B with pyridine.

A portion of solid 1B (1.0g) was stirred in pyridine (10 cm^3) at ambient temperature for 48h, to give 1D. Silica (8.0g) was stirred in and the solvent removed at 50 ^{o}C/0.3 mm Hg. The impregnated silica was then placed on a 26 x 4 cm silica chromatography column and eluted as shown in Table 5.3.

Chromatographic behaviour of solid 1C.

A portion of solid 1C (3.0g) was dissolved in acetone (25 cm^3) and silica (8.0g) was added with stirring. The solvent was then removed by passing nitrogen over the solution and the impregnated silica was placed on a 15 x 4 cm silica chromatography column and eluted as shown in Table 5.4.

Table 5.2 The chromatographic separation of solid 1B

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)	$1B_1$/0.24/colourless	Ph_3P	T.l.c. and i.r.
	$1B_2$/0.0112/yellow	1-nitroso-2-naphthol	T.l.c.
Toluene	$1B_3$/0.688/brown	$Fe(1\text{-}nqo)_3$	T.l.c.
		6-hydroxy-dibenzo-[i,mn]-acridine-8-one	T.l.c.
Toluene/ethyl acetate (1:1)	$1B_4$/0.084/green	multicomponent mixture	
	$1B_5$/1.175/green	green solid, Found: C,69.4; H,4.0; Fe,6.7; N,4.9; P,3.7%	
Ethyl acetate	$1B_6$/1.295/green	Ph_3P	T.l.c.
		$Fe(1\text{-}nqo)_3$	T.l.c.
Methanol	$1B_7$/0.264/brown-green	1-amino-2-naphthol	T.l.c. and i.r.
		$Fe(1\text{-}nqo)_2$ (minor)	T.l.c.
Methanol/HCl and neutralisation with $NaHCO_3$	$1B_8$/0.722/green	$Fe(1\text{-}nqo)_2$	T.l.c. and i.r

Table 5.2 cont.

Interaction of solid $1B_5$ with methyl iodide.

A portion of solid $1B_5$ (0.35g) was refluxed in methyl iodide (10 cm^3) for 6h. The resulting mixture was filtered hot to give a green solid (0.068g)(mainly bis(1,2-naphthoquinone-1-oximato)iron(II) by t.l.c.) and a green/brown filtrate. The filtrate was cooled and diethyl ether (100 cm^3) added. This solution was left to stand for 5 min. and filtered to give a pale green solid (0.356g) and a brown filtrate. T.l.c. examination of the solid showed it to be a complex mixture containing triphenylmethylphosphonium iodide.

Interaction of solid $1B_5$ with hydrogen sulphide.

Hydrogen sulphide was bubbled through a suspension of solid $1B_5$ (0.8g) in methanol (50 cm^3) for 9 h. The saturated solution was then left stirring for a further 16 h and filtered to give a small amount of bis(1,2-naphthoquinone-1-oximato)iron(II) (0.053g). T.l.c. examination of the filtrate showed it to contain unreacted $1B_5$ and small amounts of 1-amino-2-naphthol and triphenylphosphine oxide. The experiment was repeated in toluene with the same result.

Table 5.3 The chromatographic sepatation of solid 1D.

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 ^{o}C)	$1D_1$ /0.042/off-white	Ph_3P	T.l.c and i.r.
	$1D_2$ /0.014/yellow	1-nitro-2-naphthol	
Light petrol/ Toluene (3:1)	$1D_3$ /0.049/pink	1-phenylamino-2-naphthol and at least 3 other unidentified substances	T.l.c.
Toluene	$1D_4$ /0.019/pink	1-phenylamino-2-naphthol, 1-nitroso-2-naphthol, 6-hydroxy-dibenzo-[i,mn]-acridine-8-one and at least 2 other unidentified substances	T.l.c.
Toluene/ethyl acetate (3:1)	$1D_5$ /0.012/pink	1-phenylamino-2-naphthol (minor) 1-nitroso-2-naphthol, 6-hydroxy-dibenzo-[i,mn]-acridine-8-one and one other unidentified substance	T.l.c.
Toluene/ethyl acetate (1:1)	$1D_6$ /0.302/green	$Fe(1\text{-}nqo)_2 \cdot 2py$	T.l.c. and i.r.

Table 5.3. (continued)

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Ethyl acetate	$1D_7$ /0.034/green	$Fe(1\text{-}nqo)_2 \cdot 2py$	T.l.c.
	$1D_8$ /0.329/off-white	Ph_3PO	T.l.c. and I.r.
	$1D_9$ /0.016/yellow	Ph_3PO and 1 other minor unidentified substance	T.l.c.
Methanol	$1D_{10}$ /0.094/yellow	1-amino-2-naphthol	T.l.c. and i.r.
Methanol/HCl and neutralisation with $NaHCO_3$	$1D_{11}$ /0.02/green	$Fe(1\text{-}nqo)_2$	

Table 5.4 Chromatographic separation of solid 1C.

Eluting solvent	Code/weight (g)/colour of meterial isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)	$1C_1$/2.45/off-white	Ph_3P	T.l.c. and i.r.
	$1C_2$/0.062/yellow	1-nitro-2-naphthol	T.l.c. and i.r.
Toluene	$1C_3$/0.0212/pink	1-phenylamino-2-naphthol and 1 other unidentified substance	T.l.c.
Toluene/ethyl acetate (3:1)	$1C_4$/0.0226/pink	6-hydroxy-dibenzo-[i,mn]-acridine-8-one	T.l.c.
	$1C_5$/0.0212/pink	6-hydroxy-dibenzo-[i,mn]-acridine-8-one and 1 other unidentified substance	T.l.c.
Ethyl acetate	$1C_6$/0.425/white	Ph_3PO	T.l.c. and i.r.

Interaction of solid 1B with triphenylphosphine.

Triphenylphosphine (1.0g, 3.8 mmol) was added to a stirred solution of solid 1B (1.0g) in acetone (50 cm^3). The mixture was stirred for 20 h at ambient temperature and then the solvent was removed at 30 °C/0.3 mm Hg to leave a green solid, 1E (2.0g). Extraction of solid 1E with light petrol (b.p. 30-40 °C)(4 x 100 cm^3) gave a green solid, 1F (1.08g). Evaporation of the light petrol at 40 °C/0.3 mm Hg gave an off-white solid, 1G (0.91g). Solids 1F and 1G were placed on silica (8.0g for each). The impregnated silica was placed on 15 x 4 cm silica chromatography columns and eluted as shown in Tables 5.5 and 5.6.

Interaction of solid 1B with methyl iodide.

A portion of solid 1B (0.5g) was refluxed in methyl iodide (10 cm^3) for 4 h. The resulting mixture was filtered hot to give a green solid (0.301g)(mainly bis(1,2-naphthoquinone-1-oximato)iron(II) by t.l.c.) and a brown filtrate. The filtrate was cooled and diethyl ether (100 cm^3) added. The solution was left to stand for 5 min. and filtered to give a pale green solid (0.282g) and a brown filtrate. T.l.c. examination of the solid showed it to be a complex mixture containing triphenylmethylphosphonium iodide, unreacted solid 1B and a trace of triphenylphosphine oxide.

Table 5.5 The chromatographic separation of solid 1F.

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)	$1F_1$/0.0076/yellow	1-nitro-2-naphthol	T.l.c.
Toluene	$1F_2$/0.0312/pink	6-hydroxy-dibenzo-[i,mn]-acridine-8-one	T.l.c. and i.r.
Toluene/ethyl acetate (1:1)	$1F_3$/0.096/green	Fe(1-nqo)$_2$(Ph$_3$P)$_2$ ahd 1 other (minor) unidentified substance	T.l.c.
	$1F_4$/0.288/green	Fe(1-nqo)$_2$(Ph$_3$P)$_2$	i.r. and elemental analysis[a]
Ethyl acetate	$1F_5$/0.1772/off-white	Ph_3PO	T.l.c. and i.r
Methanol	$1F_6$/0.136/yellow	1-amino-2-naphthol	T.l.c., i.r. and elemental analysis[b]
Methanol/HCl and neutralisation with $NaHCO_3$	$1F_7$/0.340/green	Fe(1-nqo)$_2$	

[a] Found: C,73.1; H,4.68; Fe,6.1; N,3.05; p,6.76. $C_{56}H_{42}FeN_2O_4P_2$ requires C,72.7, H,4.5; Fe,6.1 N,3.03; P,6.7%

[b] Found: C,74.8; H,5.92; N,8.7. Calc. for $C_{10}H_9NO$: C,75.5; H,5.7; N,8.8%

Table 5.6 The chromatographic separation of solid 1G

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of Characterisation
Light petrol (b.p. 30-40 °C)	$1G_1$ /0.78/white	Ph_3P	T.l.c. and i.r.
	$1G_2$ /0.009/yellow	1-nitro-2-naphthol	T.l.c.
Toluene	$1G_3$ /0.011/yellow	1-phenylamino-2-naphthol, 6-hydroxy-dibenzo-[i,mn]-acridine-8-one and 1 other unidentified substance	T.l.c.
Ethyl acetate	$1G_4$ /0.154/white	Ph_3PO	T.l.c. and i.r.

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with triphenylphosphine.

Triphenylphosphine (8.46 g, 32.3 mmol) was added to a stirred solution of tris(1,2-naphthoquinone-2-oximato)iron(III) (6.02 g, 10.5 mmol) in acetone (200 cm^3). The mixture was stirred for 30 min. at room tempetature and then the solvent was removed at 30 °C/ 0.3 mm Hg to leave a dark green solid 2A (14.14 g). 13.48 g of solid 2A was stirred with light petrol (b.p. 30-40 °C)(3 x 200 cm^3) and filtered to give a dark green solid 2B (7.19 g)(Found: Fe,7.0; P,3.6%). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave an off-white solid 2C (5.57 g).

In another experiment triphenylphosphine (4.10 g, 15.6 mmol) was interacted with tris(1,2-naphthoquinone-2-oximato)iron(III) (2,89 g, 5.05 mmol) under the same conditions as those used for the foregoing experiment. After stirring with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) the mixture was filtered to give a green solid 2B' (3.95 g) (Found: Fe,7.01; P,4.0%), shown by i.r. and t.l.c. to contain the same components as solid 2B . Evaporation of the filtrate at 40 °C/0.3 mm Hg gave an off-white solid 2C' (3.0 g), shown by i.r. and t.l.c. to contain the same components as solid 2C.

Chromatographic behaviour of solid 2B.

A portion of solid 2B (4.5g) was dissolved in acetone (50 cm^3) and silica (15g) added with stirring. The solvent was then removed by passing nitrogen over the solution and the impregnated silica was placed on a 13 x 4 cm silica chromatography column and eluted as shown in Table 5.7.

Interaction of solid 2B with pyridine.

A portion of solid 2B (1.0g) was stirred in pyridine (10 cm^3) for 48 h. to give 2D in solution. Silica was then added with stirring and the solvent removed at 50 °C/0.3 mm Hg. The impregnated silica was placed on a 26 x 4 cm silica chromatography column and eluted as shown in Table 5.8.

Decomposition of solid 2B' in diethyl ether.

A portion of solid 2B' (3.25g) was stirred in diethyl ether (200 cm^3) for 4 weeks at ambient temperature. Removal of the solvent at 30 °C/0.3 mm Hg gave a green/black solid. This solid was stirred with ethyl acetate (3 x 100 cm^3) and filtered to give bis(1,2-naphthoquinone-2-oximato)iron(II) (identified by i.r. and t.l.c.). Evaporation of the filtrate at 50 °C/0.3 mm Hg gave a purple solid, $2B'_1$. T.l.c. examination of this solid showed it to be a complex mixture. The results of this examination are given in Table 5.9.

<u>Table 5.7</u> <u>The chromatographic separation of solid 2B.</u>

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Methol of characterisation
Light petrol (b.p. 30-40 ^{o}C)	$2B_1$/0.0229/yellow	2-nitro-1-naphthol	T.l.c. and i.r.
	$2B_2$/0.0687/purple	dibenzo[b,i]phenazine-5,12-diol	T.l.c. and i.r.
	$2B_3$/0.812/green	green solid, Found: C,69.6; H, 4.13; Fe,6.7; N,5.09; P,3.8%	
	$2B_4$/1.114/green	major component same as and Fe(2-nqo)$_2$	T.l.c.
	$2B_5$/0.0708/green	minor component same as Fe(2-nqo)$_2$ (major) and trace of 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine	T.l.c.
Ethyl acetate	$2B_6$/0.321/purple	2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine	T.l.c.
	$2B_7$/0.8504/yellow	Ph_3PO	T.l.c. and i.r.
Methanol/HCl and neutralisation with $NaHCO_3$	$2B_8$/1.164/green	Fe(2-nqo)$_2$	T.l.c. and i.r.

Table 5.8 The chromatographic separation of solid 2D.

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)	$2D_1$/0.0053/yellow	2-nitro-1-naphthol	T.l.c.
Toluene	$2D_2$/0.0046/pink	dibenzo[b,i] phenazine-5,12-diol and 1 other (major) unidentified substance	T.l.c.
	$2D_3$/0.0223/purple	dibenzo[b,i] phenazine-5,12-diol	T.l.c. and i.r.
	$2D_4$/0.0183/blue	dibenzo[b,i] phenazine-5,12-diol and 1 other (major) unidentified substance	T.l.c.
	$2D_5$/0.0075/dk.green	dibenzo[b,i] phenazine-5,12-diol and $Fe(2\text{-}nqo)_2 \cdot 2py$	T.l.c.
	$2D_6$/0.445/green	$Fe(2\text{-}nqo)_2 \cdot 2py$	T.l.c. and i.r.
Toluene/ethyl acetate (1:1)	$2D_7$/0.092/brown	$Fe(2\text{-}nqo)_2 \cdot 2py$ and at least 4 other minor substances	T.l.c.
	$2D_8$/0.0777/purple	$Fe(2\text{-}nqo)_2 \cdot 2py$ 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine (major product)	T.l.c.

Table 5.8 (continued)

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Ethyl acetate	$2D_9$ /0.0508/purple	2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine	T.l.c. and i.r.
	$2D_{10}$/0.2808/purple	2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine (minor) and Ph_3PO [a]	T.l.c.
Methanol	$2D_{11}$/0.0061/brown	2 unidentified substances	
Methanol/pyridine	$2D_{12}$/0.153/green	$Fe(2\text{-nqo})_2 \cdot 2py$	T.l.c. and i.r.

[a] Recrystallisation of $2D_{10}$ from light petrol (b.p. 30-40 °C) gave Ph_3PO (0.28 g) (identified by t.l.c. and i.r.)

Table 5.9

a) Using chloroform for t.l.c. examination.

Material	R_f value and appearance of spots on t.l.c. (silica plates)
2B'/diethyl ether	0.64(int.)purple, 0.56(int.)blue, 0.53(int.)purple, 0.23(med.)[a], 0.16(med.)yellow, 0.08(int.)[a], 0.0(weak)green, 0.0(int.) purple, 0.71(med)yellow.
Ph_3P	0.83[a]
Ph_3PO	0.08[a]
2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine	0.27 purple
dibenzo[b,i] phenazine-5,12-diol	0.53 purple
2-nitro-1-naphthol	0.71 yellow

b) Using solvent B*for t.l.c. examination

Material	R_f value and appearance of spots on t.l.c. (silica plates)
2B'/diethyl ether	0.79(int.)purple, 0.74(int.)red, 0.69(int.)blue, 0.55(int.)[a], 0.44(weak)green, 0.38(med.) yellow, 0.0(v.weak)green, 0.0 (v.int.)purple, 0.82(med)yellow.
Ph_3P	0.83[a]
Ph_3PO	0.55[a]

Table 5.9 (continued)

Material	R_f value and appearance of spots on t.l.c.
2-amino-N(4)-(1-hydroxy-2-naphthyl-1,4-naphthoquinone monoimine	0.84 purple
dibenzo[b,i] phenazine-5,12-diol	0.78 purple
2-nitro-1-naphthol	0.82 yellow

[a] spot made visible after exposure of t.l.c. plate to iodine vapour

* solvent system B = toluene:ethanol: ethylacetate, 9:2:1

Chromatographic behaviour of solid 2C.

A portion of solid 2C (3.0g) was dissolved in acetone (25 cm^3) and silica (8.0g) was added with stirring. The solvent was removed by passing nitrogen over the solution and the impregnated silica was placed on a 15 x 4 cm silica chromatography column and eluted as shown in Table 5.10.

Interaction of solid 2B with methyl iodide.

A portion of solid 2B (0.5g) was refluxed in methyl iodide (10 cm^3) for 4 h. The resulting mixture was filtered hot to give a green solid and a purple filtrate. T.l.c. examination of the solid showed it to contain bis(1,2-naphthoquinone-2-oximato)iron(II) and at least 5 other substances. T.l.c. examination of the filtrate showed it to contain at least 7 substances, at least two of which were also present in the green solid, and one that was identified as triphenylphosphine oxide. There was no indication of triphenylmethylphosphonium iodide being present.

Interaction of solid 2B with triphenylphosphine.

Triphenylphosphine (0.5g, 1.91 mmol) was added to a stirred solution of solid 2B (0.5g) in acetone (50 cm^3). The mixture was stirred for 20 h. at ambient temperature and then examined by t.l.c. This showed the solution to contain bis(1,2-naphthoquinone-2-oximato)iron(II),

Table 5.10 The chromatogtaphic separation of solid 2C.

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 ^{o}C)	$2C_1$ /2.70/colourless	Ph_3P	T.l.c. and i.r.
	$2C_2$ /0.053/yellow	2-nitro-1-naphthol	T.l.c. and i.r.
Toluene	$2C_3$ /0.027/purple	dibenzo[b,i] phenazine-5,12-diol	T.l.c. and i.r.
Ethyl acetate	$2C_4$ /0.20/colourless	Ph_3PO	T.l.c. and i.r.

triphenylphosphine, unreacted 2B and various organic products. The solvent was removed at 30 °C/0.3 mm Hg and the solid obtained extracted with light petrol (b.p. 30-40 °C)(4 x 100 cm^3) to give an off-white solid. Column chromatography of the solid gave triphenylphosphine (0.47g).

Interaction of solid $2B_3$ with hydrogen sulphide.

Hydrogen sulphide was bubbled through a suspension of solid $2B_3$ (0.9g) in methanol (30 cm^3) for 6h. The resulting mixture was filtered to give a black solid (0.568g) and a brown filtrate. The solvent was removed at 40 °C/0.3 mm Hg to leave a purple/brown solid. This solid was dissolved in toluene (100 cm^3) and extracted with 10% sodium bicarbonate solution (5 x 50 cm^3). Extraction of the sodium bicarbonate solutions with toluene (5 x 60 cm^3) gave a purple solution. Removal of the solvent at 40 °C/0.3 mm Hg gave dibenzo[b,i]phenazine-5,12-diol (0.081g)(identified by i.r. and t.l.c.). Neutralisation of the sodium bicarbonate solution with aqueous hydrochloric acid (15%) and extraction with diethyl ether gave no further products. Removal of the solvent at 40 °C/0.3 mm Hg from the original toluene solution gave a purple/brown solid (0.61g)(solid 2E). Solid 2E was stirred in acetone (20 cm^3) and silica (8.0g) added. The solvent was removed by passing nitrogen over the solution and the impregnated silica placed on a 20 x 4 cm silica chromatography column and eluted as shown in Table 5.11.

Table 5.11 The chromatographic separation of solid 2E.

Eluting solvent	Code/weight (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)	$2E_1$ /0.0092/yellow	2-nitro-1-naphthol	T.l.c.
	$2E_2$ /0.0962/yellow	Sulphur	T.l.c. and i.r.
Light petrol/ Toluene (1:1)	$2E_3$ /0.0087/purple	dibenzo[b,i]phenazine-5,12-diol and at least 2 other unidentified substances	T.l.c.
Toluene	$2E_4$ /0.0101/purple	dibenzo[b,i]phenazine-5,12-diol	T.l.c. and i.r.
Toluene/ethyl acetate(3:1)	$2E_5$ /0.0148/red	dibenzo[b,i]phenazine-5,12-diol and 2-nitroso-1-naphthol	T.l.c.
Toluene/ethyl acetate (1:1)	$2E_6$ /0.0174/orange	2-nitroso-1-naphthol	T.l.c. and i.r.
	$2E_7$ /0.1361/purple	at least 3 unidentified substances	
Ethyl acetate	$2E_8$ /0.0951/brown	Ph_3PO (major component) and 1 other unidentified substance	T.l.c.
	$2E_9$ /0.2049/yellow	Ph_3PO	T.l.c. and i.r.
Methanol	$2E_{10}$/0.0147/brown	at least 1 unidentified substance	

Interaction of bis(1,2-naphthoquinone-1-oximato)iron(II) with triphenylphosphine and 1,2-naphthoquinone-1-oxime.

1,2-Naphthoquinone-1-oxime (0.22g, 1.3 mmol) was added to a stirred solution of bis(1,2-naphthoquinone-1-oximato)iron(II) (0.5 g, 1.25 mmol) in acetone (50 cm^3) under nitrogen. The mixture was stirred at room temperature for 30 min. and then triphenylphosphine (0.34 g, 1.3 mmol) was added and the reaction mixture stirred for a further 24 h. The solvent was removed at 30 °C/0.3 mm Hg and the residue examined by t.l.c. The results are given in Table 5.12.

Similar results were obtained when the quinone monooxime was first mixed with triphenylphosphine and the iron complex added at a later stage.

Interaction of bis(1,2-naphthoquinone-2-oximato)iron(II) with triphenylphosphine and 1,2-naphthoquinone-2-oxime.

1,2-Naphthoquinone-2-oxime (0.23g, 1.33 mmol) was added to a stirred solution of bis(1,2-naphthoquinone-2-oximato)iron(II) (0.25 g, 1.3 mmol) in acetone (50 cm^3) under nitrogen. The mixture was stirred at room temperature for 30 min. and then triphenylphosphine (0.36 g, 1.37 mmol) was added and the reaction mixture stirred for another 24 h. The solvent was removed at 30 °C/0.3 mm Hg and the residue examined by t.l.c. The results are given in Table 5.12.

Similar results were obtained when the quinone monooxime was first mixed with triphenylphosphine and the iron complex added at a later stage.

Table 5.12

a) Using chloroform for t.l.c. examination.

Material	R_f value and appearance of spots on t.l.c. (on silica plates unless otherwise indicated).
Fe(1-nqo)$_2$/Ph$_3$P/ 1-nqoH, reaction mixture	0.51(v.weak)[a], 0.25(weak)pink, 0.16(weak)pink[b], 0.08(med.)[a], 0.0(v.int.)green, 0.93(v.int., cellulose plate used)green, 0.00 (med.,cellulose plate used)green.
Ph$_3$P	0.83[a]
Ph$_3$PO	0.08[a]
1-amino-2-naphthol	0.03[a]
1-phenylamino-2-naphthol	0.51[a]
6-hydroxy-dibenzo-[i,mn]-acridine-8-one	0.16 red[b]
1B$_5$	0.0 green, 0.95 green (on cellulose plate)
Fe(1-nqo)$_2$	0.00 green, 0.00 green (on cellulose plate)
Fe(2-nqo)$_2$/Ph$_3$P/ 2-nqoH	0.82(med)[a], 0.34(v.int.)purple, 0.12(v.int.)red/purple, 0.09 (med.)[a], 0.0(v.int)green, 0.0 (v.int.,cellulose plate used)
Ph$_3$P	0.83[a]
Ph$_3$PO	0.08[a]
Fe(2-nqo)$_2$	0.0 green, 0.0 green (on cellulose plate)
2B$_3$	0.0 green, 0.83 green(on cellulose plate)

Table 5.12 (continued)

b) Using solvent system B* for t.l.c. examination

Material	R_f value and appearance of spots on t.l.c. (silica plates unless otherwise indicated).
Fe(1-nqo)$_2$/Ph$_3$P/ 1-nqoH	0.71(v.weak)[a], 0.68(weak)pink, 0.55(med.)[a], 0.05(weak)pink, 0.0(v.int.)green, 0.92(v.int., cellulose plate used)green, 0.0 (int., cellulose plate used)green.
Ph$_3$P	0.88[a]
Ph$_3$PO	0.55[a]
1-amino-2-naphthol	0.29[a]
1-phenylamino-2-naphthol	0.70[a]
6-hydroxy-dibenzo-[i,mn]-acridine-8-one	0.62 red[b]
1B$_5$	0.0 green, 0.92 green(on cellulose plate)
Fe(1-nqo)$_2$	0.0 green, 0.0 green (on cellulose plate)
Fe(2-nqo)$_2$/Ph$_3$P/ 2-nqoH	0.88(med.)[a], 0.75(v.int.)purple, 0.60(v.weak)purple, 0.55(med.)[a], 0.05(int.)purple, 0.0(v.int.)green
Ph$_3$P	0.88[a]
Ph$_3$PO	0.55[a]
Fe(2-nqo)$_2$	0.0 green

Table 5.12(continued)

Material	R_f value and appearance of spots on t.l.c.
$2B_3$	0.78 green

[a] spot made visible after exposure t.l.c. plate to iodine vapour

[b] spot exhibited a pink fluorescence under u.v. light

* solvent system B = toluene : ethanol : ethyl acetate; 9:2:1

Decomposition of tris(1,2-naphthoquinone-2-oximato)iron(III) in acetone.

Tris(1,2-naphthoquinone-2-oximato)iron(III) (2.85 g, 5.0 mmol) was stirred in acetone for 2 weeks. T.l.c. examination of the resulting mixture showed it to contain unreacted tris-chelate, Fe(2-nqo)$_2$, 2-nitroso-1-naphthol and traces of other compounds.

Decomposition of tris(1,2-naphthoquinone-1-oximato) iron(III) in acetone.

Tris(1,2-naphthoquinone-1-oximato)iron(III) (2,86 g, 5.0 mmol) was stirred in acetone for 2 weeks. T.l.c. examination of the resulting mixture showed it to contain unreacted tris-chelate, Fe(1-nqo)$_2$, 1-nitroso-2-naphthol and traces of other compounds.

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with triphenylphosphine oxide.

Triphenylphosphine oxide (7.0 g, 25 mmol) was added to a stirred soution of tris(1,2-naphthoquinone-2-oximato)iron(III) (2.85 g, 5 mmol) in acetone. The mixture was stirred for 7 days and then silica (8.5 g) was added and the solvent removed by passing nitrogen over the solution. The impregnated silica was placed on a 25 x 4 cm silica chromatography column and eluted with solvents of increasing polarity. Triphenylphosphine oxide (6.98g, 99.7%) and Fe(2-nqo)$_3$ (1.98g, 69.3%) were recovered together with other products obtained from the

Decomposition of tris(1,2-naphthoquinone-2-oximato)iron(III) in acetone.

Tris(1,2-naphthoquinone-2-oximato)iron(III) (2.85 g, 5.0 mmol) was stirred in acetone for 2 weeks. T.l.c. examination of the resulting mixture showed it to contain unreacted tris-chelate, Fe(2-nqo)$_2$, 2-nitroso-1-naphthol and traces of other compounds.

Decomposition of tris(1,2-naphthoquinone-1-oximato) iron(III) in acetone.

Tris(1,2-naphthoquinone-1-oximato)iron(III) (2,86 g, 5.0 mmol) was stirred in acetone for 2 weeks. T.l.c. examination of the resulting mixture showed it to contain unreacted tris-chelate, Fe(1-nqo)$_2$, 1-nitroso-2-naphthol and traces of other compounds.

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with triphenylphosphine oxide.

Triphenylphosphine oxide (7.0 g, 25 mmol) was added to a stirred soution of tris(1,2-naphthoquinone-2-oximato)iron(III) (2.85 g, 5 mmol) in acetone. The mixture was stirred for 7 days and then silica (8.5 g) was added and the solvent removed by passing nitrogen over the solution. The impregnated silica was placed on a 25 x 4 cm silica chromatography column and eluted with solvents of increasing polarity. Triphenylphosphine oxide (6.98g, 99.7%) and Fe(2-nqo)$_3$ (1.98g, 69.3%) were recovered together with other products obtained from the decomposition of the tris-chelate (mainly Fe(2-nqo)$_2$ and 2-nqoH by t.l.c.).

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with triphenylphosphine oxide.

Triphenylphosphine oxide (6.9g, 25 mmol) was added to a stirred solution of tris(1,2-naphthoquinone-1-oximato)-iron(III) (2.86g, 5 mmol) in acetone (100 cm^3). The mixture was stirred for 7 days at ambient temperature and then silica (8.0g) was added and the solvent removed by passing nitrogen over the solution. The impregnated silica was placed on a 26 x 4 cm silica chromatography column and eluted with solvents of increasing polarity. Triphenylphosphine oxide (6.85g, 99.3%) and Fe(1-nqo)$_3$ (2.01g, 70.5%) were recovered together with other products obtained from the decomposition of the tris-chelate (mainly Fe(1-nqo)$_2$ and 1-nqoH by t.l.c.).

Interaction of bis(1,2-naphthoquinone-1-oximato)iron(II) with triphenylphosphine.

Triphenylphosphine (3.30 g, 12.6 mmol) was added to a stirred solution of bis(1,2-naphthoquinone-1-oximato)iron(II) (1.0 g, 2.5 mmol) in acetone (50 cm^3). The mixture was stirred for 10 days at room temperature and then the solvent was removed at 30 °C/0.3 mm Hg. The residue was extracted with light petroleum (b.p. 30-40 °C) (4 x 100 cm^3) to give unreacted triphenylphosphine (3.24 g, 12.4 mmol). T.l.c. examination of the green solid remaining showed it to be unreacted bis(1,2-naphthoquinone-1-oximato)iron(II) with a trace of triphenylphosphine.

Interaction of bis(1,2-naphthoquinone-1-oximato)dipyridine-iron(II) with triphenylphosphine.

Triphenylphosphine (3.30 g, 12,6 mmol) was added to a stirred solution of bis(1,2-naphthoquinone-1-oximato)dipyridine iron(II) (1.40 g, 2.5 mmol) in acetone (50 cm^3). The mixture was stirred for 14 days at room temperature and then the solvent was removed at 30 °C/0.3 mm Hg. The residue was extracted with light petrol(b.p. 30-40 °C) (4 x 100 cm^3) to give unreacted triphenylphosphine (3.21 g, 12.3 mmol). T.l.c. examination of the green solid remaining showed it to be unreacted bis(1,2-naphthoquinone-1-oximato) dipyridine iron(II) with a trace of triphenylphosphine.

Interaction of iron pentacarbonyl with 1,2-naphthoquinone-1-oxime and aniline.

1,2-Naphthoquinone-1-oxime (5.3g, 31 mmol) was added to a stirred solution of iron pentacarbonyl (2.0 g, 10 mmol) and aniline (4.6 g, 49 mmol) in tetrahydrofuran (100 cm^3) under nitrogen. The mixture was refluxed for 24 h and then stirred for a further 16 h at room temperature before filtering. Filtration yielded a green solid, 3A (2.7g). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown tar, 3B (8.0g).

Interaction of solid 3A with pyridine.

A portion of solid 3A (2.0 g) was stirred in pyridine (10 cm^3) for 72 h to give solid 3C . Silica (15 g) was stirred in and the solvent was then removed at 50 °C/0.3 mm Hg. The impregnated silica was then placed on a 26 x 4 cm silica chromatography column and eluted as shown in Table 5.13.

Separation of solid 3B.

Solid 3B (8.0 g) was dissolved in acetone (50 cm^3) and silica (15 g) was stirred in. The solvent was then removed by passing nitrogen over the solution and the impregnated silica was placed on a 20 x 4 cm silica chromatography column and eluted as shown in Table 5.14.

Interaction of iron pentacarbonyl with 1,2-naphthoquinone-1-oxime and aniline.

1,2-Naphthoquinone-1-oxime (5.3g, 31 mmol) was added to a stirred solution of iron pentacarbonyl (2.0 g, 10 mmol) and aniline (4.6 g, 49 mmol) in tetrahydrofuran (100 cm^3) under nitrogen. The mixture was refluxed for 24 h and then stirred for a further 16 h at room temperature before filtering. Filtration yielded a green solid, 3A (2.7g). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown tar, 3B (8.0g).

Interaction of solid 3A with pyridine.

A portion of solid 3A (2.0 g) was stirred in pyridine (10 cm^3) for 72 h to give solid 3C . Silica (15 g) was stirred in and the solvent was then removed at 50 °C/0.3 mm Hg. The impregnated silica was then placed on a 26 x 4 cm silica chromatography column and eluted as shown in Table 5.13.

Separation of solid 3B.

Solid 3B (8.0 g) was dissolved in acetone (50 cm^3) and silica (15 g) was stirred in. The solvent was then removed by passing nitrogen over the solution and the impregnated silica was placed on a 20 x 4 cm silica chromatography column and eluted as shown in Table 5.14.

Table 5.13 The chromatographic separation of solid 3C.

Eluting solvent	Code/mass(g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)/ toluene 1:1	$3C_1$/0.3599/red	N(4)phenylimino(N)-2-phenylamino-1,4-naphthoquinone	t.l.c., i.r., m.s., elemental analysis.
Toluene	$3C_2$/0.2375/brown	$3C_1$ and 1,4-diphenyl amino-2-naphthol	t.l.c.
Toluene/ethyl acetate 3:1	$3C_3$/1.0270/green	Fe(1-nqo)$_2$.2py	t.l.c. and i.r.
ethyl acetate	$3C_4$/0.6757/green	bis(4-phenylamino-1-imino-1,2-naphthoquinone)dipyridine-iron(II)	t.l.c. i.r. and elemental analysis.
Methanol/ pyridine 1:1	$3C_5$/0.2400/green	mixture of iron complexes	

Table 5.14 The chromatographic separation of solid 3B.

Eluting solvent	Code/mass(g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)/ toluene 1:1	$3B_1$/0.7517/red	N(4)phenylimino-(N)-2-phenylamino-1,4-naphthoquinone	t.l.c., i.r., m.s., elemental analysis
	$3B_2$/1.0900/red	$3B_1$ (major) and at least 4 other comps. recrystallisation gave $3B_1$ (0.91 g)	t.l.c.
Toluene	$3B_3$/0.3500/orange	N(4)-phenylamino-1,2-naphthoquinone	t.l.c., i.r., m.s., elemental analysis.
	$3B_4$/0.1513/brown	mixture containing phenylaminonaphthol	t.l.c.
	$3B_5$/0.8230/purple	phenoxazine (3.8 in text)	t.l.c., i.r. elemental analysis
methanol/ pyridine 1:1	$3B_6$/1.3200/green	Mixture of iron complexes. Further separation gave $Fe(1\text{-}nqo)_2(py)_2$ (0.86 g) + mixture of iron complexes (0.40g)	t.l.c.

Pyrolysis of bis(4-phenylamino-1-imino-1,2-naphthoquinone)-dipyridine iron(II).

Bis(4-phenylamino-1-imino-1,2-naphthoquinone)dipyridine-iron(II) (1.0g, 1.4 mmol) was pyrolysed at 150 °C/0.3 mm Hg to give bis(4-phenylamino-1-imino-1,2-naphthoquinone)iron(II) (0.79g, 1.4 mmol) (Found: C,69.4; H,3.9; Fe,10.1; N,10.5. $C_{32}H_{22}FeN_4O_2$ requires C,69.8; H,3.9; Fe,10.2; N,10.2%).

Reaction of bis(4-phenylamino-1-imino-1,2-naphthoquinone)-iron(II) with hydrochloric acid.

Bis(4-phenylamino-1-imino-1,2-naphthoquinone)iron(II) (0.2g, 0.36 mmol) was shaken with aqueous hydrochloric acid (15%, 50 cm^3) for 10 min. After neutralisation with sodium bicarbonate, chloroform was added and the mixture shaken for 5 min. The chloroform layer was separated from the aqueous layer, which was then further extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give (N)4-phenylamino-1,2-naphthoquinone (0.16g, 90%)(identified by t.l.c. and i.r.)

Reaction of bis(4-phenylamino-1-imino-1,2-naphthoquinone)-iron(II) with hydrogen sulphide.

Hydrogen sulphide was bubbled through a suspension of bis(4-phenylamino-1-imino-1,2-naphthoquinone)iron(II) (0.2g, 0.36 mmol) in toluene (25 cm^3) for 60 min. Filtration of the solution gave a black iron-containing solid (0.08g). Evaporation of the toluene under reduced pressure gave (N)4-phenylamino-1,2-naphthoquinone (0.11g, 61%)(identified by t.l.c. and i.r.)

Reaction of (N)4-phenylamino-1,2-naphthoquinone with aniline.

(N)4-Phenylamino-1,2-naphthoquinone (0.5g, 2.0 mmol) and aniline (0.94g, 10.0 mmol) were refluxed in tetrahydrofuran (50 cm^3) under nitrogen for 24 h. Silica (10g) was stirred in and the solvent removed at 50 °C/0.3 mm Hg. The impregnated silica was placed on a 10 x 4 cm silica chromatography column. Elution with toluene/light petrol (b.p. 30-40 °C)(1:1) gave (N)4-phenylimino-(N)-2-phenylamino-1,4-naphthoquinone (0.42g, 65%)(Found: C,81.5; H,5.0; N,8.6. Calc. for $C_{22}H_{16}N_2O$: C,81.5; H,4.9; N,8.6%)

Interaction of iron pentacarbonyl with aniline and 1,2-naphthoquinone-2-oxime.

1,2-Naphthoquinone-2-oxime (5.3g, 31 mmol) was added to a stirred solution of iron pentacarbonyl (2.0g, 10 mmol) and aniline (4.6g, 49 mmol) in tetrahydrofuran (100 cm^3) under nitrogen. The mixture was refluxed for 24 h and then stirred for a further 16 h at ambient temperature before filtering. Filtration yielded a green solid, 4A (2.3g). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown tar, 4B (9.8g).

Interaction of solid 4A with pyridine.

A portion of solid 4A (1.8g) was stirred in pyridine (10 cm^3) for 72 h to give 4C in solution. Silica (15g) was stirred in and the solvent removed at 50 °C/0.3 mm Hg. The impregnated silica was placed on a 20 x 4 cm silica chromatography column and eluted as shown in Table 5.15.

Separation of solid 4B.

Solid 4B (9.0g) was dissolved in acetone (50 cm^3) and silica (15g) stirred in. The solvent was removed by passing nitrogen over the solution and the impregnated silica was placed on a 20 x 4 cm silica chromatography column and eluted as shown in Table 5.16.

Pyrolysis of bis(4-phenylamino-2-imino-1,2-naphthoquinone)-dipyridine iron(II).

Bis(4-phenylamino-2-imino-1,2-naphthoquinone)dipyridine-iron(II) (1.0g, 1.4 mmol) was pyrolysed at 150 °C/0.3 mm Hg to give bis(4-phenylamino-2-imino-1,2-naphthoquinone)iron(II) (0.8g, 1.4 mmol)(Found: C,69.3; H,3.8; Fe,10.3; N,9.8. $C_{32}H_{22}FeN_4O_2$ requires: C,69.8; H,4.0; Fe,10.2; N,10.2%).

Reaction of bis(4-phenylamino-2-imino-1,2-naphthoquinone)-iron(II) with hydrochloric acid.

Bis(4-phenylamino-2-imino-1,2-naphthoquinone)iron(II) (0.2g, 0.36 mmol) was shaken with aqueous hydrochloric acid (15%, 50 cm^3) for 10 min. After neutralisation with

Table 5.15 The chromatographic separation of solid 4C

Eluting solvent	Code/mass (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)/ Toluene 1:1	$4C_1$/0.1730/orange	2-nitro-1-naphthol + $4B_1$ + $4B_2$	t.l.c.
Toluene	$4C_2$/0.0490/purple	dibenzo[b,i]phenazine-5,12-diol	t.l.c.
Toluene/ethyl acetate 3:1	$4C_3$/0.0330/brown	multicomponent mixture	
	$4C_4$/1.9200/green	Fe(2-nqo)$_2$.2py	t.l.c., i.r.
Ethyl acetate	$4C_5$/0.2850/green	bis(4-phenylamino-2-imino-1,2-naphthoquinone)dipyridine iron(II)	t.l.c., i.r., elemental analysis
Methanol	$4C_6$/0.0330/green	$4C_5$ + other components	t.l.c.

Table 5.16 The chromatographic separation of solid 4B .

Eluting solvent	Code/mass (g)/colour of material isolated	Nature of material	Method of characterisation
Light petrol (b.p. 30-40 °C)/ Toluene 1:1	$4B_1$ /2.7100/red	(N)4-phenylimino-(N)-2-phenylamino-1,4-naphthoquinone	t.l.c., i.r., m.s., elemental analysis
Toluene	$4B_2$ /1.0480/orange	(N)4-phenylimino-2-amino-1,4-naphtho quinone	t.l.c., i.r., m.s., elemental analysis
	$4B_3$ /0.4000/orange	(N)4-phenylamino-1,2-naphthoquinone	t.l.c.
Toluene/ethyl acetate 3:1	$4B_4$ /0.1183/purple	dibenzo[b,i] phenazine-5,12-diol	t.l.c., i.r.
	$4B_5$ /0.6800/brown	oily mixture	
Methanol/ pyridine 1:1	$4B_6$ /0.7200/green	mixture of iron complexes. Further separation gave, $Fe(2\text{-}nqo)_2.2py$ (0.51 g) + $4C_5$ (0.12g)	t.l.c., i.r.

sodium bicarbonate, chloroform was added and the mixture shaken for 5 min. The chloroform layer was separated from the aqueous layer, which was then further extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give (N)4-phenylimino-2-amino-1,4-naphthoquinone (0.16g, 87%) (identified by t.l.c. and i.r.)

Reaction of bis(4-phenylamino-2-imino-1,2-naphthoquinone)-iron(II) with hydrogen sulphide.

Hydrogen sulphide was bubbled through a suspension of bis(4-phenylamino-2-imino-1,2-naphthoquinone)iron(II) (0.2g, 0.36 mmol) in toluene for 60 min. Filtration of the solution gave a black iron-containing solid (0.07g). Evaporation of the filtrate under reduced pressure gave (N)4-phenylimino-2-amino-1,4-naphthoquinone (0.12g, 67%) (identified by t.l.c. and i.r.).

The interaction of iron pentacarbonyl with 1,2-naphthoquinone-1-oxime.

1,2-Naphthoquinone-1-oxime (5.3g, 31 mmol) was added to a stirred solution of iron pentacarbonyl (2.0g, 10 mmol) in tetrahydrofuran (100 cm^3) under nitrogen. The mixture was refluxed for 24 h and then stirred for a further 16 h at ambient temperature before filtration. Filtration yielded bis(1,2-naphthoquinone-1-oximato)iron(II) (1.76g, 44%)(Found: C,59.9; H,2.9; Fe,14.1; N,6.9. Calc. for $C_{20}H_{12}FeN_2O_4$: C,60.0; H,3.0; Fe,14.0; N,7.0%).

Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown tar, 5A (3.9g).

Separation of solid 5A.

Solid 5A (3.9g) was dissolved in acetone (50 cm^3) and silica (15g) stirred in. The solvent was removed by passing nitrogen over the solution and the impregnated silica was placed on a 20 x 4 cm silica chromatography column and eluted in the order toluene, toluene/ethyl acetate 1:1, ethyl acetate. This gave unreacted 1,2-naphthoquinone-1-oxime (1.3g, 25%) as the main component, with trace amounts of the dioxazine, oxazine and phenazine (3.5-3.7 in text)(identified by t.l.c.).

The interaction of iron pentacarbonyl with 1,2-naphthoquinone-2-oxime.

1,2-Naphthoquinone-2-oxime (5.3g, 31 mmol) was added to a stirred solution of iron pentacarbonyl (2.0g, 10 mmol) in tetrahydrofuran (100 cm^3) under nitrogen. The mixture was refluxed for 24 h and then stirred for a further 16 h at ambient temperature before filtering. Filtration yielded bis(1,2-naphthoquinone-2-oximato)iron(II) (3.64g, 91%)(Found: C,60.2; H,2.7; Fe,13.9; N,6.8. Calc. for $C_{20}H_{12}FeN_2O_4$: C,60.0; H,3.0; Fe,14.0; N,7.0%). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown tar, 6A (1.82g).

Separation of solid 6A.

Solid 6A (1.8g) was dissolved in acetone (50 cm^3) and silica (15g) stirred in. The solvent was removed by passing nitrogen over the solution and the impreganted silica was placed on a 20 x 4 cm silica chromatography column and eluted in the order light petrol (b.p. 30-40 °C)/ toluene 1:1, toluene, toluene/ethyl acetate 1:1, ethyl acetate. This gave unreacted 1,2-naphthoquinone-2-oxime (0.42g, 8.0%) as the major product with a trace amount of 2-nitro-1-naphthol and small amounts of dibenzo[b,i]phenazine-5,12-diol and 2-amino-(N)4-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine.

The interaction of carbon monoxide with selected metal complexes.

Small scale experiments (0.10g of complex) were carried out qualitatively with the following complexes:

$Fe(1\text{-}nqo)_2.2py$
$Fe(2\text{-}nqo)_2.2py$
$Fe(1\text{-}nqo)_2$
$Fe(2\text{-}nqo)_2$
$Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2.2py$
$Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2.2py$
$Co(1\text{-}nqo)_3$
$Fe(1\text{-}nqo)_3$
$Fe(2\text{-}nqo)_3$

Carbon monoxide was bubbled through a solution or suspension of the complex in toluene and then on through a cold trap (-80 °C) and a trap containing baryta water, for 15 h. At the end of this period the solvent was removed by evaporation under nitrogen and the solid remaining examined by t.l.c. Elemental analyses of the complexes previous to reaction and of the reaction products were obtained. The results are summarised in Table 5.17.

The interaction of tris(1.2-naphthoquinone-2-oximato)iron(III) with carbon monoxide.

Carbon monoxide was bubbled through a solution of tris(1,2-naphthoquinone-2-oximato)iron(III) (1.02g, 1.78 mmol) and then on through a cold trap (-80 °C) and a trap containing baryta water for 15 h. Filtration of the reaction mixture gave a black solid which was washed with toluene (2 x 20 cm^3) and methanol (2 x 20 cm^3) to leave green

Table 5.17 The interaction of carbon monoxide with selected metal complexes.

Complex	Results
$Fe(1\text{-}nqo)_2 \cdot 2py$	No reaction
$Fe(2\text{-}nqo)_2 \cdot 2py$	T.l.c. examination showed $Fe(2\text{-}nqo)_2$ to be the main component of the reaction mixture with traces of 5 other compounds (1 green, 2 purple and 2 yellow)
$Fe(1\text{-}nqo)_2$	No reaction
$Fe(2\text{-}nqo)_2$	No reaction
$Fe(4\text{-}PhNH\text{-}1\text{-}imnq)_2 \cdot 2py$	No reaction
$Fe(4\text{-}PhNH\text{-}2\text{-}imnq)_2 \cdot 2py$	No reaction
$Co(1\text{-}nqo)_3$	No reaction
$Fe(1\text{-}nqo)_3$	Some reaction, but t.l.c. examination of reaction mixture showed $Fe(1\text{-}nqo)_3$ to be the main component
$Fe(2\text{-}nqo)_3$	T.l.c. examination showed a mixture of products, one of which (green) is also seen in the $Fe(2\text{-}nqo)_2 \cdot 2py$ system. C:N ratio of reaction mixture = 11.8:1 C:N ratio of $Fe(2\text{-}nqo)_3$ = 10.0:1 Precipitate of $Ba(CO_3)_2$ from baryta water

bis(1,2-naphthoquinone-2-iminato)iron(II) (0.49g, 74%) (Found: C,65.9; H,3.5; Fe,14.9; N,7.5. $C_{20}H_{12}FeN_2O_2$ requires C,65.2; H,3.3; Fe,15.2; N,7.6%). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave a brown solid (0.34g), which was dissolved in acetone (5.0 cm^3) and spotted onto a 6"x6" preparative silica chromatography plate. The plate was developed with ethyl acetate to give six bands, two major, purple, bands, three minor, orange/yellow, bands and a green band which was left at the bottom of the plate. Removal of the purple bands, followed by extraction with ethyl acetate, gave dibenzo[b,i]phenazine-5,12-diol (0.16g, 55%) and 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine (0.10g, 35%)(identified by t.l.c.)

Reaction of bis(1,2-naphthoquinone-2-iminato)iron(II) with hydrochloric acid.

Bis(1,2-naphthoquinone-2-iminato)iron(II) (0.20g, 0.54 mmol) was shaken with aqueous hydrochloric acid (15%, 50 cm^3) for 10 min. After neutralisation with sodium bicarbonate, chloroform was added and the mixture shaken for 5 min. The chloroform layer was separated from the aqueous layer, which was then further extracted with chloroform. The combined chloroform extracts were dried ($MgSO_4$), filtered and evaporated under reduced pressure to give a purple solid. T.l.c. examination of the solid showed the major components to be dibenzo[b,i]phenazine-5,12-diol and 2-amino-N(4)-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone monoimine, with at least four other, minor, components.

The interaction of nitric oxide with selected metal complexes.

Small scale experiments (0.1g of complex) were carried out qualitatively with the following complexes:

$Fe(1\text{-}nqo)_2 \cdot 2py$
$Fe(2\text{-}nqo)_2 \cdot 2py$
$Co(1\text{-}nqo)_3$
$Fe(1\text{-}nqo)_3$
$Fe(2\text{-}nqo)_3$

Nitric oxide was bubbled through a solution or suspension of the complex in toluene and then on through a cold trap (-80 °C) for 3 h. At the end of this period the solvent was removed by evaporation under nitrogen and the solid remaining examined by t.l.c. Elemental analyses of the complexes previous to reaction and of the reaction products were obtained. The results are summarised in Table 5.18.

Table 5.18 Interaction of nitric oxide with selected metal complexes.

Complex	Initial C:N ratio*	Final C:N ratio	Results of t.l.c. study
$Fe(1\text{-}nqo)_2 \cdot 2py$	7.6:1	5.3:1	Multicomponent mixture with at least 9 components, none of which could be identified.
$Fe(1\text{-}nqo)_3$	10:1	5.9:1	Same components as those seen in the reaction of $Fe(1\text{-}nqo)_2 \cdot 2py$
$Fe(2\text{-}nqo)_2 \cdot 2py$	7.3:1	5.6:1	Multicomponent mixture with at least 8 components, none of which could be identified.
$Fe(2\text{-}nqo)_3$	9.7:1	6.1:1	Same components as those seen in the reaction of $Fe(2\text{-}nqo)_2 \cdot 2py$
$Co(1\text{-}nqo)_3$	10:1	10:1	No reaction

*As estimated by analysis of the samples used

Interaction of bis(1,2-naphthoquinone-1-oximato)copper(II) with nicotine.

Nicotine (3.2g, 20.0 mmol) was added to a stirred solution of the copper complex (2.05g, 5 mmol) in acetone (100 cm^3). After 1h the solvent was removed at 30 °C/0.3 mm Hg to give a brown residue (5.4g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give brown bis(1,2-naphthoquinone-1-oximato)-mononicotine copper(II) (2.85g, 98%)(Found: C,64.3; H,4.6; Cu,11.0; N,9.7. $C_{30}H_{26}CuN_4O_4$ requires C,63.2; H,4.6; Cu,11.1; N,9.8%)

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with nicotine.

Nicotine (3.2g, 20.0 mmol) was added to a stirred solution of the iron complex (2.85g, 5.0 mmol) in acetone (100 cm^3). After 1h the solvent was removed at 30 °C/0.3 mm Hg to give a green residue (5.9g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give a light green, diamagnetic solid (3.3g) (Found: C,62.8; H,4.4; Fe,7.6; N,9.0%)(one component by t.l.c.). A portion (1.5g) of this solid was chromatographed on silica gel. Toluene eluted a brown solid (0.52g) (mainly 1-nitroso-2-naphthol by t.l.c.). Toluene/ethyl acetate (1:1) eluted a yellow/brown solid (0.5g)(multicomponent by t.l.c.). Methanol eluted a green substance which decomposed on evaporation of the solvent at 45 °C/0.3 mm Hg to a brown compound (0.15g) and nicotine (0.05g)(identified by t.l.c.). Methanol/pyridine (10:1) eluted bis(1,2-naphthoquinone-1-oximato)di(pyridine)iron(II) (1.1g)(identified by t.l.c. and i.r.).

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with pyridine.

The iron complex (2.85g, 5 mmol) was stirred in pyridine (30 cm^3) for 4 days at ambient temperature. The resultant solution was added dropwise to light petrol (b.p. 30-40 °C)(100 cm^3) and filtered to give a dark green solid. This was washed with light petrol (b.p. 30-40 °C) (3 x 50 cm^3) to leave a green solid (3.1g). Evaporation of the light petrol extracts at 45 °C/0.3 mm Hg gave a yellow solid (0.40g)(shown by comparative t.l.c. to be 1-nitroso-2-naphthol plus two other minor components). A portion of the green solid (0.80g) was chromatographed on silica gel. Toluene eluted tris(1,2-naphthoquinone-1-oximato)iron(III) (0.26g)(identified by t.l.c.). Ethyl acetate eluted bis(1,2-naphthoquinone-1-oximato) di(pyridine)iron(II) (0.44g)(identified by i.r. and comparative t.l.c.). Methanol/pyridine (10:1) eluted a further amount of the pyridine adduct (0.06g).

Interaction of tris(1,2-naphthoquinone-1-oximato)iron(III) with pyrrole.

Pyrrole (1.6g, 25 mmol) was added to a stirred solution of the iron complex (2.85g, 5.0 mmol) in acetone (100 cm^3). After 5h the solvent was removed at 30 °C/0.3 mm Hg to give a green oil (5.1g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give a dark green diamagnetic solid (3.55g) which decomposed on a silica t.l.c. plate. Evaporation of the light petrol at 45 °C/0.3 mm Hg gave a brown oil (1.14g) (multicomponent by t.l.c.).

Interaction of bis(1,2-naphthoquinone-2-oximato)copper(II) with nicotine.

Nicotine (3.2g, 20.0 mmol) was added to a stirred solution of the copper complex (2.05g, 5.0 mmol) in acetone (100 cm^3). After 4h the solvent was removed at 30 °C/0.3 mm Hg to give a red/brown residue (5.6g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give dark red bis(1,2-naphthoquinone-2-oximato) mono-nicotine copper(II) (2.80g, 96%)(Found: C,63.8; H,4.5; Cu,11.2; N,9.6. $C_{30}H_{26}CuN_4O_4$ requires C,63.2; H,4.6; Cu,11.1; N,9.8%).

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with nicotine.

Nicotine (3.2g, 20.0 mmol) was added to a stirred solution of the iron complex (2.85g, 5.0 mmol) in acetone (100 cm^3). After 1h the solvent was removed at 30 °C/0.3 mm Hg to give a green oil (5.0g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give a green, diamagnetic solid (3.72g). (one component by t.l.c.). A portion of this solid (1.5g) was chromatographed on silica gel. Toluene eluted 2-nitro-1-naphthol (0.03g)(identified by comparative t.l.c.). Toluene/ethyl acetate (1:1) eluted a brown solid (0.02g) (multicomponent by t.l.c.) and a yellow solid (0.05g) (shown by t.l.c. to be a mixture of 2-nitroso-1-naphthol and bis(1,2-naphthoquinone-2-oximato)iron(II)). Methanol eluted a green solid which after evaporation of the methanol at 45 °C/0.3 mm Hg gave a yellow solid (0.26g) (extracted with methanol)(shown to be mainly 2-nitroso-1-naphthol by comparative t.l.c.) and a green solid (0.45g)(shown to be mainly bis(1,2-naphthoquinone-2-oximato)iron(II) by comparative t.l.c.). Methanol/pyridine (10:1) eluted bis(1,2-naphthoquinone-2-oximato)di(pyridine)iron(II) (0.6g)(identified by i.r. and comparative t.l.c.).

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with pyridine.

The iron complex (2.85g, 5.0 mmol) was stirred in pyridine for 24h at ambient temperature. The resultant solution was added dropwise to light petrol (b.p. 30-40 °C) (100 cm^3) and filtered to give a green solid which was washed with light petrol (b.p. 30-40 °C)(3 x 50 cm^3) to give impure bis(1,2-naphthoquinone-2-oximato)di(pyridine)-iron(II) (2.83g). Evaporation of the light petrol at 45 °C/0.3 mm Hg gave a yellow solid (0.81g)(shown by comparative t.l.c. to be 2-nitroso-1-naphthol plus one other minor component). A portion of the impure pyridine adduct (1.0g) was chromatographed on silica gel. Toluene eluted 2-nitroso-1-naphthol (0.02g)(identified by comparative t.l.c.). Ethyl acetate eluted bis(1,2-naphthoquinone-2-oximato)di(pyridine)iron(II) (0.84g) (identified by i.r. and comparative t.l.c.). Methanol/pyridine (10:1) eluted a further amount of the pyridine adduct (0.2g) (identified by comparative t.l.c.).

Interaction of tris(1,2-naphthoquinone-2-oximato)iron(III) with pyrrole.

Pyrrole (1.6g, 25 mmol) was added to a stirred solution of the iron complex (2.85g, 5.0 mmol) in acetone (100 cm^3). After 1h. the solvent was removed at 30 °C/0.3 mm Hg to give a green residue (3.58g). This was stirred with light petrol (b.p. 30-40 °C)(3 x 100 cm^3) and filtered to give a dark green, diamagnetic solid (2.85g) which decomposed on a silica t.l.c. plate. Evaporation of the light petrol at 45 °C/0.3 mm Hg gave an orange/brown solid (0.70g)(multicomponent by t.l.c.). A portion of the iron-containing solid (0.50g) was chromatographed on silica gel. Elution with a series of solvents increasing in polarity gave seven fractions which upon removal of the solvent all gave a blue compound with identical t.l.c.

behaviour (total weight of fractions 0.20g)(multicomponent by t.l.c.). Methanol/pyridine (10:1) eluted a green compound which upon removal of the solvent at 45 °C/0.3 mm Hg gave bis(1,2-naphthoquinone-2-oximato) di(pyridine)iron(II) (0.35g)(identified by i.r. and comparative t.l.c.).

Interaction of tris(diethyldithiocarbamato)iron(III) and bis(diethyldithiocarbamato)copper(II) with selected Lewis bases.

Small scale experiments were carried out qualitatively with the following Lewis bases: Aniline, pyridine, triphenylphosphine and acetonitrile. A 5:1 ratio of base to complex* was used. All reactions were carried out in toluene at ambient temperature and followed by t.l.c. examination. These reactions are summarised in Table 5.19.

* Prepared as described by Golding et al[2]

Interaction of tris(acetylacetonato)iron(III) with triphenylphosphine.

The iron complex (1.26g, 3.6 mmol) was refluxed in acetone (50 cm^3) with triphenylphosphine (4.49g, 17.1 mmol) for 7 days. The solvent was removed at 30 °C/0.3 mm Hg to leave a red/brown solid. The solid was stirred in light petrol (b.p. 30-40 °C)(3 x 200 cm^3) and filtered to give unreacted tris(acetylacetonato)iron(III) (1.20g, 3.4 mmol). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave crude triphenylphosphine (4.5g)(by t.l.c.)

Interaction of tris(acetylacetonato)iron(III) with pyridine.

The iron complex (1.20g, 3.4 mmol) was refluxed in pyridine (20 cm^3) for 7 days. The resultant mixture was added dropwise to light petrol (b.p. 30-40 °C)(100 cm^3) and filtered to give unreacted tris(acetylacetonato)iron(III) (1.16g, 3.3 mmol).

Table 5.19 Summary of the interaction of $Cu(Et_2NCSS)_2$ and $Fe(Et_2NCSS)_3$ with selected Lewis bases.

Complex	Base	Nos of hrs before evidence of reaction observed by t.l.c.	Results
$Cu(Et_2NCSS)_2$	py	—	No reaction
$Cu(Et_2NCSS)_2$	$PhNH_2$	408	Slow reaction. $(Et_2NCSS)_2$ identified by t.l.c.
$Cu(Et_2NCSS)_2$	Ph_3P	1	$Cu(Et_2NCSS)(Ph_3P)_2^{*}$, Ph_3PS and $(Et_2NCSS)_2$ (minor) identified by t.l.c.
$Cu(Et_2NCSS)_2$	MeCN	350	Slow reaction. $(Et_2NCSS)_2$ identified by t.l.c.
$Fe(Et_2NCSS)_3$	py	12	Column chromatographic separation gave $(Et_2NCSS)_2$ (identified by m.pt., C.H.N. analysis and i.r.) + a brown, paramagnetic iron-containing solid.
$Fe(Et_2NCSS)_3$	$PhNH_2$	30	$(Et_2NCSS)_2$ identified by t.l.c. Evaporation of solvent gave a brown, paramagnetic iron-containing solid.
$Fe(Et_2NCSS)_3$	Ph_3P	72	Ph_3PS + $(Et_2NCSS)_2$ (minor) identified by t.l.c. Evaporation of solvent gave a brown, paramagnetic iron-containing solid.

Table 5.19 cont.

$Fe(Et_2NCSS)_3$	MeCN	36	$(Et_2NCSS)_2$ identified by t.l.c. Evaporation of solvent gave a brown, paramagnetic iron-containing solid.

* Identified by comparison with an authentic sample prepared as directed by Kowala et al[3]

Interaction of tris(benzohydroximato)iron(III) monohydrate with triphenylphosphine.

The iron complex* (1.0g, 2.0 mmol) was refluxed in acetone (50 cm^3) with triphenylphosphine (2.6g, 10.0 mmol) for 7 days. The solvent was removed at 30 °C/0.3 mm Hg to leave a red/brown solid. The solid was stirred in light petrol (b.p. 30-40 °C)(3 x 200 cm^3) and filtered to give unreacted tris(benzohydroximato)iron(III) monohydrate (0.97g, 1.9 mmol). Evaporation of the filtrate at 40 °C/0.3 mm Hg gave triphenylphosphine (2.4g, 9.9 mmol).

* Prepared as directed by Brown et al[4]

Interaction of tris(benzohydroximato)iron(III) monohydrate with pyridine.

The iron complex (1.0g, 2.0 mmol) was refluxed in pyridine(20 cm^3) for 7 days. The resultant mixture was added dropwise to light petrol (b.p. 30-40 °C)(100 cm^3) and filtered to give unreacted tris(benzohydroximato)iron(III) monohydrate (0.95g, 1.9 mmol).

Interaction of bis(acetylacetonato)copper(II) with triphenylphosphine.

The copper complex (0.93g, 3.6 mmol) was refluxed in acetone (50 cm^3) with triphenylphosphine (4.42g, 16.8 mmol) for 7 days. The solvent was removed at 30 °C/0.3 mm Hg to leave an off-white solid. The solid was extracted with diethyl ether (3 x 50 cm^3) and methanol (3 x 50 cm^3) to leave diamagnetic mono(acetylacetonato)bis(triphenylphosphine) copper(I) (2.31g, 94%) (Found: C,68.5; H,5.4; Cu,9.1; P,9.3. $C_{41}H_{37}CuO_2P_2$ requires C,71.5; H,5.4; Cu,9.2; P,9.3%) Evaporation of the ether and methanol extracts at 40 °C/0.3 mm Hg left two solids (2.1g and 0.9g). T.l.c. examination of the solids showed them to be complex mixtures containing triphenylphosphine, triphenylphosphine oxide and at least five other components.

Interaction of bis(benzohydroximato)copper(II) with triphenylphosphine.

The copper complex(1.68g, 5.0 mmol) was refluxed in acetone (50 cm^3) with triphenylphosphine (3.95g, 15.1 mmol) for 1 day. The mixture was stirred for a further 2 h at ambient temperature and filtered to give a brown filtrate and a solid. The solid was washed with acetone (3 x 50 cm^3) to give pale green, diamagnetic mono(benzohydroximato)-bis(triphenylphosphine)copper(I) (2.35g, 70%) (Found: C,71.1; H,5.1; Cu,8.7; N,2.2; P,8.5. $C_{43}H_{36}CuNO_2P_2$ requires C,71.3; H,5.0; Cu,8.8; N,1.9; P,8.6%). Evaporation of the filtrate at 30 °C/0.3 mm Hg left a brown tar. T.l.c. examination of the tar showed it to be a multicomponent mixture.

5.5 References

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