

A STUDY OF THE REACTIONS OF PHENOLS

WITH CHROMYL CHLORIDE

by

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A thesis submitted in part fulfilment of the requirements
for a C.N.A.A. Ph.D. Degree

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(ii)

To my Parents

and

Pauline

INDEX

| | | |
|------------------|--|----|
| <u>Chapter 1</u> | Introduction | 1 |
| <u>Chapter 2</u> | Chromyl Compounds | 5 |
| 2.1 | Chromyl Halides | 5 |
| 2.2 | Other Inorganic Chromyl Compounds | 8 |
| 2.3 | Organic Chromyl Compounds | 9 |
| <u>Chapter 3</u> | The Oxidation of Organic Compounds by Chromyl Chloride: The Etard Reaction | 14 |
| 3.1 | Introduction | 14 |
| 3.2 | Experimental Procedures which have been used for the Etard Reaction | 16 |
| 3.3 | Solvents used for the Etard Reaction | 17 |
| 3.4 | The Hydrolysis Stage of the Etard Reaction | 19 |
| 3.5 | Oxidation Products of the Etard Reaction | 19 |
| <u>Chapter 4</u> | The Mechanism of the Etard Reaction | 47 |
| 4.1 | Introduction | 47 |
| 4.2 | The Formation of the Etard Complex | 47 |
| 4.3 | The Structure of the Etard Complex | 59 |
| 4.4 | The Decomposition of the Addition Product | 64 |
| <u>Chapter 5</u> | Introduction to the Results Section | 66 |
| 5.1 | The Reasons for the Investigation | 66 |
| 5.2 | The Choice of Phenols | 67 |
| 5.3 | The General Mode of Reaction of Phenols with Chromyl Chloride | 69 |
| <u>Chapter 6</u> | The Products of Oxidation of Phenols by Chromyl Chloride and Chromyl Acetate | 71 |
| 6.1 | Introduction | 71 |
| 6.2 | Oxidation by Chromyl Chloride | 71 |
| 6.3 | The Reductive Hydrolysis of the Complexes | 88 |
| 6.4 | The Oxidation by Chromyl Acetate | 90 |

| | | |
|------------------|---|-----|
| <u>Chapter 7</u> | The Reactions of Phenols with Vanadium (V) Oxytrichloride and Chromium (V) Oxytrichloride | 93 |
| 7.1 | The Products of Reaction of Phenols with Vanadium (V) Oxytrichloride | 93 |
| 7.2 | The Reaction of Chromium (V) Oxytrichloride with Phenols | 106 |
| <u>Chapter 8</u> | The Properties of the Solid Complexes | 116 |
| 8.1 | The Phenol - Chromyl Chloride Complexes | 116 |
| 8.2 | The Solid Product from Chromyl Acetate Oxidations | 155 |
| 8.3 | The Electron Spin Resonance Spectra of the Complexes | 162 |
| <u>Chapter 9</u> | Discussion of the Experimental Results | 165 |
| 9.A | The Products and Mechanism of Oxidation of Phenols with Oxidants other than Chromyl Compounds | 165 |
| 9.A.1 | Reactions which involve a One-electron Transfer | 166 |
| 9.A.2 | Reactions which involve a Two-electron Transfer | 175 |
| 9.B | The Oxidation of Phenols by Chromyl Compounds | 181 |
| 9.B.1 | The Oxidation of Phenols as an Example of the Etard Reaction | 181 |
| 9.B.2 | Some General Features of the Phenol Oxidation Reactions | 184 |
| 9.B.3 | The Reaction as an Example of a Free Radical Oxidation | 186 |
| 9.B.4 | The Reaction as an Example of a Heterolytic Oxidation | 203 |
| 9.B.5 | The Formation of Products other than p-Benzoquinones | 207 |

Chapter 9 (Contd.)

| | |
|---|-----|
| 9.B.6 The Nature of the Solid Products derived from Chromyl Chloride and Chromyl Acetate Oxidations | 213 |
| 9.B.7 The Reaction of Vanadium (V) Oxytrichloride and Chromium (V) Oxytrichloride with Phenols | 221 |

| | |
|---|-----------|
| <u>Chapter 10</u> Experimental Section | 226 |
| 10.1 The Choice of Solvents for Reactions with Chromyl Compounds | 226 |
| 10.2 The Preparation and Purity of the Reagents | 228 |
| 10.3 The Preparation and Purification of the Metal Oxychlorides | 230 |
| 10.4 The Preparation and Purification of Phenols | 231 |
| 10.5 The Preparation and Handling of the Phenol - Chromyl Chloride Complexes | 238 |
| 10.6 The Oxidations with Chromyl Acetate | 244 |
| 10.7 The Reactions of Vanadium (V) Oxytrichloride with Phenols | 245 |
| 10.8 The Reaction of the Phenol - Chromyl Chloride Complexes with Water | 245 |
| 10.9 The Reductive Hydrolysis of the Phenol - Chromyl Chloride Complexes | 249 |
| 10.10 Instrumentation and Analytical Techniques | 250 |
| <u>Appendix</u> | 253 |
| Tables 22 to 64 | 254 - 297 |
| Courses of Study | 298 |
| <u>References</u> | 300 |

CHAPTER 1

INTRODUCTION

In this thesis, an investigation into the reaction between chromyl chloride and a number of phenolic compounds is described.

Such an investigation must be seen in the context of the evergrowing interest in the interaction between transition metal compounds and organic species.

Most transition metals exhibit a number of oxidation states, the higher states giving rise to oxidizing agents whilst the lower states give compounds which have reducing properties. However, the nature of the redox reaction in all cases is highly dependent on the reacting species and on the reaction environment.

Chromium compounds¹, particularly chromic acid, and those of manganese¹, principally potassium permanganate and manganese dioxide, have been used for many years as oxidants in organic chemistry.

More recently, vanadium, iron, cobalt and copper^{2,3} have been investigated in this context.

The oxidation of phenols with compounds of these and other metals is well documented and has been the subject of research from various standpoints.

The study of such reactions has received much attention, from the consideration of both synthetic application and reaction mechanism.

In the last decade, the importance of phenols and their oxidation products in relation to biologically important reaction pathways has led to a further extension of this field.

Indeed, it is evident that the application of phenol oxidation to the synthetic chemistry of natural products is in its infancy and that it will rapidly develop into an important area of organic chemistry.

Another area in which phenol oxidation is of increasing importance is in the study and application of antioxidants⁴.

The use of antioxidants to prevent the deterioration of many natural and synthetic organic materials has become widespread; phenols have been used in this context as stabilizers in rubbers, oils, plastics and foodstuffs⁴.

The oxidation of phenols with chromyl chloride or other chromyl compounds has received little attention in comparison to the application of other oxidants in this developing situation.

In Chapter 2, a brief review is presented of the preparation and properties of chromyl compounds. Their reactivity as oxidizing agents, where it is known, is also described.

Chapter 3 is devoted to a review of the reactions of chromyl chloride with organic compounds. Chromyl chloride is the best known chromyl compound⁵ (see Chapter 2) and consequently its reactions make up the bulk of the reports on the chemistry of this class of compound.

It can be seen in Chapter 3, that much of the early work on the topic suffered considerably from the limitations of the chemistry of that period: more recent work has shown that many of the early results are misleading and that the reactions are very much more complicated than earlier supposed.

The various types of mechanism which have been postulated for the reactions of chromyl chloride and other chromyl compounds are critically reviewed in Chapter 4.

The use of chromyl chloride as an oxidant requires the use of certain types of solvent. This is described fully in Chapter 3. In general these solvents are non-polar and their use leads to the isolation of solid reaction intermediates. The majority of investigations into oxidations with other metal compounds have been carried out using polar solvents, especially water or acetic acid, which precludes the isolation of such intermediates.

Although the oxidation of many classes of organic compounds by chromyl chloride has been reported, prior to this study, there has been no systematic investigation of the reactions between phenols and chromyl chloride.

Towards the end of the last century, Etard reported the reactions of chromyl chloride with phenol and certain cresols^{7,8}; he was unable to draw any significant conclusions from this work, but he suggested that the reactions involved non-stoichiometric ratios of reagents and that the products of oxidation were complex, but probably included quinones^{7,8}.

In this thesis, the results of a systematic study of the oxidation of phenols with chromyl chloride are described.

The nature and yields of the oxidation products of a number of substituted phenols have been studied, and the relationship between them, the effect of ring substituents and the mole ratio of reactants has been determined. The results of this investigation are presented in Chapter 6 and the discussion of the likely mechanisms for the oxidation process follows in Chapter 9.

Another oxidizing agent which has been studied concurrently with chromyl chloride, is chromyl acetate. This compound, in many respects, reacts with phenols in a similar way to chromyl chloride; the results obtained from the use of this reagent are included in Chapter 8.

The use of vanadium (V) oxytrichloride and chromium (V) oxytrichloride as potential oxidants for phenols has also been studied. The reactions with these compounds are outlined in Chapter 7.

The conclusions drawn from this study of the oxidation of phenols by the various metal oxyhalides are presented in Chapter 9 where proposals as to both reaction mechanism and structure of the reaction intermediates are made.

Chapter 10 comprises a description of the experimental procedures used in this study.

CHAPTER 2

CHROMYL COMPOUNDS

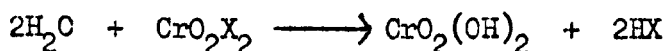
In this review, the compounds designated as 'chromyl compounds' are those which have the general formula CrO_2X_2 where X is a univalent element or group.

Chromic acid, $\text{CrO}_2(\text{OH})_2$, may be considered to be the parent chromyl compound, from which the others can be derived. However, this compound has been purposely omitted from the survey as it is not a typical chromyl compound.

Chromic acid has not been isolated, but is well known in solution in polar solvents where it is appreciably associated.

For example, in water the following ions are present: CrO_4^{2-} , HCrO_4^- , $\text{Cr}_2\text{O}_7^{2-}$ and HCrO_7^- .

By contrast other chromyl compounds are covalent and react readily with water to give chromic acid and the hydride of the group X:



Chromyl compounds, which are usually strongly coloured and monomeric, are vigorous oxidising agents towards many organic and inorganic substances.

Brief summaries of the properties of the known chromyl compounds are presented in the following sections.

2.1 Chromyl Halides

Three chromyl halides have been prepared, chromyl fluoride, chromyl chloride and chromyl bromide. Chromyl iodide has not been isolated: its existence is doubtful in view of the powerful oxidizing properties of chromium (VI). The oxidation of iodide to

iodine by chromium (VI) in aqueous solution is well known, and most evidence points to chromyl compounds being stronger oxidants than aqueous chromium (VI).

Of the three compounds, chromyl chloride, CrO_2Cl_2 , has been the subject of most study, largely because of the relative ease with which it may be handled.

2.1.1 Chromyl Chloride

Chromyl chloride was first prepared by Berzelius⁹, who found that, on distillation, a mixture of potassium chromate, sodium chloride and concentrated sulphuric acid yielded a deep red liquid. Three years later, Thomson¹⁰ characterized this red compound as 'chlorochromic acid'.

Since this original work many other preparative routes have been reported for the synthesis of chromyl chloride and its properties are now well established.

Chromyl chloride, CrO_2Cl_2 , is deep red as solid, liquid and vapour. At room temperature it is a transparent liquid, b.p. 115.7° , d_4^{20} 1.9220⁵. The melting point of the solid is -95.5° . It is unstable in the presence of light³⁸ and decomposes above 150° to give chlorine and various oxides of chromium,³⁹ including a polymeric chloro-oxide, $(\text{CrO}_2)_n\text{Cl}^{40}$. This decomposition also occurs to a small extent at room temperature, even if the compound is stored in the dark and under nitrogen¹⁴.

The physical properties of chromyl chloride are those of a typical non-metal halide: molecular weight-determinations in the vapour and in solution in phosphorus oxytrichloride show that it is a monomeric compound⁴¹. Electron diffraction studies⁴² have

shown that the chromyl chloride molecule has a distorted tetrahedral structure.

Chromyl chloride is soluble in non-polar solvents such as carbon tetrachloride and carbon disulphide, without apparent reaction, but the oxidizing power of chromium (VI) is such that many organic liquids, though potential solvents for chromyl chloride, are rapidly oxidized.

Many oxidations by chromyl chloride in both inorganic^{43,44,45} and organic chemistry have been studied.

The use of this reagent as an oxidant in organic chemistry will be examined in detail in Chapters 3 and 4.

2.1.2 Chromyl Fluoride

Chromyl fluoride was first prepared in 1824 by Unverdorben¹¹, who treated chromyl chloride with hydrogen fluoride, but the product was very impure and later attempts^{12,13} at purification failed. Engelbrecht and Grosse¹⁴ have since isolated this compound in a pure state as a violet-red crystalline solid (m.p. 31.6°); they found that it hydrolysed very readily and exploded on contact with organic compounds such as paraffins.

2.1.3 Chromyl Bromide

Zellner¹⁵ succeeded in preparing chromyl bromide at low temperature by the action of chromyl chloride on liquid hydrogen bromide, but the compound contained unreacted chromyl chloride. Isolation of the pure compound by other workers¹⁶, has shown it to be a deep violet solid, stable only below -70° .

No other chemical properties of chromyl fluoride and bromide have been reported.

2.2 Other Inorganic Chromyl Compounds

Chromyl nitrate was first reported¹⁷ as an oily, red liquid, formed when nitric acid vapour was passed over warmed chromium trioxide, but the compound was not isolated until Schmeisser and Lutzow¹⁸ prepared it as one of the products of the reaction between dinitrogen pentoxide and chromyl chloride at -60° . It is a powerful oxidizing agent, causing many hydrocarbons e.g. benzene, to inflame on contact¹⁹. In carbon tetrachloride solution, however, its oxidizing action is less violent, and complexes, analagous to the Etard adducts are formed in the reaction¹⁹ with toluene.

Cady and Lustig²⁰ claimed to have prepared chromyl fluorosulphonate, $\text{CrO}_2(\text{SO}_3\text{F})_2$, but other workers²¹ have shown that the compound isolated was in fact a product which resulted from the decomposition of the initially formed fluorosulphonate. Pure chromyl fluorosulphonate²¹ is a moss-green, non-volatile solid, which reacts violently with water.

The meta-borate, $\text{CrO}_2(\text{BO}_2)_2$, prepared by Haider et al²², is a brown, crystalline solid which undergoes hydrolysis readily. The reactivity of chromyl metaborate with organic compounds is

dissimilar to that of most other chromyl compounds: it is insoluble in ether, chloroform and benzene, but may be recrystallized from dry acetone without reaction. It dissolves readily in ethanol but reaction with this solvent does take place and the meta-borate cannot be recovered unchanged.

Chromyl azide is a deep violet crystalline solid which hydrolyses readily; it decomposes with explosion at temperatures above about -60° ²³.

Chromyl perchlorate is similarly very susceptible to hydrolysis, though it is relatively stable towards heat, existing as a deep red solid below 1° , and as a similarly coloured liquid at temperatures above this ¹⁹. It is a vigorous oxidant, causing many organic compounds to inflame on contact. Solutions of chromyl perchlorate in carbon tetrachloride are, however, quite stable; molecular weight determinations in this solvent have shown that the compound is monomeric ¹⁹.

Other chromyl compounds which have been reported are the sulphates $\text{CrO}_2(\text{S}_2\text{O}_7)_2$, ²⁴ $\text{CrO}_2(\text{OH})\text{HSO}_4$ and $\text{CrO}_2(\text{HSO}_4)_2$ ²⁵. It is suggested that these are formed in chromium trioxide/sulphuric acid solutions, but they have not been isolated in pure form.

A summary of the methods of preparation of these chromyl compounds is presented in Table 1.

2.3 Organic Chromyl Compounds

A variety of compounds of general formula CrO_2X_2 , where X^- is an anion derived from an organic acid, have been prepared, the best known being chromyl acetate, $\text{CrO}_2(\text{O.COCH}_3)_2$.

TABLE 1

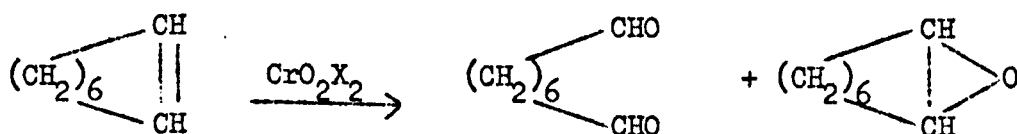
The Preparation of Inorganic Chromyl Compounds

| Compound | Preparation | Ref |
|---------------------------|---|--------|
| Chromyl Fluoride | $\text{CrO}_3 + 2\text{HF} \xrightarrow{\text{excess HF}} \text{CrO}_2\text{F}_2$ <p style="text-align: center;">(anhydrous)</p> | 14 |
| Chromyl Chloride | $\text{K}_2\text{CrO}_4 + 2\text{NaCl} + 2\text{H}_2\text{SO}_4 \longrightarrow \text{CrO}_2\text{Cl}_2$ | 37 |
| Chromyl Bromide | $\text{CrO}_3 + 2\text{CF}_3\text{COBr} \xrightarrow[-135^\circ]{\text{CCl}_4} \text{CrO}_2\text{Br}_2$ | 16 |
| Chromyl Nitrate | $\text{CrO}_2\text{Cl}_2 + 2\text{N}_2\text{O}_5 \xrightarrow{-60^\circ} \text{CrO}_2(\text{NO}_3)_2$ | 18, 19 |
| Chromyl Fluoro-sulphonate | $\text{CrO}_2\text{Cl}_2 + \text{S}_2\text{O}_6\text{F}_2 \longrightarrow \text{CrO}_2(\text{SO}_3\text{F})_2$ | 21 |
| Chromyl Borate | $\text{CrO}_2\text{Cl}_2 + 2\text{AgBO}_2 \longrightarrow \text{CrO}_2(\text{BO}_2)_2$ <p style="text-align: center;">(solid)</p> | 22 |
| Chromyl Azide | $\text{CrO}_3 + 2\text{HN}_3 \xrightarrow[\text{CF}_2\text{Cl}_2/-78^\circ]{\text{P}_2\text{O}_5} \text{CrO}_2(\text{N}_3)_2$ | 23 |
| Chromyl Perchlorate | $\text{CrO}_3 + \text{Cl}_2\text{O}_6 \xrightarrow{+6^\circ} \text{CrO}_2(\text{ClO}_4)_2$ | 19 |

Over fifty years ago, solutions of chromium trioxide in acetic anhydride were used as oxidants in organic chemistry²⁶ and it has now been shown that these solutions contain chromyl acetate²⁷. Thus if chromium trioxide is dissolved in acetic anhydride or acetic anhydride/carbon tetrachloride and the excess solvent removed under reduced pressure, chromyl acetate can be isolated as a red, crystalline solid (m.p. 30.5°)²⁷. The solution of chromium trioxide in anhydrous acetic acid may contain chromyl acetate, but the formation of the solvated chromate ion or the acetochromate ion ($\text{CH}_3\text{COCrO}_2\text{O}^-$) is more likely²⁸.

The preparations of chromyl benzoate and chromyl trichloroacetate can be effected by mixing chromium trioxide with the respective acid anhydrides and boiling the mixtures under reflux until the trioxide has dissolved^{29,30}.

All three compounds, the acetate, trichloroacetate and benzoate have been used as oxidants; very few comparative studies have been carried out, although all are reported²⁹ to oxidize cyclo-octene to the corresponding dialdehyde together with the epoxide:



Neither product was obtained in a yield higher than 25%. The oxidation of alkanes by chromyl acetate gives mainly ketones and acids³¹, but the mechanistic aspect of these reactions has received little study.

Three chromyl compounds which have been prepared recently³² are chromyl trifluoroacetate, $\text{CrO}_2(\text{O.COCF}_3)_2$, chromyl chlorodifluoroacetate, $\text{CrO}_2(\text{O.COCF}_2\text{Cl})_2$, and chromyl perfluorobutyrate, $\text{CrO}_2(\text{O.COCF}_2\text{CF}_2\text{CF}_3)_2$. All three compounds are yellow or yellow-brown crystalline solids which are hygroscopic and light sensitive. The chemical reactivity of these compounds has yet to be studied.

Chromyl compounds derived from alcohols have been prepared. Thus, di-iso-propyl chromate³³ and di-t-butyl chromate^{34,35} are prepared by treating the corresponding alcohol with chromium trioxide in a non-polar solvent at 0° . Both are red crystalline solids, unstable at temperatures above 0° , but are relatively stable in solution. Typical oxidations effected by these reagents include the conversion of primary alcohols to aldehydes, and the oxidation of secondary alcohols to ketones, both in high yields^{34,35}.

Other dialkyl chromates have been prepared in solution but they have not been isolated³⁶.

The preparation of these chromyl compounds has been summarized in Table 2.

TABLE 2

The Preparation of Organic Chromyl Compounds

| Compound | Preparation | Ref |
|--------------------------------|---|----------|
| Chromyl Acetate | $\text{CrO}_3 + (\text{CH}_3\text{CO})_2\text{O} \xrightarrow[\text{4}]{\text{CCl}_4} (\text{CH}_3\text{COO})_2\text{CrO}_2$ | 27 |
| Chromyl Benzoate | $\text{CrO}_3 + (\text{PhCO})_2\text{O} \xrightarrow[\text{40}^\circ]{\text{CCl}_4} (\text{PhCOO})_2\text{CrO}_2$ | 29 |
| Chromyl Tri-chloroacetate | $\text{CrO}_3 + (\text{CCl}_3\text{CO})_2\text{O} \xrightarrow[\text{77}^\circ]{\text{CCl}_4} (\text{CCl}_3\text{COO})_2\text{CrO}_2$ | 29,30 |
| Chromyl Tri-fluoroacetate | $\text{CrO}_3 + (\text{CF}_3\text{CO})_2\text{O} \xrightarrow{\text{Room temp.}} (\text{CF}_3\text{COO})_2\text{CrO}_2$ | 32 |
| Chromyl Difluoro-chloroacetate | $\text{CrO}_3 + (\text{CF}_2\text{ClCO})_2\text{O} \xrightarrow{\text{Room temp.}} (\text{CF}_2\text{ClCOO})_2\text{CrO}_2$ | 32 |
| Chromyl Perfluoro-butyrate | $\text{CrO}_3 + (\text{CF}_3\text{CF}_2\text{CF}_2\text{CO})_2\text{O} \xrightarrow{\text{Room temp.}} (\text{CF}_3\text{CF}_2\text{CF}_2\text{COO})_2\text{CrO}_2$ | 32 |
| Di-iso-propyl-chromate | $\text{CrO}_3 + 2^i\text{PrOH} \xrightarrow[\text{0}^\circ]{\text{Benzene}} (^i\text{PrO})_2\text{CrO}_2$ | 33 |
| Di-tert-butyl-chromate | $\text{CrO}_3 + 2^t\text{BuOH} \xrightarrow[\text{0}^\circ]{\text{Benzene}} (^t\text{BuO})_2\text{CrO}_2$ | 34 35 |

CHAPTER 3

THE OXIDATION OF ORGANIC COMPOUNDS BY CHROMYL CHLORIDE; THE ETARD REACTION

3.1 Introduction

The action of chromyl chloride on a wide variety of organic compounds was reported^{10,45} shortly after its discovery. Detailed studies of these reactions were hampered by the vigour of the oxidations: with many organic materials the oxidizing action of chromyl chloride was so vigorous that, on mixing the reagents, ignition took place, because of the low rate of dissipation of heat of oxidation. Some examples of the organic substances which were reported to inflame on contact with chromyl chloride, at room temperature, are turpentine¹⁰, olive oil⁴⁵, methanol and ethanol⁴³, various commercial hydrocarbon fractions⁴⁶, pyridine, aniline⁴⁷, and ethylene glycol⁵.

As a consequence, early workers were not able to carry out product analysis or to isolate intermediates in most of the reactions studied; only in a few isolated cases, in which the oxidation was less vigorous, was any progress made¹⁰.

The first controlled reactions were carried out by Carstanjen^{48,49}, a few years before Etard published his first report on the topic⁵⁰. Carstanjen appreciated the need for a solvent system for the reaction, to allow for homogeneous reaction and dissipation of evolved heat.

The solvent which Carstanjen chose for the reaction was glacial acetic acid, in which chromyl chloride dissolved readily, without any apparent change over a short period of time. Using this

system, the oxidation of benzene and other aromatic hydrocarbons was studied^{48,49}, the reactions being carried out at room temperature and without any of the violence characteristic of the earlier experiments.

A more comprehensive study of these reactions was carried out by the French chemist Etard, during the period 1877 - 1895^{7,8,38,50-59}. By using a similar technique to that of Carstanjen but employing relatively inert, non-polar solvents such as carbon tetrachloride and carbon disulphide, he was able to isolate intermediates in all the oxidations he studied. The addition of chromyl chloride to an organic compound, the isolation of the oxidation intermediate and its subsequent hydrolysis are now known as the Etard reaction⁵, although frequently this title is restricted to the description of the reaction of toluene with chromyl chloride.

Etard carried out a large number of reactions between chromyl chloride and a wide range of organic compounds^{7,8,38,50-59}. He found that each reaction led to the formation of a dark brown, precipitate, insoluble in carbon disulphide or tetrachloride. In many cases, these solids had the composition of 'adducts', the ratio of organic molecule to chromyl chloride being 1:2, e.g. the empirical formula of the toluene adduct was $C_6H_5CH_3 \cdot 2CrO_2Cl_2$ ³⁸. Hydrolysis of these adducts gave oxidation products of the original organic compound similar to those obtained by Carstanjen.

A detailed study of the empirical composition of the adducts and of their hydrolysis products enabled Etard to formulate structures for these complexes and to suggest a likely course for the reaction³⁸.

Many other workers have continued the studies initiated by Cartsanjen and Etard and the topic has been the subject of two reviews^{5,60}.

As a result of later work, many of the postulates and conclusions of the early workers have been modified but the mechanism of the reaction and the true nature of the solid intermediates are still not clearly understood.

3.2 Experimental Procedures which have been used for the

Etard Reaction

As indicated earlier, the Etard reaction must be carried out under strictly controlled conditions to ensure that, firstly, the solid intermediate may be isolated and secondly that there is no ignition or explosion. In general these conditions have been met by adding the oxidant, in an inert solvent, to a solution of the organic compound in the same solvent, with stirring to ensure homogeneity and external cooling to control the reaction temperature.

The initial stage of the reaction is complete when the insoluble complex is formed; this can then be separated by filtration. The final stage of the reaction is the hydrolysis of the complex.

Whilst many reactions are very rapid^{61,62} others may be comparatively slow^{63,64}. Wheeler⁶⁵, who studied the reaction of chromyl chloride with various substituted toluenes in carbon tetrachloride, found that the reaction time could be considerably reduced if, after allowing to stand for a short time, the reaction mixture was heated under reflux for several hours. He reported no significant change in the adduct composition when prepared by this means.

One requirement, for the successful completion of the Etard reaction, is that all apparatus and reagents are quite dry, as both oxidant and the intermediate complexes are very susceptible to hydrolysis.

3.3. Solvents used for the Etard Reaction

The choice of solvent for carrying out the Etard reaction has been found to be very limited. It is desirable that there is no significant interaction between oxidant and solvent; the solvents which have been most often used are carbon tetrachloride and carbon disulphide, although both of these are reported^{5,66} to react slowly with chromyl chloride.

Etard carried out much of his work using carbon disulphide as solvent. An important advantage in the use of this solvent is that, under atmospheric pressure, the temperature of the reaction cannot rise above the boiling point of the solvent (46°). Since chromyl chloride is not decomposed at this temperature, side reactions due to the presence of free chlorine are eliminated. The disadvantages of this solvent are its inflammability and its reactivity with the oxidant. Recent evidence⁶ suggests that the interaction between chromyl chloride and carbon disulphide occurs to a greater extent than is indicated in the literature.

Carbon tetrachloride appears to be the most suitable solvent for the study of the Etard reaction. Chromyl chloride is readily soluble in this solvent and there is no observable reaction below 100°. One disadvantage with carbon tetrachloride is that it

is very difficult to remove from the Etard adducts. This aspect is discussed in greater detail in Chapter 10.

Other solvents which have been used for studying the Etard reaction are glacial acetic acid^{48,49}, ethyl acetate⁶⁷, chloroform^{38,68} and dichloromethane⁶⁹.

The first two of these solvents are relatively good complexing agents and as a consequence they keep the chromium in solution, thus preventing the formation of the insoluble Etard complexes. The exact nature of the species produced when chromyl chloride is dissolved in acetic acid or ethyl acetate is not known; that interaction between the oxidant and acetic acid occurs has already been established (see page 11), and acetic acid and acetaldehyde are formed in solutions of chromyl chloride in ethyl acetate⁶⁷.

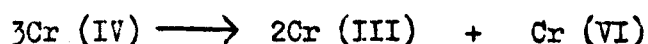
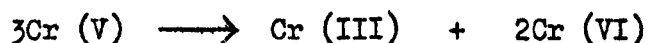
It has been reported⁵ that chromyl chloride dissolved in acetic acid is a stronger oxidant than the analagous solution in carbon tetrachloride; both chlorination reactions^{48,49} and carbon-carbon bond cleavage⁷⁰ take place in the former solution, but much less readily in the latter. The strongly oxidizing conditions also result in toluene being oxidized to benzoic acid. When the comparable reaction is conducted in carbon tetrachloride benzaldehyde is the major product.

Although chloroform and dichloromethane have been used only infrequently as solvents for Etard reactions, both give satisfactory results^{38,67,69}. There is evidence that both may react to some extent with the oxidant, especially in the presence of light; for example Etard reported the formation of phosgene as a product of the reaction between chromyl chloride and chloroform³⁸.

Alternative solvents such as benzene³⁸, pyridine^{47,70,71} ether³⁸ and acetone⁴⁷ have all proved unsatisfactory because of their reactivity with the oxidant.

3.4 The Hydrolysis Stage of the Etard Reaction

The Etard reaction is completed by the hydrolysis of the adduct; this hydrolysis is rapid and exothermic, resulting in a mixture of oxidized organic species and reduced chromium compounds. Generally the hydrolysis is carried out by adding the adduct to a large excess of cold water, but the presence of reducing agents³⁸ in the water ensures that no further oxidation of the organic product occurs at this stage. Possible oxidants liberated by hydrolysis are species of chromium (V) and (IV), or probably chromium (VI) species formed by disproportionation reactions such as:-



Reductants such as sodium bisulphite³⁸, sulphurous acid⁷², formic acid⁷³ and ferrous sulphate⁷³ have been used with success. However, most workers in this field have found that a large excess of cold water is equally satisfactory⁵.

3.5 Oxidation Products of the Etard Reaction

In this section is presented a review of the different types of Etard reaction. The emphasis is put on the examination of the products which have been obtained by oxidizing the various classes of organic compound with chromyl chloride.

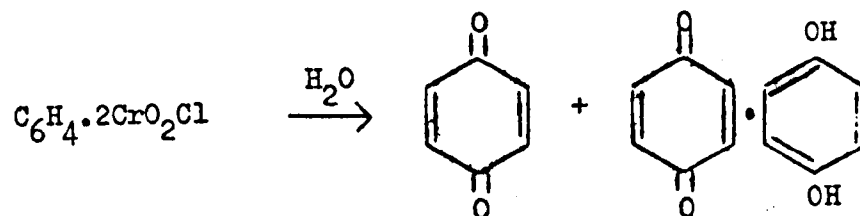
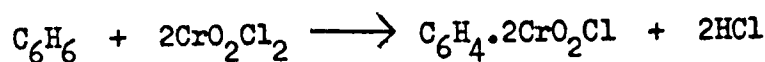
In each case the headings refer to the type of compound which has been oxidized, rather than the types of product which can be formed.

While the earlier workers studied a large number of different reactions, there is good reason, as this review illustrates, to re-examine these reactions using modern separational techniques. Indeed many of the results reported must be treated with a great deal of caution, as is shown particularly in sub-sections 3 - 5.

3.5.1 Benzene and Halogenated Benzenes

The first work in this field was carried out by Carstanjen⁴⁸. He found that when chromyl chloride, diluted with glacial acetic acid, was added carefully to benzene, an exothermic reaction occurred. Hydrolysis of the reaction mixture with cold water gave a deep green solution from which a yellow organic layer separated which consisted of unreacted benzene and trichloro-p-benzoquinone. It has been suggested⁵ that the extent of chlorination may have been due to free chlorine in the oxidant.

The study of the oxidation of benzene was continued by Etard³⁸. He found that when an excess of benzene was boiled with chromyl chloride without a diluent, a brown precipitate formed and hydrogen chloride was evolved; the precipitate had a composition corresponding to the formula $C_6H_4 \cdot 2CrO_2Cl$. Decomposition of this product by a large excess of cold water gave a green aqueous solution and an organic layer from which quinhydrone and p-benzoquinone were isolated:



A recent study by Gragerov and Sulima⁷⁴ has shown that the adduct formed when benzene and chromyl chloride are mixed at 0° and the mixture allowed to stand for seven days, has an empirical formula corresponding to $\text{C}_6\text{H}_6 \cdot 2\text{CrO}_2\text{Cl}_2$. The evolution of hydrogen chloride in Etard's experiment can be attributed to the vigorous reaction conditions that he employed. Gragerov and Sulima, like Etard, obtained *p*-benzoquinone on hydrolysis of the adduct.

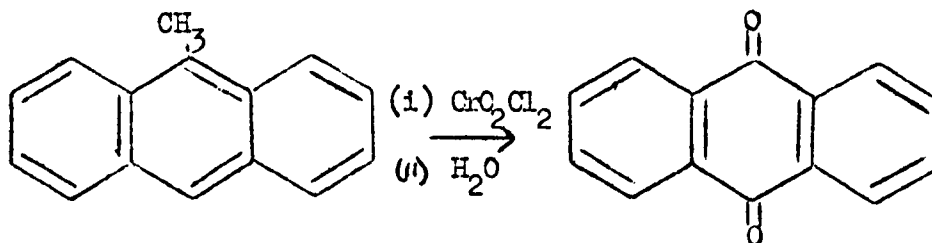
By comparison, benzene is relatively resistant to oxidation by chromic acid, the oxidation proceeding very slowly in sulphuric acid, giving only carbon dioxide⁷⁵.

The reactions of halogenated benzenes with chromyl chloride yield quinones; thus bromo-1,4-benzoquinone, *p*-dibromo-1,4-benzoquinone, chloro-1,4-benzoquinone and *p*-dichloro-1,4-benzoquinone can be prepared by heating the corresponding halogenated benzenes with chromyl chloride³⁸.

3.5.2 Polynuclear Aromatic Hydrocarbons

Polynuclear hydrocarbons such as naphthalene, anthracene and phenanthrene all yield Etard adducts^{38,76}. Hydrolyses of these adducts yielded compounds classified as 'quinones' and 'chloroquinones'⁵⁷; intractable resins were also reported⁷⁶. Wheeler⁷⁷, using chromatographic techniques, confirmed the formation of 1,4-benzoquinones in moderate yields on hydrolysis of the Etard complexes derived from various polycyclic aromatic compounds.

Exceptions were naphthalene which gave only traces of a red oil, and, 9-methylanthracene, which gave only 9,10-anthraquinone, indicating complete removal of the ring substituent:



Invariably, uncrystallizable oils and tars were also formed⁷⁷. Earlier workers had difficulty in isolating the quinones formed in these reactions, as they appeared to be strongly retained by the chromium residues^{7,76,63}.

Polynuclear hydrocarbons in which the rings are joined by one carbon in each ring, for example diphenyl, also undergo reaction with chromyl chloride. Thus diphenyl reacts vigorously, in glacial acetic acid solution to give benzoic acid⁴⁹.

3.5.3 Alkyl Substituted Aromatic Hydrocarbons

The first reported oxidation of an alkyl substituted benzene was carried out by Carstanjen⁴⁸ who treated toluene with chromyl chloride in glacial acetic acid. No solid intermediates were observed and the evolution of acetyl chloride was reported. The product of oxidation was benzoic acid. Other products such as complex chromium acetates, acetochromates and chlorinated products have been found by other workers⁶⁰. Using carbon disulphide as solvent, Etard obtained a brown precipitate when repeating this reaction⁵⁰. Analysis showed that this solid had the stoichiometry of an adduct: $\text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{CrO}_2\text{Cl}_2$. Hydrolysis of this adduct, gave

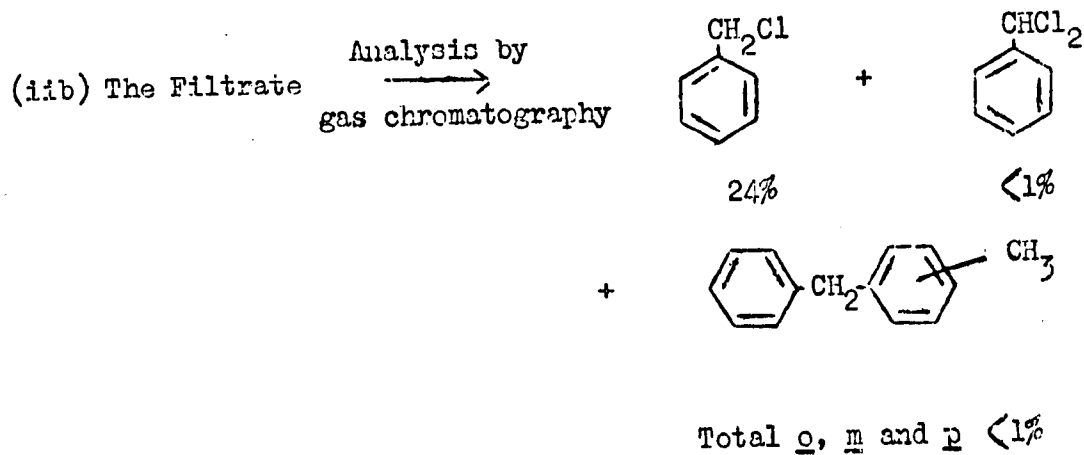
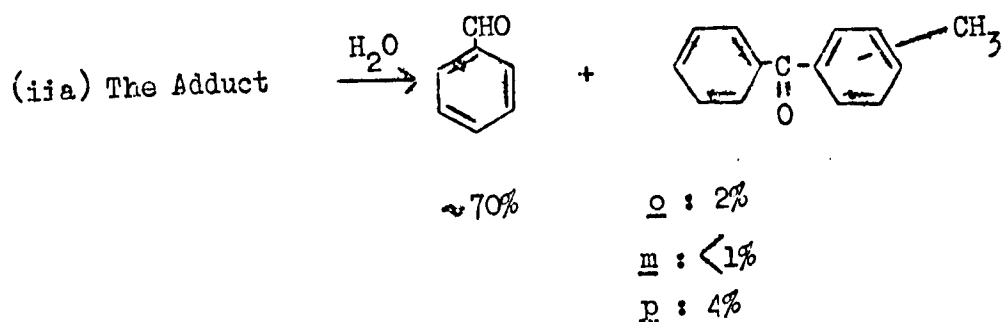
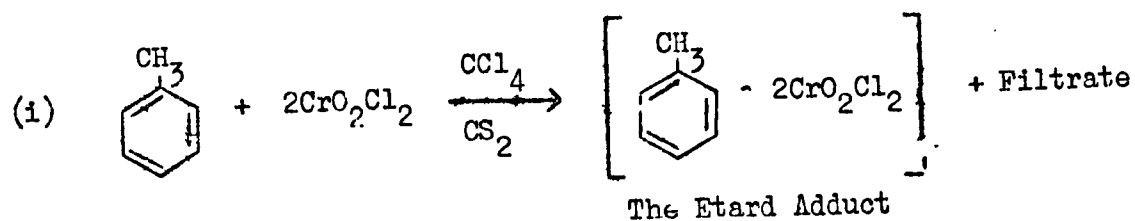
a high yield of benzaldehyde, of the order of 90%, together with small quantities of other products⁵³. Distillation of the solvent from the adduct filtrate gave an oil which contained mainly benzyl chloride but also some benzylidene chloride. It was suggested⁵ that these compounds resulted from chlorination, due to photochemical decomposition of the oxidant, but recently it has been shown⁷⁹ that these are indeed products of the toluene-chromyl chloride reaction.

The use of modern analytical techniques, such as gas chromatography, has now indicated the presence of products of the Etard reaction not found by early workers. Thus, small quantities of ortho, meta and para methyldiphenylmethanes, together with the chlorinated products described above, have been found in the filtrate resulting from the filtration of the toluene-chromyl chloride reaction mixture. If excess oxidant is present, the coupled products undergo further reaction and are in turn precipitated as their Etard complexes. Thus, careful analysis of the hydrolysis product from the Etard complex showed the presence of small amounts of the corresponding methylbenzophenones⁷⁸. The reaction of toluene and chromyl chloride is outlined in Figure 1, where the yields of the various products described above are given.

The coupled products formed in this reaction probably result from a Friedel-Crafts reaction; similar compounds have been isolated when toluene has been oxidized by manganese dioxide/sulphuric acid⁸⁰ and chromic acid⁸¹.

FIGURE 1

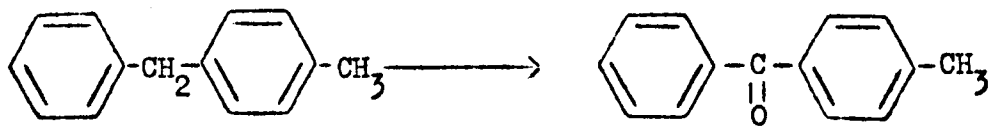
The Products of Oxidation of Toluene by Chromyl Chloride⁷⁸



The relative ratios of the products are dependent on the method of adduct preparation and other workers have reported different yields.

The oxidation of dimethyl and trimethyl benzenes is very similar to that of toluene. The experimental evidence shows that only one methyl group is oxidized. The products are dependent on the solvent used: in glacial acetic acid, the methyl group is oxidized to the acid⁴⁹, whilst in carbon disulphide and carbon tetrachloride the corresponding aldehyde results⁶⁷. The oxidation of a single methyl group is in contrast to similar oxidations by chromic acid, in which two or more methyl groups may be oxidized simultaneously⁸³. Mixed aldehydes however, have been reported as the products of the reaction between asymmetric polymethylbenzenes and chromyl chloride⁸².

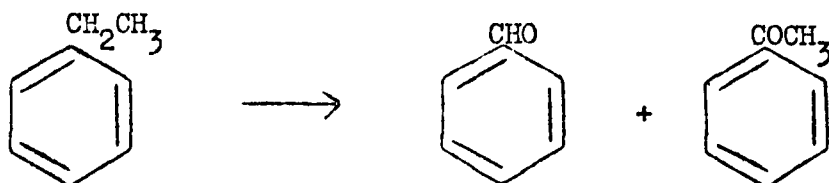
Weiler⁸⁵ found that various coupled toluenes gave the customary 2:1 chromyl chloride to toluene adduct. Decomposition of this with water gave a small amount of *p*-tolylbenzaldehyde, though the main product was a brown resin. *p*-Tolylphenylmethane gave a 62% yield of the ketone.



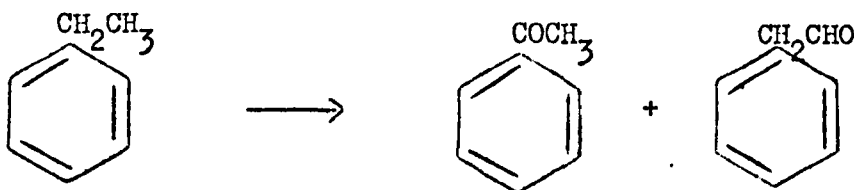
This suggests that the methylene group is more susceptible to attack by chromyl chloride than the methyl.

Oxidation of alkylbenzenes C_6H_5R where R is an aliphatic group with two or more carbon atoms leads to a multiplicity of products. While earlier workers^{38,86,87} carried out these reactions, it is only relatively recently that the full complexity of these oxidations has become apparent. Thus whereas Miller and Rohde⁸⁶ reported the formation of benzaldehyde and

acetophenone from the oxidation of ethylbenzene:



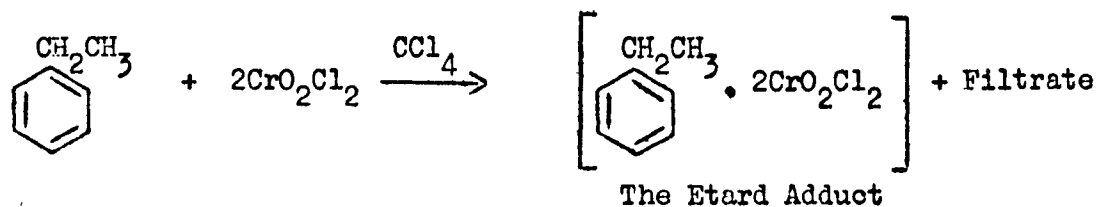
Wheeler⁸⁸ found acetophenone and phenylacetaldehyde (identified as their 2,4-dinitrophenylhydrazones):



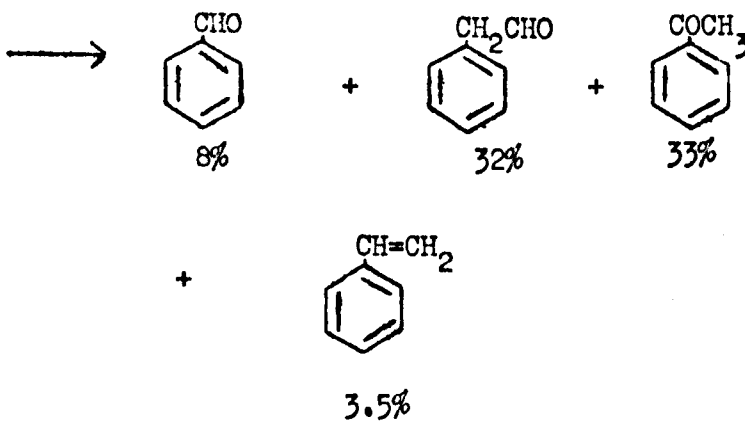
A recent systematic investigation⁸⁹ of this reaction has shown that all the previously reported products are in fact formed, the yields varying with the method of decomposition of the Etard complex and the period of time that elapses between this decomposition and subsequent work-up of the hydrolysis mixture. Other products were also reported in this investigation both from the adduct filtrate and the hydrolysis mixture. Two unexpected products were the olefins trans-1,3-diphenyl-1-butene and styrene. The latter was found in the filtrate and as a product of hydrolysis. Only one chlorinated product was found, α -chloroethylbenzene, which was present in the filtrate in low concentration. Other compounds shown to be present in the filtrate were ortho, meta and para coupled phenylethanes⁷⁸; these were thought to have been formed by a Friedel-Crafts or similar reaction. The products of the oxidation of ethylbenzene by chromyl chloride are summarised in Figure 2.

FIGURE 2

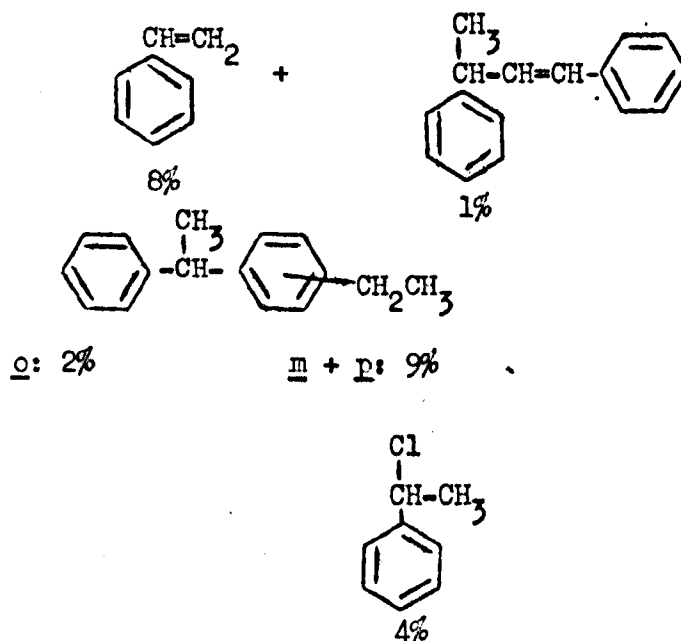
The Products of Oxidation of Ethylbenzene by Chromyl Chloride⁷⁸



Adduct Hydrolysis



Analysis of the Filtrate



The oxidation of n-propylbenzene by chromyl chloride similarly leads to a diversity of products. Amongst those reported were 'hydrocinnamaldehyde',³⁸ ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CHO}$), methylbenzylketone, benzaldehyde and propiophenone^{86,90} as well as unidentified chloroketones⁸⁷.

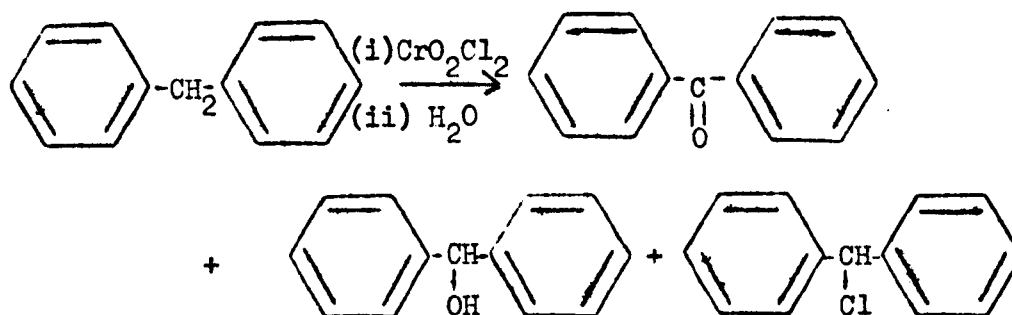
Wiberg and his co-workers¹⁰⁴ have identified three components in the adduct hydrolysis mixture:

| | | |
|---------------------------|--|--------|
| 1-Chloro-1-phenylpropane: | $\text{C}_6\text{H}_5\text{CHCl}\cdot\text{CH}_2\text{CH}_3$ | (60%) |
| Methylbenzylketone: | $\text{C}_6\text{H}_5\text{CH}_2\text{COCH}_3$ | (18%) |
| Propiophenone: | $\text{C}_6\text{H}_5\text{COCH}_2\text{CH}_3$ | (3.3%) |

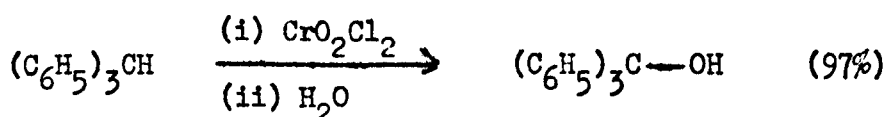
The first two components were also present in the adduct filtrate (24% and 6% respectively). It has recently been shown⁹¹ that, as in the case of ethylbenzene oxidation, the ratio of products is dependent on the method of preparation and method of hydrolysis of the n-propylbenzene-chromyl chloride adduct. In the adduct preparation, both temperature and ratio of oxidant to hydrocarbon have a significant effect on the subsequent hydrolysis products. The use of reducing agents, e.g. sulphur dioxide, in the hydrolysis solution leads to the formation of small quantities of 1-phenylpropan-1-ol, a compound which is not formed if the adduct is hydrolysed by distilled water alone.

Other substituted benzenes e.g. iso-propylbenzene and p-methyl-iso-propylbenzene also give typical Etard adducts⁹². No doubt the products of hydrolysis of these adducts are more varied than those reported by early workers^{63,85,93,94} but there have been no recent investigations of these systems.

The oxidation of diphenylmethane was initially reported to give only benzophenone in high yield^{63,85}. A recent investigation has shown that benzhydrol and benzhydryl chloride are also formed⁷³.



The case of triphenylmethane is somewhat different, as there is only one hydrogen which may be removed by the oxidant (assuming ring attack does not occur). As a consequence, hydrolysis of the triphenylmethane-chromyl chloride complex gives a high yield of triphenylcarbinol⁹⁵.



3.5.4 Halogenated Derivatives of Toluene

The effect of substituting chlorine for hydrogen in the methyl group of toluene was studied by Etard⁵⁰ and more recently by Tucker⁷⁹. Both the stoichiometry of the adduct and the rate of reaction are modified. The rate of reaction is reduced by the presence of the halogen and the ratio of reactants in the Etard complex is changed from 2:1 to 1:1 as indicated

below:

| <u>Toluene Derivative</u> | <u>Adduct Composition</u> |
|--|---|
| $\text{C}_6\text{H}_5\text{CH}_3$ | $(\text{C}_6\text{H}_5\text{CH}_3)(\text{CrO}_2\text{Cl}_2)_2$ |
| $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ | $(\text{C}_6\text{H}_5\text{CH}_2\text{Cl})(\text{CrO}_2\text{Cl}_2)$ |
| $\text{C}_6\text{H}_5\text{CHCl}_2$ | $(\text{C}_6\text{H}_5\text{CHCl}_2)(\text{CrO}_2\text{Cl}_2)$ |
| $\text{C}_6\text{H}_5\text{CCl}_3$ | No reaction |

The reaction of chromyl chloride with ring-halogenated toluenes is similar to that with toluene itself, though halogenation reduces reactivity^{65,96}. All monohalogenated toluenes form Etard complexes, and the products of hydrolysis depend on ring substituent and its position. In general *p*-halogenotoluenes react to give high yields of the corresponding benzaldehydes⁶⁵. Ortho-substituted toluenes react less readily and yields of benzaldehyde are not as high as with *p*-homologues. Some side-chain chlorination occurs; with ortho-substituted toluenes, the proportion of benzal chloride to aldehyde formed increases in the order chloro-, bromo-, iodo⁷². Thus with o-iodotoluene, the main product of oxidation is o-iodobenzal chloride, only a trace of aldehyde being formed.

Toluenes having other ortho or para substituents e.g. cyano, chloromethyl, methoxy, and mercapto gave only low yields of the expected aldehyde, though in some cases the corresponding benzoic acids were formed⁶⁵. Ring oxidation was proposed to account for the small yields of side-chain oxidation products.

3.5.5 Nitrobenzenes and Nitrotoluenes

The nitrotoluenes afford further examples of compounds, the reported oxidation products of which, vary with the investigators.

Etard^{8,51} reported the formation of nitrotoluquinones on oxidation of nitrotoluenes by chromyl chloride, whilst von Richter⁵⁷ reported the formation of nitrobenzoic acid and nitrobenzaldehyde with a large recovery of nitrotoluene. Duffin and Tucker⁹⁸ have shown that o-nitrobenzoic acid is the main product in the case of o-nitrotoluene. One reason for this conflict of observations is the coordinating power of the oxidation products. Duffin and Tucker found that the chromium in the hydrolysate was firmly complexed by the carboxylic acid, and the acid could not be extracted from the aqueous solution by solvents such as ether. This type of behaviour could have led to the presence of the carboxylic acid being overlooked by earlier workers.

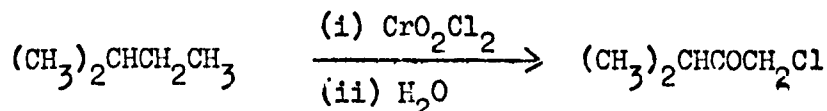
Nitrobenzene does react slowly with chromyl chloride though the stoichiometry of the product, $C_6H_5NO_2 \cdot 2CrO_2Cl_2$, is only approximate³⁸. Decomposition of this complex by water was reported to give a 'nitroquinone' but the nature of this compound has not been reinvestigated and in view of conflicting reports in the early literature⁹⁹ it would be unwise to draw any conclusion regarding this reaction.

Carstanjen⁴⁹ obtained trichloronitrobenzoic acid, by treating nitrotoluene with chromyl chloride in glacial acetic acid, but this was later shown to have been derived from an impurity in the original reagent⁹⁷.

As in the case of dinitrotoluenes, no reaction takes place between chromyl chloride and di- and trinitrobenzenes⁵.

3.5.6 Alkanes

Etard found that when substituted aliphatic hydrocarbons were treated with chromyl chloride in an inert solvent insoluble 'addition products' similar to those formed with toluene were produced^{38,52}. Thus 2-methylbutane yielded an insoluble adduct, $C_5H_{12} \cdot 2CrO_2Cl_2$. Decomposition of this complex with water gave a chlorinated ketone of composition C_5H_9OCl , which was identified, as its bisulphite compound, to be 1-chloro-3-methyl-2-butanone, i.e.

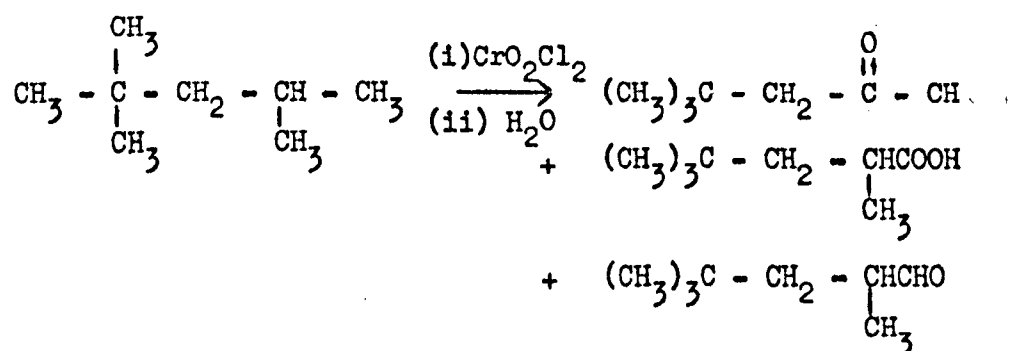


Other unidentified compounds were also said to be present in the hydrolysis mixture. Hexane and n-heptane were treated in a similar manner and the formation of chlorinated ketones was reported³⁸.

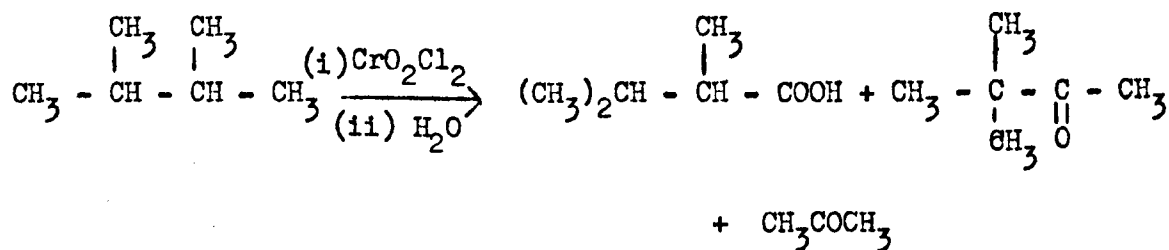
Hobbs and Houston¹⁰⁰, using various alkanes, repeated the work of Etard and reported the formation of a number of isomeric ketones. Thus n-hexane gave both 2- and 3-hexanone but no chlorinated products, but 2-methylbutane gave 3-methyl-2-butanone as well as the chlorobutanone reported by Etard. All the hydrocarbons oxidized by Hobbs and Houston gave typical Etard adducts though the stoichiometry of certain of the complexes was unusual: 2,5-dimethylheptane gave an adduct of composition

$C_9H_{20} \cdot 3CrO_2Cl_2$, whilst certain others gave adducts of composition intermediate between $RH \cdot 2CrO_2Cl_2$ and $RH \cdot 3CrO_2Cl_2$. This compares with the work of Crook¹⁰¹ who found that the chain length of an alkane was an important factor in determining the adduct stoichiometry. With long chain alkanes e.g. 2,7-dimethyloctane adducts with a ratio of hydrocarbon to chromyl chloride as high as 1:4 were obtained.

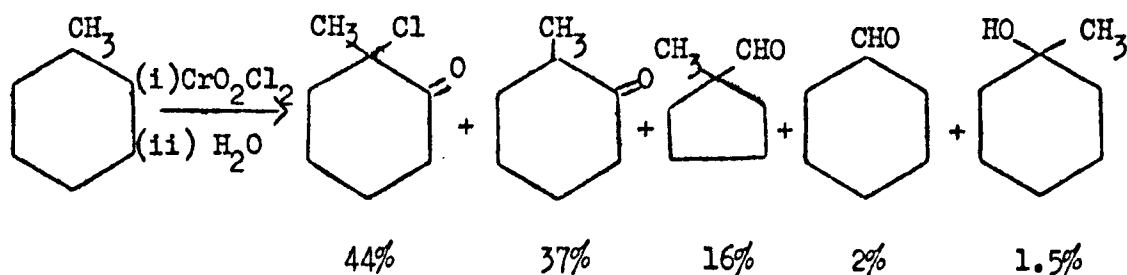
The yields of the complexes prepared by Hobbs and Houston were found to be dependent on the presence of a tertiary carbon atom - where such an atom was present, the yield was essentially quantitative; when the hydrocarbon did not possess a tertiary carbon, the reaction was noticeably slower, and the yield of adduct was not quantitative. The adducts, on hydrolysis, yielded mixtures of aldehydes, ketones and in certain cases acids. The tertiary or terminal positions were usually the sites where oxidation occurred. Thus 2,2,4-trimethylpentane gave the following products:



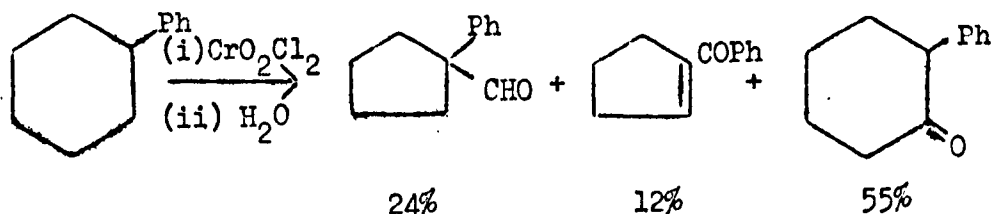
and 2,3-dimethylbutane gave 2,3-dimethylbutanoic acid, the rearranged product 3,3-dimethyl-2-butanone and some acetone, a product of carbon-carbon bond cleavage:



The reactions of cyclic aliphatic hydrocarbons with chromyl chloride give the expected Etard complexes^{100,102,103}, though the reactions are not rapid. In some cases, a trace of olefin (less than 1%) added to the reaction mixture initiates a relatively fast reaction¹⁰². Hydrolysis of the complexes gives ketonic and chlorinated products but no ring fission has been reported. For example cyclohexane yields either cyclohexanone¹⁰⁰ or cyclohexylchloride¹⁰³ depending on reaction conditions. Methylcyclohexane shows little tendency to react with chromyl chloride at room temperature but addition of a trace of olefin as above initiates a reaction which gives a good yield of adduct (85%)¹⁰². The product of the decomposition of the adduct by water was reported as hexahydrobenzaldehyde but Wiberg et al¹⁰⁴ repeated this work and suggested the main product was the isomeric 2-methylcyclohexanone. They also identified a chlorinated product, 2-chloro-2-methylcyclohexanone. This situation has recently been clarified⁹¹, and all the above products have been shown to be present along with others not previously reported; namely 1-methylcyclopentylaldehyde (a product of rearrangement) and 1-methylcyclohexanol⁹¹:



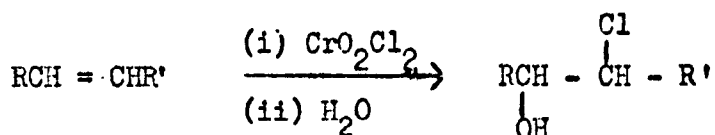
Phenylcyclohexane is oxidized by chromyl chloride in a manner similar to that of methylcyclohexane. The products of oxidation show that considerable ring contraction occurs:



3.5.7. Alkenes and other Olefins

Chromyl chloride reacts readily with olefins: typical adducts of approximate stoichiometry $\text{RCH} = \text{CHR}' \cdot 2\text{CrO}_2\text{Cl}_2$ ^{57,58,103,106} are formed.

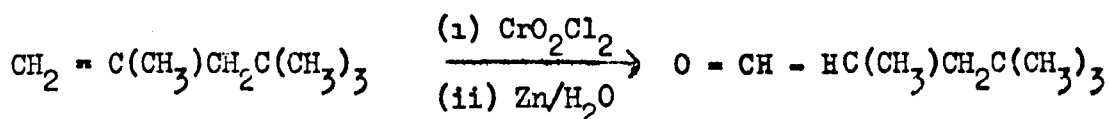
Hydrolysis of the adducts obtained from simple aliphatic olefins yields mainly the chlorohydrin corresponding to trans addition¹⁰³:



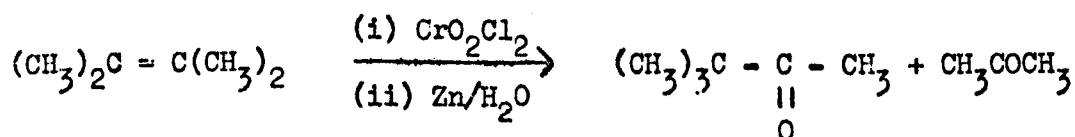
Terminal olefins, i.e. those where $\text{R}' = \text{H}$, give the chlorohydrin corresponding to anti-Markovnikoff addition of hypochlorous acid¹⁰³. Cyclic olefins give similar chlorohydrins and it has been shown⁷⁴ by the use of ^{18}O tracers that, in the case of cyclohexene, all the oxygen in the 2-chloro-cyclo-hexanol comes from the chromyl chloride. The minor products of these oxidations have been investigated and are chloroketones and aldehydes, as well as small amounts of cis-chlorohydrins¹⁰⁶.

A modification of the Etard reaction with olefins, conducted by Freeman and co-workers¹⁰⁷, has led to the preparation of aldehydes and ketones in good yields. Their procedure differs from previous methods primarily by the introduction of a reductive hydrolysis step. Instead of isolating the Etard complex and then hydrolysing it, the reaction mixture itself, containing excess oxidant and Etard complex, is treated with an excess of powdered zinc shortly after mixing of reactants is complete. The zinc decomposes any excess chromyl chloride¹⁰ and prevents further oxidation. A mixture of ice and water is then added, the complex thus being hydrolysed in situ in the presence of an excess of zinc. By this method, secondary reactions such as further oxidation, chlorination and bond cleavage which may occur during isolation of the adduct and during non-reductive hydrolysis, are reduced to a minimum.

In typical reactions carried out as above, 2,4,4-trimethyl-1-pentene yielded 2,4,4-trimethyl-1-pentanal (76%):

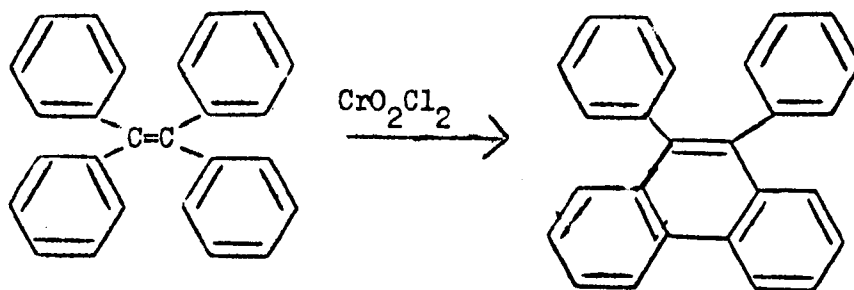


2,3-Dimethyl-2-butene gave pinacolone (50%) with only a small amount of acetone, the cleavage product¹⁰⁷:

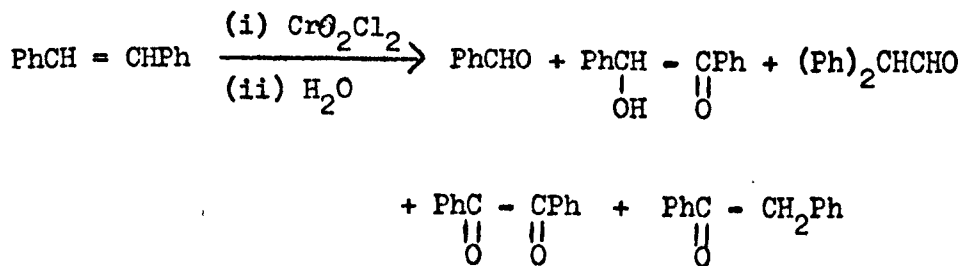


Likewise 1-phenylpropene gave only benzylmethyl ketone and benzaldehyde and no other products⁶⁹. By comparison, the oxidation of 1-phenylpropene by the usual Etard scheme yields six products, including chlorinated and rearranged compounds⁹¹.

The reaction of chromyl chloride with tetraphenylethene¹⁰⁸ occurs rapidly, even at low temperature, to form the usual brown precipitate. Hydrolysis of the filtered solid however, gives only a small yield of yellow oil but the filtrate contains 9,10-diphenylphenanthrene, in a 70% yield:



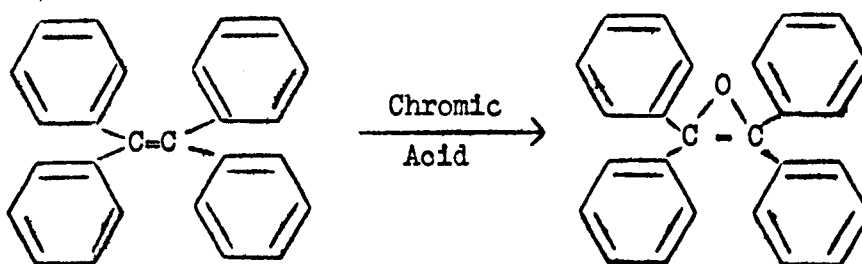
This cyclization has no parallel in other olefin oxidations by chromyl chloride: the oxidation of both cis and trans-stilbene yields only aldehydic or ketonic products¹¹⁶ such as benzaldehyde, benzoin, diphenylacetaldehyde, benzil and phenylbenzyl ketone. No phenanthrene or phenanthraquinone, the chromyl chloride oxidation product of phenanthrene, have been detected¹⁰⁸.



Chromyl chloride also fails to cause ring closure with 1,1-binaphthyl, hexaphenylbenzene or *o*-terphenyl¹⁰⁸, though Lewis acids such as aluminium chloride or stannic chloride are effective in these cases.

This suggests that chromyl chloride, even in this special case, does not act as a Lewis acid, despite earlier suggestions that it does^{77,69}.

By comparison the oxidation of tetraphenylethene by chromic acid gives the corresponding epoxide and benzophenone as the only products, their ratio depending on the amount of oxidant used;¹⁰⁹

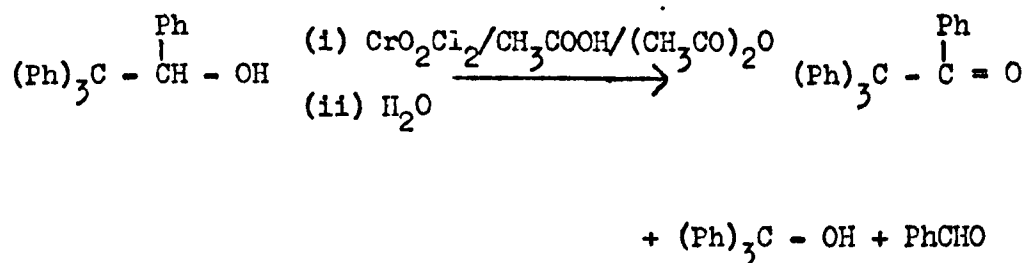


3.5.8 Alcohols

Very little work has been carried out on the reaction of alcohols with chromyl chloride. Walter⁴³ found that many alcohols were spontaneously ignited by chromyl chloride, so he abandoned the work.

Mosher and Celeste⁷⁰ reported the reactions of chromyl chloride with many secondary alcohols; they found that solid complexes of empirical formula $\text{ROH} \cdot 2\text{CrO}_2\text{Cl}_2$ could be isolated when the reaction was carried out in carbon tetrachloride.

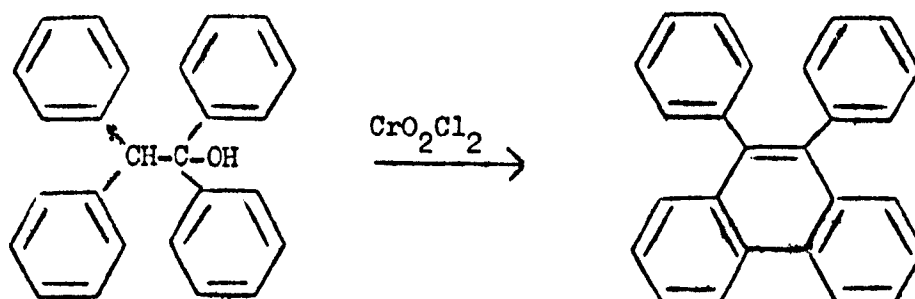
Similar reactions, carried out in other solvent systems, e.g. acetic acid/acetic anhydride, were examined but no intermediates were isolated; in these cases the reaction mixture was treated directly with water and the organic products extracted by solvent. The organic products were ketones, formed by direct oxidation of the hydroxyl group, and cleavage products, e.g. with benzpinacolyl alcohol:



The major product was always the ketone; it was observed that addition of a small amount of pyridine to the reaction mixture reduced the amount of cleavage considerably.

Primary and tertiary alcohols also give typical Etard adducts¹¹⁰. Hydrolysis of those derived from primary alcohols gives a mixture of components, of which the ester derived from the alcohol is the major constituent. The hydrolysis products of adducts derived from tertiary alcohols are complex and their characterization has yet to be carried out.¹¹⁰

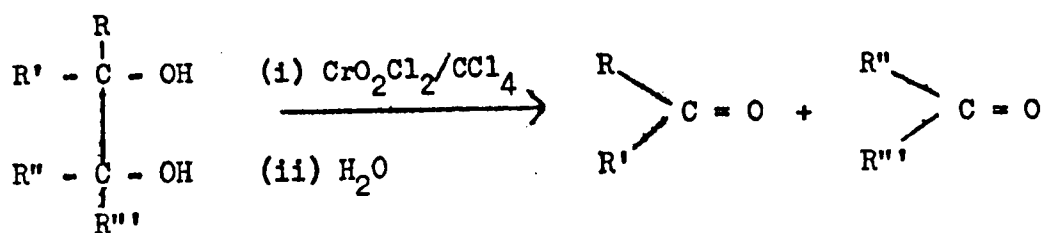
There is one exception to this, and that is the oxidation of 1,1,2,2-tetraphenylethanol¹¹¹. Reaction of this alcohol with chromyl chloride gives a high yield (>80%) of 9,10-diphenylphenanthrene



This is the same product which is obtained on oxidation of tetraphenylethene¹⁰⁸ (see section 5.7 of this Chapter).

3.5.9 Glycols

The oxidation of glycols takes place, via the usual Etard scheme and results in carbon-carbon bond fission to give aldehydes or ketones, or mixtures of the two, depending on the structure of the original glycol¹¹²:



R, R'' = alkyl or aryl groups

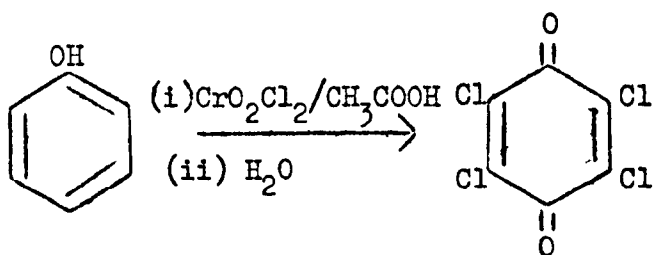
R''', R' = alkyl or aryl groups

or hydrogen atoms

The products, characterized by their 2,4-dinitrophenylhydrazones, were not formed quantitatively. By carrying out similar reactions, but in glacial acetic acid rather than carbon tetrachloride, and adding the reaction mixture directly to a solution of 2,4-dinitrophenylhydrazine reagent containing excess ferrous sulphate, quantitative fission was achieved. Evidently the free aldehydes were susceptible to further oxidation under the hydrolysis conditions employed.

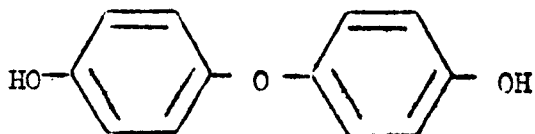
3.5.10 Phenols

Carstanjen⁴⁹ treated phenol with chromyl chloride in glacial acetic acid and reported a vigorous reaction. On addition of a large excess of water, a yellow-brown solid resulted from which chloranil and unspecified chloroquinones were obtained.



Etard⁷ reported that the direct treatment of phenol with chromyl chloride was very violent. As a result he carried out the reaction with both phenol and oxidant in dry carbon disulphide. The reaction took place smoothly to give a brown solid; analysis showed that this solid did not have the exact stoichiometry expected for an adduct.

Hydrolysis of the solid with dilute alkali gave chromium salts and an uncrystallizable, whitish solid, of empirical formula $\text{C}_{12}\text{H}_{10}\text{O}_3$. Oxidation of this product gave 1,4-benzoquinone, so Etard^{7,38} considered it to be the 'ether of hydroquinone':



Both ortho and para-cresol gave similar brown solids⁸ with chromyl chloride. Decomposition by water, in the presence of sulphur dioxide, gave alkali soluble compounds which 'had the nature of quinones'. Elemental analysis of the compound from o-cresol gave the empirical formula as $\text{C}_7\text{H}_6\text{O}_3$; that from

p-cresol as $C_{14}H_{10}O_3$, but no further identification was carried out.

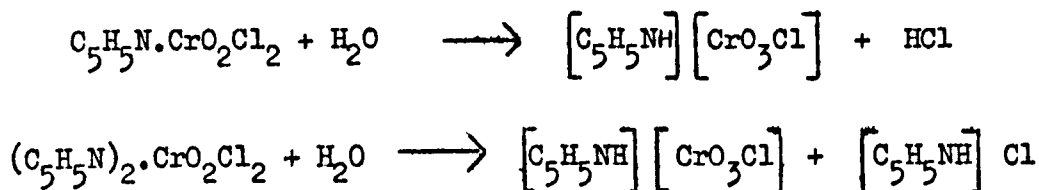
Etard³⁸ did not consider the brown solids formed in the phenol and cresol reactions to be true 'addition compounds', such as those between toluene and chromyl chloride. This was due to their non-stoichiometric composition, which Etard ascribed to the presence of the -OH group. He believed that this group led to the partial decomposition of the 'addition compound', in a manner similar to that by water, with the subsequent formation of acids of chromium and other products and hence non-stoichiometric complexes.

Similar complexes have been reported for chlorophenols and phenoxytrichlorosilanes¹¹³, i.e. phenols with the phenolic hydrogen replaced by $-SiCl_3$. These complexes yield, on hydrolysis, p-benzoquinones and resinous, apparently polymeric, material. The yield of 1,4-benzoquinone was shown to be dependent on the degree of chlorination of the original phenol: thus o-chlorophenol gives only a small yield of 2-chloro-1,4-benzoquinone, whilst pentachlorophenol gives a yield of chloranil in excess of 70%.

The only report other than that of Etard, of an oxidation of an alkyl-substituted phenol, is that of Wheeler⁶⁵. He attempted to oxidize the methyl group of p-cresol with chromyl chloride, but hydrolysis of the intermediate complex gave only an intractable tar and some starting material. Addition of 2,4-dinitrophenylhydrazine reagent to the hydrolysis product gave no precipitate, indicating the absence of an aldehydic product.

3.5.11 Heterocyclic Compounds

Various heterocyclic compounds have been reported to give Etard adducts. Pyridine⁷¹, for example, when treated with chromyl chloride in carbon tetrachloride solution at -20° gives either $\text{CrO}_2\text{Cl}_2 \cdot \text{C}_5\text{H}_5\text{N}$ or $\text{CrO}_2\text{Cl}_2 \cdot 2\text{C}_5\text{H}_5\text{N}$, depending on the mole ratio of reactants. Both complexes are brown solids which hydrolyse readily and are decomposed by light at room temperature. The products of hydrolysis by a large volume of water are complex brown oils containing oxidation products of pyridine, and chromium (III) species. However, controlled hydrolysis, using moist air gives pyridinium chlorochromates:



The reaction of 2-picoline and 2-picoline-N-oxide with chromyl chloride in carbon tetrachloride and at room temperature, results in brown solids, similar in appearance to other Etard adducts, being formed⁷⁷. On decomposition by water, only the original starting material could be recovered, and it was concluded that these complexes were salts between the base and chromyl chloride, the latter acting as a Lewis acid. Similarly the complex between 3-methylthiophene and chromyl chloride yielded no oxidation products on hydrolysis, only the original thiophene.

Similar results were obtained with tetrahydrofuran, dioxan and 4-picoline by Makhija and Stairs¹¹⁴, who initially thought the Etard adducts of these compounds to be Lewis complexes. Magnetic susceptibility measurements later disproved this postulate, showing that the chromium was present as chromium (IV) and not as chromium (VI).

As a consequence, a more careful study of the hydrolysis products of these complexes was carried out, and in all cases oxidation products were identified.

3.5.12 Miscellaneous Compounds

The reaction between chromyl chloride and compounds containing nitrogen, phosphorus, arsenic, oxygen and sulphur has been investigated recently¹¹⁴. It was believed that the presence of potential electron donating atoms or groups might modify the usual course of the Etard reaction. Complexes of varying stoichiometries were prepared¹¹⁴ and their hydrolysis products are shown in Table 3.

The infrared spectra of the triphenylphosphine and triphenylarsine complexes show bands which have been assigned to $P = O$ and $As = O$ stretching vibrations, shifted to lower frequency. This was considered to be evidence for the presence, in the complexes, of triphenylphosphine and arsine oxides coordinated to a reduced chromium species¹¹⁴.

Many ethers undergo oxidative cleavage on reaction with chromyl chloride; thus diethyl ether gives acetaldehyde as well as ethyl acetate¹¹⁴ (see Table 3).

Nenitzescu et al¹¹⁵ have shown that, unlike other chromyl chloride oxidations, the oxidation of an ether results in a considerable part of the reaction product remaining in solution, only a fraction of the product being found on hydrolysis of the Etard complex. Analysis of the complexes derived from various

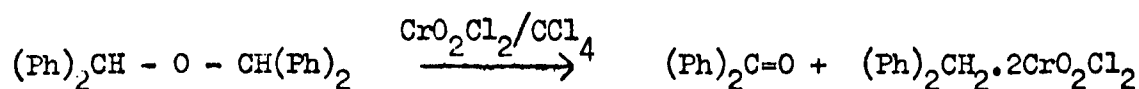
TABLE 3

The Reaction of Compounds containing Electron-donating Atoms,

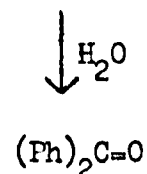
with Chromyl Chloride¹¹⁴

| Starting Material | Ratio $\text{CrO}_2\text{Cl}_2:\text{X}$ in complex | Product of Complex Hydrolysis | Yield % |
|--------------------|---|--------------------------------------|------------|
| Dimethylsulphoxide | 1:2 | Dimethylsulphone | - |
| Acetone | 1:2 | Acetone | - |
| Diethyl ether | 1:1 | Ethylacetate and Acetaldehyde | - |
| Triphenylamine | 2:1 | Tetraphenylbenzidine | 60 |
| Triphenylphosphine | 1:1 | Triphenylphosphine oxide | 75 |
| Triphenylarsine | 1:1 | Triphenylarsine oxide monohydrate | 75 |

ethers and of their corresponding filtrates shows that the oxidative cleavage takes place during the formation of the Etard complex, prior to its hydrolysis. A typical example¹¹⁵ was the reaction of dibenzylhydryl ether with chromyl chloride to give benzophenone. Most of the ketone formed was found in the filtrate which remained after the insoluble complex was removed:



In solution The Etard complex



The oxidative cleavage was, in this case, quantitative. It is significant to note that the above Etard complex was said to be identical to that formed by the reaction of chromyl chloride with diphenylmethane⁷³.

CHAPTER 4

THE MECHANISM OF THE ETARD REACTION

4.1 Introduction

In this chapter a review is made of the postulated mechanisms for the different forms of the Etard reaction.

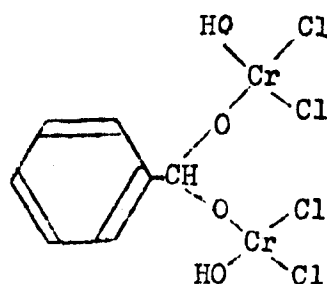
4.2 The Formation of the Etard Complex

Although the Etard reaction has been known and studied for almost a century, most of the reported work on the reaction has only been concerned with identification of the products of hydrolysis of the Etard complexes. In many cases there has been little or no attempt to correlate the formation of various products with a definite mechanism, and in the few cases where this has been done, the results have been contradictory. Although there are some similarities in the mode of reaction of chromyl chloride with different classes of organic compounds, there is evidence that the role of the oxidant towards hydrocarbons (both aromatic and aliphatic), olefins, and hydroxy compounds is different in each case, and hence each class of organic compound will be considered separately.

4.2.1 Aromatic Hydrocarbons

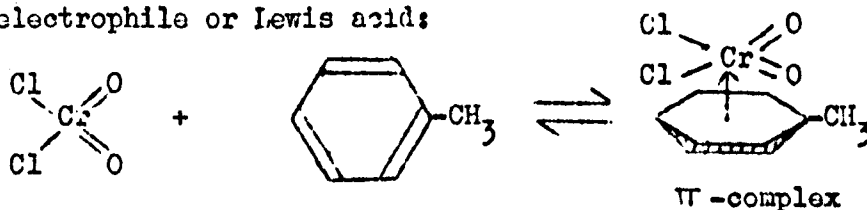
Although many different structures were suggested for the Etard complexes of aromatic hydrocarbons, by early workers, there were very few proposals for a reaction pathway⁵.

In the case of toluene oxidation, Etard considered that the hydrocarbon had been oxidized before complex formation occurred and he proposed the following structure for the complex³⁸:

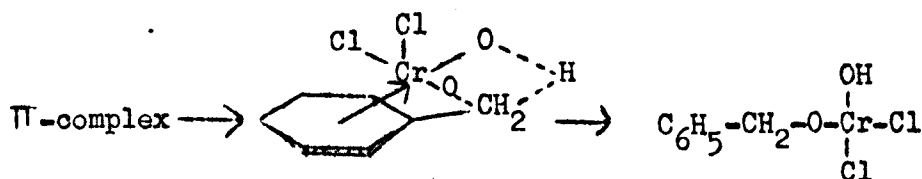


Despite the suggestion of other workers (see section 3 of this chapter) it is now generally accepted that Etard complexes of hydrocarbons do in fact contain oxidized organic species and reduced forms of chromium^{95,117,118,119}; magnetic susceptibility measurements suggest that the chromium is present in oxidation states between (III) and (VI)^{88,119,120}. Thus the first stage in the reaction must be attack by the oxidant on the hydrocarbon, leading to carbon-hydrogen bond cleavage.

Both Wheeler⁸⁸ and Stairs⁹⁶ believed that the initial stage of the reaction was the formation of a π -complex between the aromatic ring and the oxidant, the chromyl chloride acting as an electrophile or Lewis acid:



followed by rearrangement through a cyclic transition state to give a chromium (IV) ester⁹⁶:

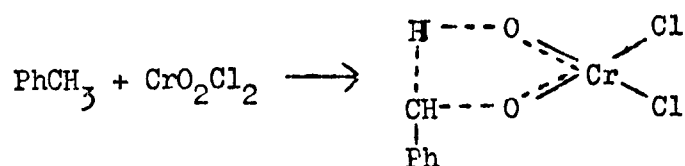


The kinetics of the toluene-chromyl chloride reaction were found to be first order in chromyl chloride¹²¹, it was hence thought that only one molecule of the oxidant is involved in the transition state. It is the addition of the second molecule of chromyl chloride to the ester which would then give the Etard complex⁹⁶.

The evidence for the formation of the π -complex was obtained from both kinetic⁹⁶ and spectroscopic⁸⁶ observations.

The reaction rates of the oxidation of a number of substituted toluenes by chromyl chloride was studied by Stairs⁹⁶, and Duffin and Tucker¹²².

Duffin and Tucker described the reaction in terms of the direct formation of the cyclic transition state:



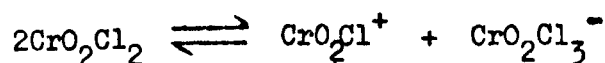
However, they concluded that it was still not clear whether the initial role of the oxidant was that of an electrophile or a free radical reagent.

Stairs⁹⁶ analysed his kinetic results by means of a Hammett treatment and claimed support from this for π -complex formation. In a later paper, Duffin and Tucker¹²³ disputed this conclusion, claiming that invalid assumptions had been made.

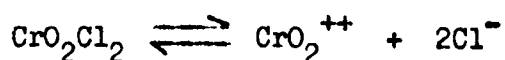
On the basis of further experimental evidence, they affirmed their proposal that the first stage involves the formation of a cyclic transition state.

Bartecki¹¹⁹ has suggested that the spectroscopic results⁸⁸ have been misinterpreted and that the spectra are not explicable in terms of the complexes as proposed. He argued further that the spectra differed only slightly from those of the starting materials and were completely different from the spectra of the Etard complexes obtained by himself.

An alternative interpretation of the kinetic measurements suggests¹²⁴ that the reaction takes place via an ionic mechanism, following an initial ionization step:



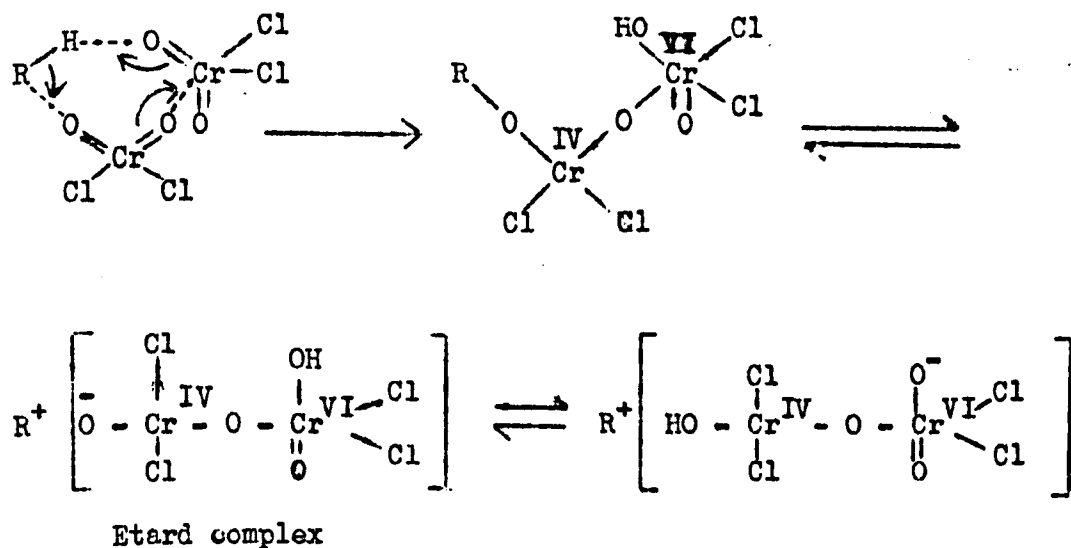
but Wheeler¹²⁵ considered this unlikely in view of the non-polar nature of the solvents used for the reaction. The only evidence¹²⁶ for the ionization of chromyl chloride in these solvents has been interpreted in terms of the dissociation:



However, no mechanisms which involve the presence of the CrO_2^{++} ion have been postulated by any of the workers investigating the Etard reaction.

Neitzescu and his co-workers⁹⁵ proposed a mechanism for the oxidation of hydrocarbons, which is similar to that used to explain the analagous oxidations by chromic acid.

Their conclusions have been based on a study of the products of hydrolysis of the Etard complexes of various alkylated benzenes. A cyclic transition state, similar to that proposed by Rocek¹²⁷ for the chromic acid oxidation of hydrocarbons, was proposed. It differed only in the suggestion that two moles of oxidant were involved rather than one:

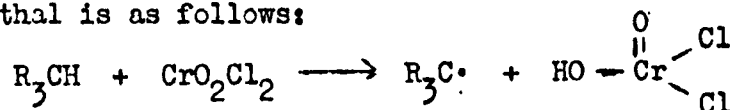


Chromyl chloride was considered⁹⁵ to be a strongly electrophilic reagent, causing the hydride abstraction illustrated above. The evidence for both chromium (VI) and chromium (IV) in the Etard complexes was obtained from the electron spin resonance spectrum of the Etard complex formed from triphenylmethane.

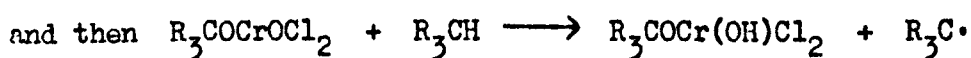
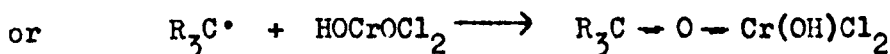
Wiberg and Eisenthal¹¹⁸ did not agree with this interpretation and indicated that the results of Nenitzescu et al⁹⁵ were in agreement with the argument that both chromium atoms were in a (IV) oxidation state. The other proposals of Nenitzescu and his co-workers⁹⁵ were considered to be inconsistent with the experimental results, and Wiberg and Eisenthal¹¹⁸ suggested that hydrogen atom abstraction was the initial step.

They also considered that there was little evidence for the formation of the cyclic intermediates in chromic acid oxidation and further indicated that there was no reason to expect the formation of such intermediates with the structurally similar chromyl chloride.

The first stage in the oxidation, as proposed by Wiberg and Eisenthal is as follows:

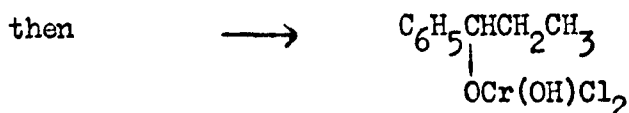
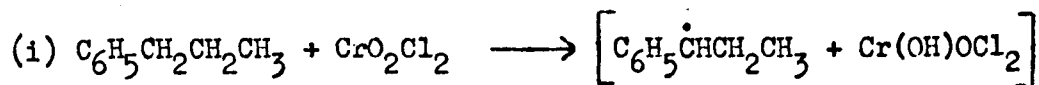


This is followed by further reaction of the radical with the chromium (V) species or with excess chromyl chloride:

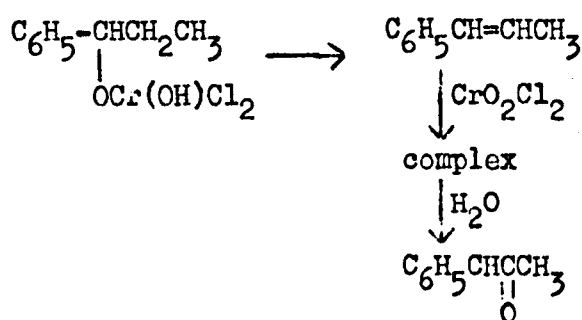


Wiberg also interpreted¹⁰⁴ the oxidation of n-propylbenzene by chromyl chloride with a similar mechanistic scheme.

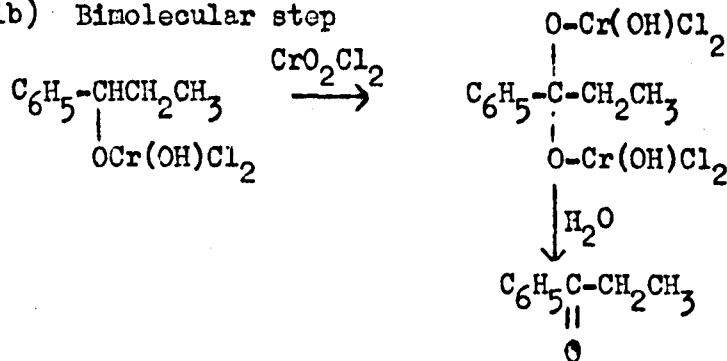
He proposed that the observed dependence of product ratio on the concentration of chromyl chloride was due to competition between two secondary steps, one of which is unimolecular and one of which is bimolecular.



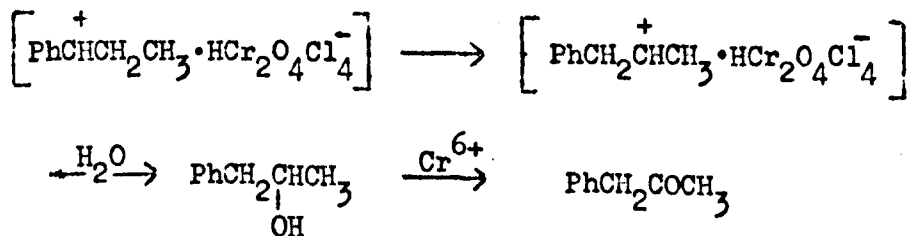
(iia) Unimolecular step



(iib) Bimolecular step

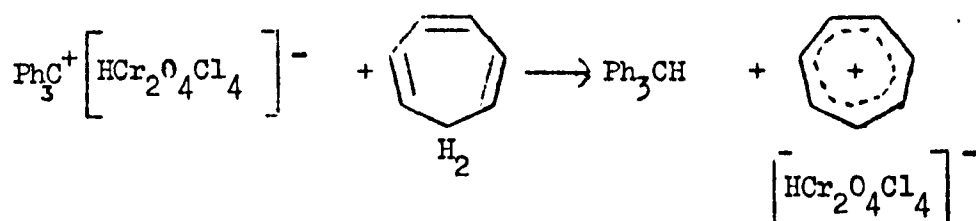


The comparable sequence proposed by Nonitzescu et al⁹⁵ using their ionic mechanism is as follows:



Wiberg and Eisenthal¹¹⁸ disapproved of this scheme because the major product, benzylmethyleketone is derived from the least stable carbonium ion.

Despite these objections, in a subsequent report, Nenitzescu et al⁹¹ again proposed a carbonium ion mechanism for the oxidation of n-propylbenzene and other hydrocarbons. Indeed, they claim that there is further evidence for this scheme, in the results obtained from the reaction of the Etard complex of triphenylmethane with hydride donors such as cycloheptatriene and xanthene^{73,111} e.g.



In both cases nearly quantitative yields of triphenylmethane were obtained, the tropylium and xanthylum ions being isolated as their perchlorates. All of the subsequent oxidations carried out by Nenitzescu and his coworkers have been interpreted using the carbonium ion mechanism^{78,89,91,105,111,115,116,128,129}.

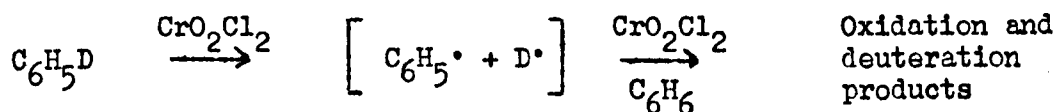
Duffin and Tucker¹²² have pointed out that, if chromyl chloride is the strong electrophile suggested by Nenitzescu et al then attack of the aromatic ring would occur during the oxidation of alkylbenzenes by chromyl chloride, but as yet no evidence of such a reaction has been reported. Ring attack does occur during the oxidation of certain aromatic hydrocarbons by chromic acid at elevated temperature¹³⁰; for example t-butyl benzene is oxidised via trimethyl acetic acid to acetic acid itself.

Despite the differences between the mechanisms as proposed by the different groups of workers, there appears to be agreement that the rate determining step, in the oxidation of hydrocarbons is the breaking of a carbon-hydrogen bond. Both Wheeler¹²⁵, and

Gragerov and Ponomarchuk¹³¹ found a significant deuterium isotope effect in the oxidation of toluene, but such an effect was not observed during the oxidation of benzene, where the rate-determining step was assumed to be formation of a molecular complex¹³¹.

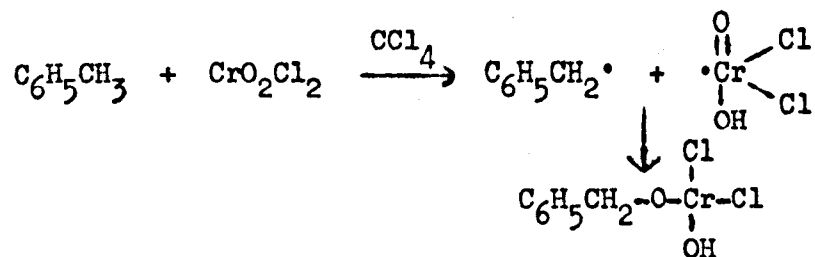
The evidence does not indicate unambiguously whether hydride ion or hydrogen atom transfer takes place, and, in this respect the position is still unclear.

Some recent work¹³² tends to support a free radical mechanism. When an excess of monodeuterated benzene was treated with chromyl chloride, residual, apparently unreacted, benzene contained species with a higher degree of deuteration, this was explained in terms of the following scheme:

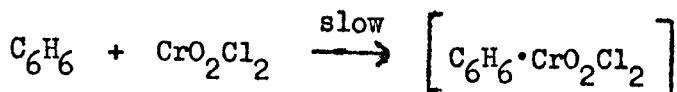


Control experiments supported this as the most probable mechanism, and eliminated the possibility that the exchange is catalysed by hydrogen chloride. Similar effects were reported for toluene, diphenylmethane and polynuclear aromatic hydrocarbons such as naphthalene and anthracene, deuterated to various degrees. The mechanism¹³² suggested for these reactions is as follows:

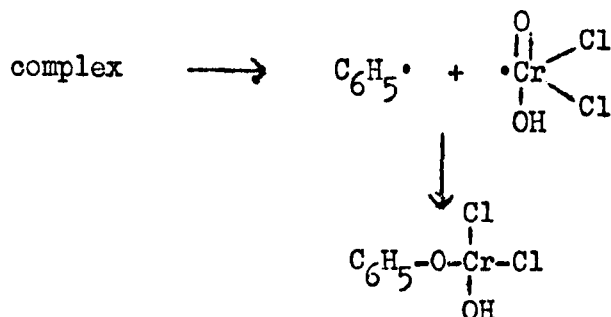
(a) Toluene etc.



(b) Benzene, naphthalene etc.



π -complex



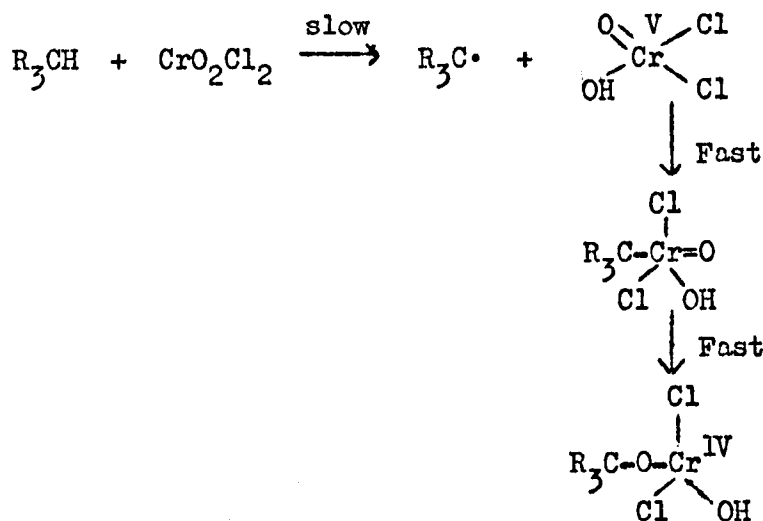
A second reaction then occurs with the second molecule of chromyl chloride.

The free radical mechanism has received substantial support from the direct observation¹³³ of radicals in these reactions. Aromatic compounds similar to those above were treated with chromyl chloride in carbon disulphide at temperatures between -80° and -50° , and the resulting solutions studied by electron spin resonance spectroscopy. In all cases radical signals were observed but these did not correspond to the expected species. Thus there was no evidence for the radicals $\text{C}_6\text{H}_5\text{CH}_2\cdot$ (from toluene) or $(\text{C}_6\text{H}_5)_3\text{C}\cdot$ (from triphenylmethane). Only in the case of 2,6-di-*t*-butyl-4-methylphenol was the expected radical signal observed.

The e.s.r. spectra were interpreted as being due to either secondary radical formation, or the formation of mixtures of radicals by the further reaction of the chromium (V) species produced in the initial reaction. An earlier reference¹³⁴ to electron spin resonance signals observed in chromyl chloride

oxidations appears to have been overlooked by some of the later workers: e.s.r. signals were obtained from mixtures of chromyl chloride with aliphatic and aromatic acids. It was further reported that the signals altered with time.

In their review, Hartford and Darrin⁵ proposed a free radical mechanism, analogous to that suggested by Slack and Waters¹³⁵ for the oxidation of hydrocarbons by chromium trioxide in glacial acetic acid:

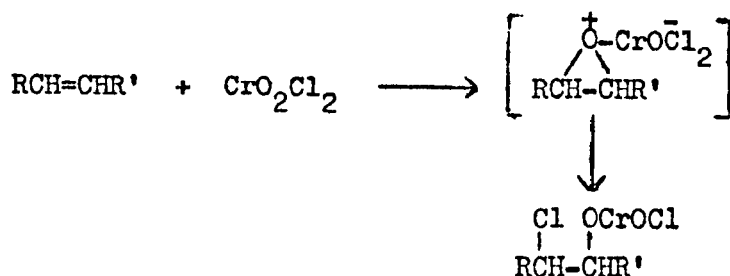


However, although they proposed this scheme as a possible reaction pathway, Hartford and Darrin concluded that the solid complex was more likely to be based on a hydrogen bonded system containing chromium (VI) (see page 61).

4.2.2 Olefins

The mechanism of the oxidation of olefins by chromyl chloride appears to be better understood than that of the oxidation of hydrocarbons.

One mole of chromyl chloride takes part in the main reaction, which probably involves electrophilic attack on the double bond by an oxygen of chromyl chloride^{103,106,116,136}. A cyclic oxonium ion intermediate would then account for the observed products of reaction (see Chapter 3, section 5.7).

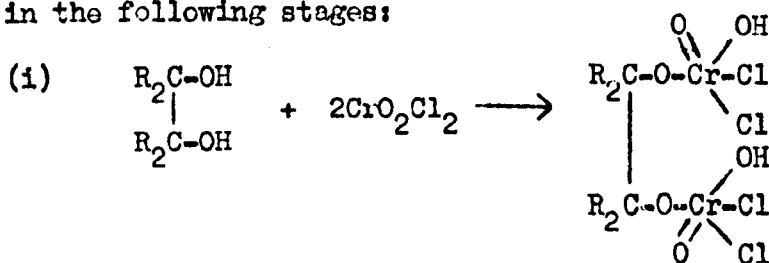


Sulima and Gragerov⁷⁴ have shown, by the use of ¹⁸O tracers, that, in the case of the oxidation of cyclohexene, all the oxygen in the 2-chlorocyclohexanol is derived from the chromyl chloride.

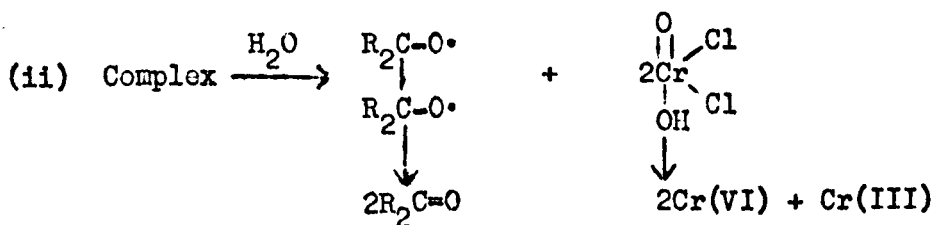
The oxidation of tetraphenylethene to 9,10-diphenylphenanthrene (see page 37) has been explained using a modified version of the above mechanism¹⁰³.

4.2.3 Hydroxycompounds

Slack and Waters¹¹² studied the oxidation of glycols by chromyl chloride, and suggested the reaction proceeded in the following stages:

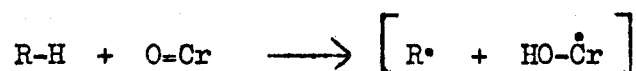


The Etard Complex

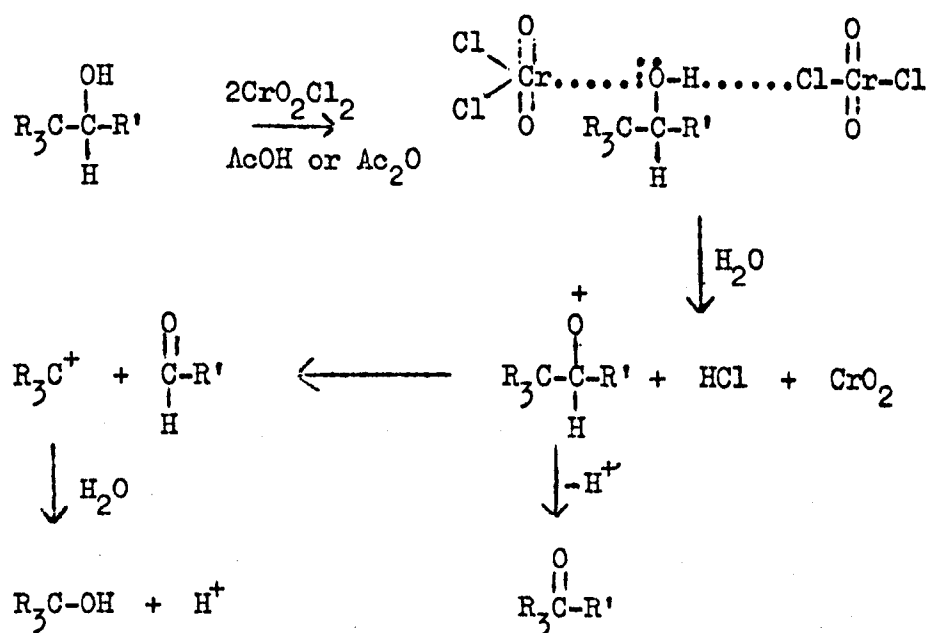


They considered the bonds C-O-Cr as essential to the system as neither hydrogen nor chlorine was lost during complex formation.

In a subsequent paper¹³⁵, it was suggested that radicals might take part in the primary stage of the reaction, especially when hydrocarbons (as opposed to glycols) were being oxidized. This statement was qualified by the proposal that the radicals were never completely 'free', but always associated with another one:



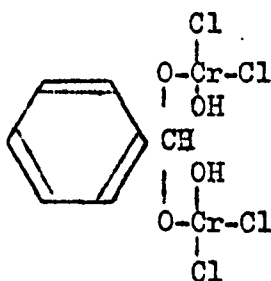
Mosher and Celeste⁷⁰, who studied the oxidation of secondary and tertiary alcohols using acetic acid or anhydride as solvent, found similar cleavage products to those formed by the oxidation of glycols. They did not agree with Slack and Waters' mechanism and suggested the following sequence involving formation of a hydrogen-bonded intermediate, followed by hydride ion abstraction:



4.3 The Structure of the Etard Complex

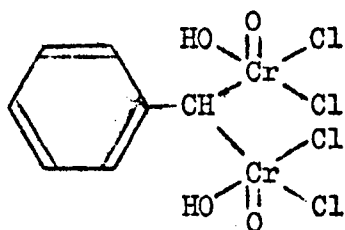
Although some progress has been made towards the elucidation of the reaction mechanism, the intermediate complex in the Etard reaction has received scant attention. This is due mainly to the considerable difficulty in applying the usual analytical techniques to the complexes. Indeed, a recent paper⁷³ states: "The determination of the structure of the Etard complexes meets with considerable difficulties, since owing to their complete insolubility in unreactive solvents, the usual purification methods are not applicable. Nor can methods of optical and nuclear magnetic resonance spectroscopy be applied". As a consequence, many of the early suggestions as to the structure of these complexes were no more than speculation, based on only the results of elemental analysis.

The structure postulated by Etard³⁸ for the toluene complex, contained two atoms of chromium (IV):



The concept of a stable solid, containing chromium in this oxidation state was not accepted by some subsequent workers⁵, though favoured by others^{118,137}. At the present time, the formation of chromium species in oxidation states between (III) and (VI) forms part of the explanation of the mechanism of chromic acid oxidations^{31,137} (see Chapter 7, section 2.1) and the existence of compounds of chromium (IV) such as barium chromate (IV)¹³⁹, chromium (IV) fluoride¹³ and chromium (IV) chloride¹⁴⁰ as well as chromium tetra-*t*-butoxide¹⁴¹, is now also well established.

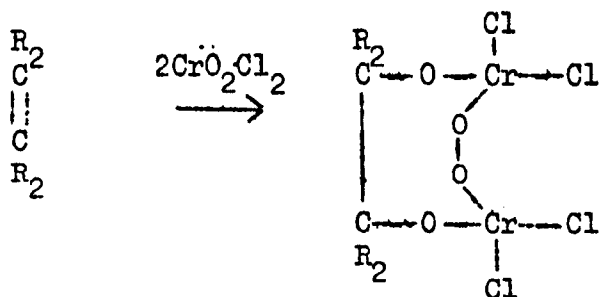
In 1901, Rohde⁶⁰ suggested an organometallic structure for the toluene complex, basing the instability of the addition compound toward water on the existence of this type of bonding.



Rohde also considered that these intermediates were formed during the reactions carried out by Carstanjen,^{48,49} but that excess acetic acid caused the benzaldehyde to be liberated before isolation of the complex could be achieved.

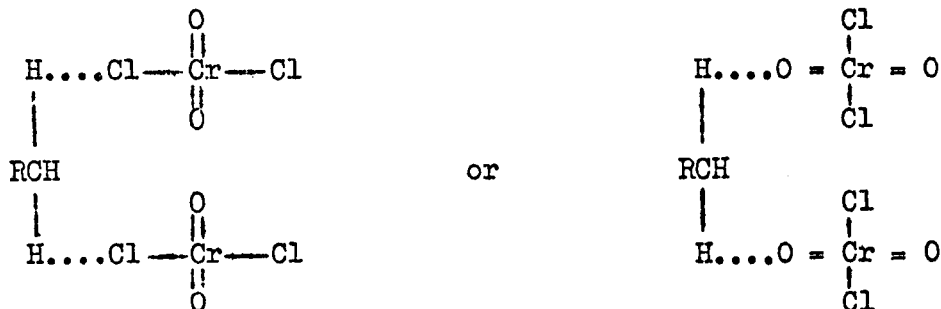
The properties of authentic organo-chromium compounds as described by Hein¹⁴², Zeiss,^{143,144} Fischer and co-workers¹⁴⁵ are dissimilar to those of the Etard complexes whether one considers σ or π bonding and the structure suggested by Rohde has received no recent support.

Sword¹⁴⁶ suggested a peroxide link to explain oxidation at a double bond:



Again, from a consideration of known chromium compounds of this type¹⁴⁷, such a structure for the Etard complex of an olefin seems unlikely.

Hartford and Darrin⁵ proposed a hydrogen-bonded structure for the Etard complex as they considered this consistent with its properties. Two forms of hydrogen bonding were believed possible:

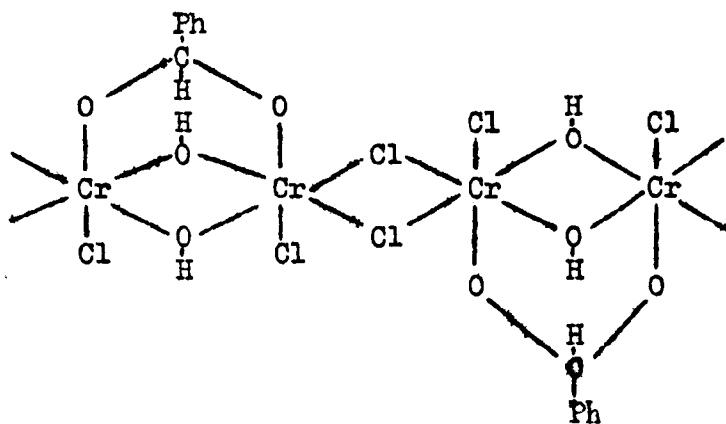


Although favouring structures such as these, containing chromium (VI), these authors were agreed that magnetic measurements must be made before a final conclusion could be drawn.

Two years later, the first magnetic measurements were in fact made on the toluene-chromyl chloride complex and these suggested⁸⁸ the presence of chromium (IV) rather than (VI).

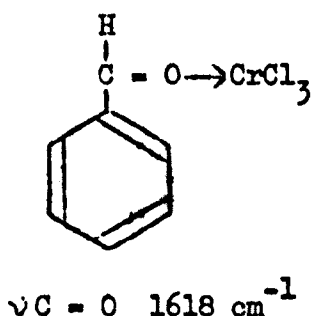
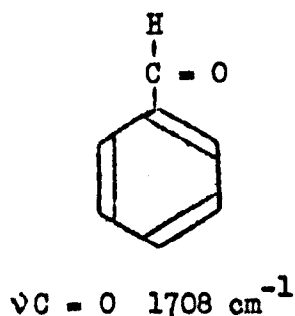
The electron spin resonance study⁹⁵ of the Etard complex derived from toluene confirmed the paramagnetism of the adduct. Bartecki and Wajda¹²⁰ extended the study of the magnetic susceptibility of the complexes derived from cyclohexane and isooctane over a wide range of temperature. Both complexes were found to be paramagnetic and the calculated magnetic moments pointed to the existence of chromium in oxidation state (IV). Further work on this topic gave similar results¹¹⁹.

The interpretation of the infrared spectrum of the toluene-chromyl chloride complex, by Stairs and Makhija¹¹⁷, led them to suggest that the complex was a polymer with hydroxy and chloro bridges:



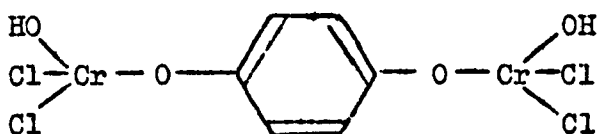
Duffin and Tucker¹⁴⁸, however, proposed that the Etard adduct of toluene contained benzaldehyde coordinated to a reduced chromium species. They recorded the infrared spectra of the adducts from toluene, benzyl chloride and benzyl alcohol, all of which give a high yield of benzaldehyde on hydrolysis. They found the spectra very similar, suggesting a common organic component. Subsequent investigations⁹⁸ showed that the spectra of the complexes formed from anhydrous chromic chloride and various benzaldehydes, were very similar to the above Etard adducts.

A feature of the spectra, common to all, was a band attributed to the carbonyl stretching in benzaldehyde. In each case the band showed a marked shift from that observed for the corresponding benzaldehyde itself. This shift was attributed to a modification of the carbonyl group by its coordination to the electrophilic chromium atom:



The presence of a strong band due to OH absorption is another feature common to these spectra which had been previously reported⁸⁸. The presence of this group was attributed to hydrogen transfer from the organic molecule to the oxygen of the chromyl chloride.

Gragerov and Ponomarchuk¹³¹ favoured a structure similar to that described by Etard, for the benzene-chromyl chloride complex,



A significant feature which emerged indirectly from this work was that the so-called Etard 'adducts' did not have an exact stoichiometry. As a consequence, Gragerov and Ponomarchuk suggested that the complexes were a mixture of compounds. Many workers^{100,103,112,135} have assumed that the complexes had a 1:2 stoichiometry on the basis of either chromium or chlorine analysis and it is noteworthy that many reported analyses do not compare well with the theoretical expectations^{95,105}.

A careful study¹⁴⁸, of the elemental analyses of toluene complexes, confirmed the findings of Gragerov and Ponomarchuk suggested and further showed that the oxidizing power, that is the percentage of chromium in oxidation state higher than (III), varied with the conditions of preparation of the complexes.

This evidence indicates that attempts to describe the 'adducts' in terms of a single simple structure are open to question.

4.4 Decomposition of the Addition Products

The Etard reaction is completed by hydrolysis of the complex, but very few attempts have been made to study this aspect of the reaction.

The only study of the hydrolysis of Etard adducts using isotopic tracers was made by Gragerov and his co-workers^{74,149}. They hydrolysed, with H_2^{18}O , the complexes derived from benzene and cyclohexene and found that the oxidation products, p-benzoquinone and chlorocyclohexanol respectively, contained oxygen derived from the oxidant.

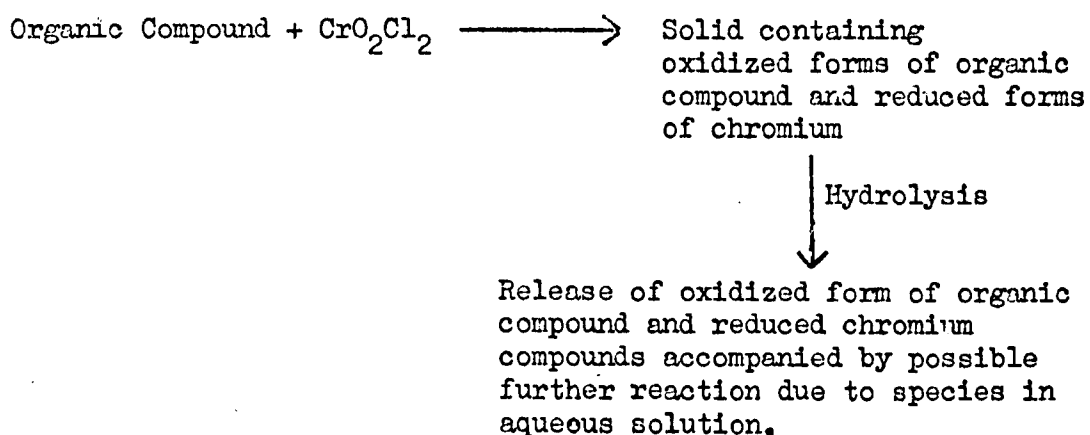
Decomposition of the Etard complexes by solvents other than water has been reported; often the published evidence is contradictory⁵. In some cases, the complexes are reported¹¹⁷ not to decompose but to react with the solvent to give a ternary complex e.g. $\text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{CrO}_2\text{Cl}_2 \cdot 2\text{D}$, where D is a molecule which can donate electrons e.g. pyridine and dioxan. Tucker⁷⁹ found that when the toluene complex was treated with these donor solvents, benzaldehyde was liberated and he suggested that this was evidence for coordination between chromium and benzaldehyde in the complex.

4.5 Conclusion

From the evidence which has been presented in the two preceding chapters, it can be seen that there is no single Etard reaction, but indeed a number of such reactions. It is quite probable that the so-called general feature of the reaction viz the formation of a complex or adduct is general only in the sense that the commonly used solvents for the reaction are poor solvents

for the constituent ligand and acceptor species which make up the complex.

It appears, most unlikely that a general mechanism for this reaction can be formulated unless it is in very general terms. The simplest form of reaction scheme that can be proposed on the basis of the work reviewed in the previous two Chapters is as follows:



CHAPTER 5

INTRODUCTION TO THE RESULTS SECTION

5.1 The Reasons for the Investigation

From a consideration of the preceeding chapters, the following conclusions can be drawn:

- (a) Although the products of oxidation of various hydrocarbons by chromyl chloride have been well investigated, there has been virtually no corresponding study of the oxidation of phenols.
- (b) There are conflicting theories concerning the mechanism of hydrocarbon oxidation by chromyl chloride, and apart from two recent reports^{113,133}, there have been no comparable proposals for the mechanism of the oxidation of phenols.
- (c) The structure of the chromyl chloride - hydrocarbon adducts has not been elucidated, though considerable research has been carried out on this topic.
- (d) Comparable oxidations by other chromyl compounds have been infrequently reported.

Thus, there is good reason to study the oxidation of phenols with chromyl chloride and hence to determine the products of oxidation, and further to investigate the nature of any reaction intermediates. A comparison of this oxidation, using other chromyl compounds appeared relevant. Chromyl acetate was chosen for this purpose because it may be readily prepared in the laboratory and its use, in contrast to other chromyl compounds, presents few experimental problems.

Furthermore, a preliminary investigation into the possible oxidation of phenols by chromium (V) oxychloride (CrOCl_3) and vanadium (V) oxychloride (VOCl_3) was carried out (Chapter 7).

Like the two chromyl compounds mentioned above, both are soluble^{150,151} in non-polar solvents such as carbon tetrachloride and carbon disulphide.

Very little is known of the oxidative properties of chromium (V) oxytrichloride and reactions with organic compounds have not yet been reported¹⁵². Although the chemistry of vanadium (V) oxytrichloride is well documented, there have been few reports² of its use as an oxidant for organic compounds.

The first stage of the investigation of the phenol-chromyl chloride reaction was the determination of the natures and yields of the oxidation products. Then, the solid intermediates formed in these processes were isolated and their structure and properties investigated.

A similar investigation was conducted into the chromyl acetate oxidations.

The results of the determination of the reaction products is described in Chapter 6 and the study of the reaction intermediates, with the attempts to elucidate their structure, is described in Chapter 8.

5.2. The Choice of Phenols

The choice of phenols for this study was based on the following considerations.

Firstly, previous studies have dealt only with the oxidation of phenol⁷, the cresols⁸ and some chlorophenols¹¹³ by chromyl chloride. Thus an investigation of the oxidation of alkylphenols appeared more likely to yield pertinent information than a further study of, for instance, halogenated phenols.

Secondly, by choosing phenols substituted with different groups in various positions on the ring, the relationship between the yields of oxidation product and the degree and position of ring substitution could be observed. Likewise, steric factors which may effect the oxidation could be studied by using phenols with suitably large groups next to likely positions of attack by the oxidant.

For this reason, mono, di- and tri-alkylated phenols were chosen, the alkyl groups being methyl, isopropyl, and t-butyl. This provided a suitable selection of phenols for the investigation, with both small and large substituents, and substituents with and without α -hydrogen atoms. This is of significance because, when the side-chain of an aromatic hydrocarbon is oxidized by chromyl chloride, the hydrogen in the α -position to the ring is preferentially attacked¹⁰⁴.

The oxidation of hydroxyphenols was carried out to determine whether one or more of the hydroxy groups would undergo oxidation.

The presence of a strong electron withdrawing group, on the aromatic ring, might be expected to modify the oxidation of a phenol. Thus ortho, meta and para-nitrophenol and 2,6-dinitrophenol were chosen as suitable examples of phenols with this class of substituent.

As the more detailed discussion in Chapter 6 reveals, the oxidation of various other substituted phenols was studied, but the results obtained with these were somewhat less significant than with those phenols discussed above.

5.3 The General Mode of Reaction of Chromyl Chloride with Phenols

The reaction of chromyl chloride with these compounds was found to be similar to the analagous reactions of the hydrocarbons.

When a solution of the phenolic compound in an inert solvent was mixed with a solution of the oxidant in the same solvent, a brown insoluble solid was rapidly formed. Subsequent hydrolysis of this solid gave oxidation products of the phenol and reduced chromium species.

There were however some exceptions to this, and these are mentioned in Chapter 6.

5.4 The General Mode of Reaction of Chromyl Acetate with Phenols

Initially, it was believed that the reaction path with chromyl acetate was similar to that taken by chromyl chloride.

On mixing a solution of a phenol with one of the oxidant (both in carbon tetrachloride), an immediate reaction occurred, with rapid precipitation of a green-brown solid. The solid product was isolated by filtration and then subjected to hydrolysis. However none of the expected phenol oxidation products were isolated from the hydrolysate; a further investigation showed them to be present wholly in the filtrate. These reactions and their products are described in Chapter 6.

It was found that, whichever phenol was oxidized by chromyl acetate, the insoluble solids always had the same infrared spectrum, suggesting that the solids were identical. This could be the case only if the solid was derived solely from the oxidant i.e. if the solid were a reduced form of chromyl acetate. This

postulate was confirmed by elemental analysis and by magnetic measurements; these results are discussed in Chapter 8.

CHAPTER 6

THE PRODUCTS OF OXIDATION OF PHENOLS BY CHROMYL CHLORIDE AND CHROMYL ACETATE

6.1 Introduction

Much of the information concerning the nature and yields of the products of oxidation is summarized in tabular form on pages 75 et seq. An amplification of the information supplied in the tables is presented below.

6.2 Oxidation by Chromyl Chloride

6.2.1 The Oxidation of Phenol

The oxidation of phenol, at room temperature and in carbon tetrachloride proceeded smoothly to give a dark brown precipitate. Hydrolysis of this solid and extraction of the aqueous solution with organic solvents yielded mainly a brown, intractable tar but also a small amount of p-benzoquinone as well as a trace of phenol. Although a number of different separation procedures were used, the coupled ether, reported by Etard⁷, was not obtained.

6.2.2 The Oxidation of Hydroxyphenols

The reactions of quinol, resorcinol and pyrogallol were somewhat different to that of phenol.

All three compounds were found to be virtually insoluble in carbon tetrachloride. As a consequence, the attempted oxidations were conducted using suspensions of these phenols in chromyl chloride/carbon tetrachloride.

No precipitate was formed in the mixtures after prolonged stirring at room temperature. The mixtures were heated under reflux for several hours but this treatment gave only a trace of brown precipitate in the quinol and pyrogallol reaction mixtures, and none at all in that containing resorcinol. Filtration of the mixtures gave almost quantitative yields of the solid starting materials. The infrared spectra of the filtrates failed to show the presence of compounds other than the solvent and the oxidant.

In order to see if the lack of reactivity of these compounds with chromyl chloride was a function of their insolubility in carbon tetrachloride, the reactions were repeated at room temperature but without solvent. Again there was a complete lack of reaction, although, after a brief induction period, phenol reacts violently under these conditions.

The action of chromyl chloride on molten quinol, resorcinol and pyrogallol was, on the contrary, violent. Ignition occurred and resulted in a charred residue which contained chromium (III) oxide.

An attempt was made to modify the process by addition of a solvent after the reaction had been initiated, but without success. Nothing resembling the usual chromyl chloride complex could be isolated.

The reaction of chromyl chloride with resorcinol in glacial acetic acid at room temperature did not give a precipitate but removal of the solvent under reduced pressure did give a black, tarry residue. Solvent extraction and chromatography failed to give a separation into recognisable compounds.

The reaction of quinol in glacial acetic acid proceeded in a similar manner but in this case extraction of the resulting brown solution gave a mixture of chlorinated quinones, with a high yield of trichloro-1,4-benzoquinone.

Because of their lack of solubility in carbon tetrachloride and carbon disulphide, the hydroxyphenols are not representative phenols for use in this type of reaction.

Alkylated phenols such as 3,5-di-t-butylcatechol and 3,5-di-t-butylpyrogallol are readily soluble in carbon tetrachloride and are thus more suitable reagents for Etard oxidation.

Both compounds reacted rapidly with chromyl chloride to give insoluble, brown complexes.

Hydrolysis of the complex derived from the substituted catechol, and subsequent extraction of the organic material with pentane, gave only a trace of a pale yellow oil. Ether extraction yielded a red solution initially. Further extraction yielded a more intensely coloured solution, suggesting that a reaction may have taken place during extraction. Removal of the solvent yielded a deep red oil which partially solidified on standing, to give a similarly coloured, non-crystalline, sticky substance.

Thin layer chromatography indicated the presence of at least two red components, but protracted chromatography (thin layer and column) failed to yield pure compounds. The infrared spectra of the sticky solid showed distinctive, sharp absorption bands which could be correlated with the presence of sterically hindered hydroxyl groups.

Other features of the spectra were absorptions similar to those assigned to the C-H stretching of t-butyl groups.

An attempt was made to obtain the n.m.r. spectra, but the solutions gave very poorly defined spectra which was attributed to the presence of a paramagnetic species.

The e.s.r. spectrum of a solution of the red compound showed the presence of an inorganic radical, but not an organic one. The e.s.r. spectrum showed one single strong absorption with four side bands due to the hyperfine splitting of the ^{53}Cr isotope (Fig. 22).

Elemental analysis of the red compound showed the presence of chromium and suggested a compound, with an approximate empirical formula $\text{C}_{14}\text{H}_{20}\text{CrO}_4$.

However, the analyses showed considerable variation, depending on the method of separation and subsequent treatment of the red material, and it is evident that a mixture of substances was present.

The possible structure of this compound is discussed in Chapter 9.

6.2.3 The Oxidation of Monoalkylphenols

The oxidations of monoalkylphenols were carried out as described in the experimental section. The reactions were very rapid and resulted in the formation of chocolate-brown, insoluble solids.

Hydrolysis of these solids and subsequent solvent extraction of the hydrolysis mixture failed to give appreciable yields of simple products.

TABLE 4

Products of Hydrolysis of Complexes derived from
Monoalkylated Phenols

| Phenol | Mole Ratio $\text{CrO}_2\text{Cl}_2:\text{ArOH}$ | % Substituted <i>p</i> -benzoquinone | Other Products |
|--------------------------|---|---|-------------------|
| Phenol | 2:1 | Trace | Brown tar |
| 2-Methylphenol | 2:1 | 1 - 2 | Intractable tar |
| 2- <i>t</i> -Butylphenol | 2:1 | 5 | Intractable tar |
| 3- <i>t</i> -Butylphenol | 2:1 | 5 | Intractable tar |
| 4- <i>t</i> -Butylphenol | 2:1 | 0 | Intractable tar |

In all cases, the main products were brown tars or resins. All attempts to crystallize these resinous substances failed, as did attempts to separate possible components by column chromatography.

The only compounds which were isolated were the p-benzoquinones. These were isolated in low yield (see Table 4) by heating the tars under reduced pressure and collecting the quinones in a cold trap after sublimation.

6.2.4. The Oxidation of Dimethylphenols

The oxidations, carried out as with the monoalkylated phenols, gave brown insoluble complexes.

The hydrolysis products of the complexes were found to be primarily the corresponding p-benzoquinones. In the case of dimethylphenol, 3,3',5,5'-tetramethyldiphenquinone was also isolated.

The yield of product was found to be dependent on the mole ratio of phenol to oxidant (see Table 5). The implications of this are discussed in Chapter 9.

The other products of hydrolysis of the complexes were again resinous materials which could not be crystallized.

The mass spectrum of the resin obtained from the hydrolysis of the 2,5-dimethylphenol-chromyl chloride complex showed the presence of a component of molecular weight 312 (the molecular weight of the phenol is 122).

A very small amount of a trimeric compound was obtained from the tar resulting from hydrolysis of the 3,5-dimethylphenol complex. This trimer was a buff, apparently crystalline solid. High resolution mass spectrometry indicated a molecular weight of 362.168, corresponding to an empirical formula $C_{24}H_{26}O_3$.

TABLE 5

Products of Hydrolysis of Complexes derived from
Dimethylphenols

| Phenol | Mole Ratio $\text{CrO}_2\text{Cl}_2:\text{ArOH}$ | % Substituted p-Benzoquinone | Other Products |
|---------------------|---|---------------------------------|---|
| 2,5-Dimethyl-phenol | 2:1 | 14.5 | Polymeric tar - one component MW of 312 |
| | 5:1 | 15.5 | |
| 2,6-Dimethyl-phenol | 2:1 | 48 | 10.3% 3,3',5,5'-tetra- methyldiphenquinone |
| | 10:1 | 16.5 | 4.7% 3,3',5,5'-tetra- methyldiphenquinone |
| 3,5-Dimethyl-phenol | 2:1 | 5 | Tars - one component of MW 362.188, molecular formula $\text{C}_{24}\text{H}_{26}\text{O}_3$ |
| | 7:1 | 19 | |
| | 100:1 | 22.5 | |

6.2.5 The Oxidation of Di-isopropylphenols

Both 2,5- and 2,6-di-isopropylphenol reacted rapidly with chromyl chloride to give high yields, (based on the amount of phenol used), of the brown complexes.

Hydrolysis of the complex derived from 2,5-di-isopropylphenol yielded a yellow oil which was extracted from the aqueous solution by pentane. The oil crystallized below room temperature to give yellow needles. Distillation of the oil under reduced pressure gave a similar yellow liquid which crystallized at 38.5° . Infrared and n.m.r. spectra of this substance were consistent with it being 2,5-di-isopropyl-1,4-benzoquinone. Mass spectral data confirmed this. Hydrolysis of the 2,6-di-isopropylphenol complex yielded both the p-benzoquinone and diphenoquinone (see Table 6).

6.2.6 The Oxidation of Di-t-butylphenols

The reaction of the 2,5- 2,6- and 3,5-di-t-butylphenols with chromyl chloride, followed the pattern shown for the dimethyl and di-isopropylphenols, brown insoluble complexes being formed very rapidly on mixing the reagents. Again, yields of the complexes (based on the amount of phenol used), were nearly quantitative.

Hydrolysis of the complexes gave the expected p-benzoquinones in better yields than hydrolysis of those derived from methylphenols. Again there was a dependence of the yield of quinone on the mole ratio of phenol:chromyl chloride.

TABLE 6

Products of Hydrolysis of Complexes derived from

Di-isopropylphenols

| Phenol | Mole Ratio $\text{CrO}_2\text{Cl}_2:\text{ArOH}$ | % Substituted p-benzoquinone | Other Products |
|-------------------------|---|---------------------------------|---|
| 2,5-Di-isopropyl-phenol | 2:1 | 42 | Yellow-brown resin |
| 2,6-Di-isopropyl-phenol | 2:1 | 56 | About 5% 3,3',5,5'-tetra- isopropyldiphen- quinone |

TABLE 7

Products of Hydrolysis of Complexes derived from

Di-t-butylphenols

| Phenol | Mole Ratio $\text{CrO}_2\text{Cl}_2:\text{ArOH}$ | % Substituted p-Benzoquinone | Other Products |
|----------------------|---|---------------------------------|---|
| 2,4-Di-t-butylphenol | 2:1 | 1 | Polymeric tar |
| 2,5-Di-t-butylphenol | 1:1 | 28 | |
| | 1.3:1 | 75 | |
| | 2:1 | 83 | |
| | 5:1 | 76 | |
| | 10:1 | 63 | |
| 2,6-Di-t-butylphenol | 1.3:1 | 36 | Traces of 3,3',5,5'-tetra-t-butyl-di-phenoquinone |
| | 2:1 | 68.5 | |
| | 5:1 | 58 | |
| 3,5-Di-t-butylphenol | 2:1 | 31 | Polymeric tar |
| | 5:1 | 49 | Polymeric tar |
| | 10:1 | 57 | Polymeric tar |

In the case of 2,6-di-*t*-butylphenol, a small amount of 3,3',5,5'-tetra-*t*-butyldiphenoquinone as well as the 2,6-di-*t*-butyl-1,4-benzoquinone was formed.

The only product obtained from the oxidation of 2,4-di-*t*-butylphenol was a trace of 2-*t*-butyl-1,4-benzoquinone, the remaining products being present as a resin which resisted all attempts to purify it. Smaller amounts of resinous materials were obtained from the oxidation of the other di-*t*-butylphenols (see Table 7).

6.2.7. The Oxidation of Trimethylphenols

2,4,6-Trimethylphenol reacted rapidly with chromyl chloride to give a dark brown precipitate. Hydrolysis of the collected solid yielded a yellow resin. All attempts at crystallization failed, cooling to -70° only gave a yellow 'glass'. The infrared spectrum of this substance suggested that it had both phenolic and quinonoid properties but the n.m.r. spectrum was complex. The mass spectrum failed to show the presence of simple compounds and suggested that the product was polymeric.

Both 2,3,5- and 2,3,6-trimethylphenol reacted with chromyl chloride giving virtually quantitative yields of brown complexes.

Hydrolysis of both complexes gave small yields of trimethyl-1,4-benzoquinone. The other product of hydrolysis was a yellow-brown, non-crystalline gum, whose infrared spectrum was identical in each case. The spectrum showed characteristic quinone carbonyl absorptions, similar but not identical to those of trimethylquinone itself.

TABLE 8

Products of Hydrolysis of Complexes derived from Trimethyl-
phenols and a Tetramethylphenol

| Phenol | Mole Ratio $\text{CrO}_2\text{Cl}_2:\text{ArOH}$ | % Substituted p-Benzoquinone | Other Products |
|--------------------------------|---|---------------------------------|---|
| 2,3,5-Trimethyl- phenol | 2:1 | 5 - 10 | Polymeric Tar |
| | 5:1 | | |
| 2,3,6-Trimethyl- phenol | 2:1 | 16.5 | Yellow resin |
| 2,4,6-Trimethyl- phenol | 1:1 | 0 | Yellow resin |
| | 2:1 | 0 | Yellow resin |
| | 5:1 | 0 | Yellow resin and some original phenol <1% |
| 2,3,5,6-Tetra- methylphenol | 2:1 | 5 - 10 | Brown resin |
| | 5:1 | | |

Some of the organic material appeared to remain in the aqueous solution and resisted attempts at its extraction. Removal of the water resulted in a black-green ~~fat~~ from which no crystallizable products could be obtained.

Alteration of the mole ratio of phenol:oxidant appeared to have little appreciable effect on the yield of quinone (see Table 8).

6.2.8 The Oxidation of Miscellaneous Phenols

All the phenols, listed in Table 9 , reacted with chromyl chloride in the manner typical of the other alkyl phenols. Reactions were rapid, and yields of the complexes based on the weights of phenol, were approximately quantitative.

It was expected that 2,6-di-sec-butyl and 2,6-dimethoxyphenol would yield both the p-benzoquinone and the diphenoquinone, in a manner analogous to that found for the corresponding 2,6-dimethyl and 2,6-di-t-butylphenols. From the hydrolysis of the di-sec-butylphenol-chromyl chloride complex, quantitative separation of the products was not achieved because the quinone, which was shown to be present by infrared spectroscopy, decomposed on both the silica and alumina which were used for the attempted chromatographic separations. The use of less active phases such as cellulose or magnesium silicate, failed to effect satisfactory separation.

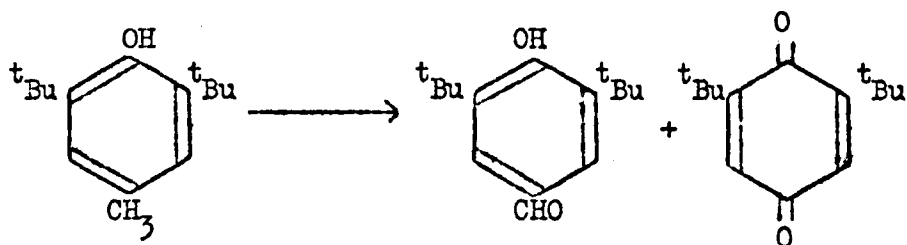
However, an examination of the infrared spectrum of the product of hydrolysis suggested that the quinone was the major component, with the diphenoquinone only present in small quantities (small amounts of each of these compounds were isolated in a pure form).

TABLE 2Products of Hydrolysis of Complexes derived from MiscellaneousPhenols

| Phenol | Mole Ratio CrO_2Cl_2 : ArOH | Products | % Yield |
|-------------------------------|--|---|---------|
| 2,6-Dimethoxyphenol | 2:1 | 2,6-Dimethoxy-1,4-benzoquinone | 26 |
| 2,6-Di-sec-butylphenol | 2:1 | Quinone and Diphen-quinone (Total yield 70%) | - |
| 2,6-Di-t-butyl-4-methylphenol | 2:1 | 2,6-Di-t-butyl-1,4-benzoquinone 3,5-Di-t-butyl-4-hydroxybenzaldehyde | 2 12 |
| 2,4-Di-t-butyl-6-methylphenol | 2:1 | Polymeric tar | - |
| 2,4,6-Tri-t-butylphenol | 2:1 | 3,5-Di-t-butyl-1,2-benzoquinone | 31 |
| 1-Naphthol | 2:1 | 1,4-Naphthoquinone | 25 |
| 2-Naphthol | 2:1 | Black-brown tar | - |

Hydrolysis of the 2,6-dimethoxyphenol-chromyl chloride complex gave 2,6-dimethoxy-1,4-benzoquinone, but none of the 3,3',5,5'-tetramethoxydiphenoquinone.

Hydrolysis of the complex derived from 2,6-di-*t*-butyl-4-methylphenol gave the hydroxy-benzaldehyde, indicating that in this case side-chain oxidation had occurred, though some quinone was also formed:



A comparable oxidation of 2,4-di-*t*-butyl-6-methylphenol was thus expected to give the corresponding aldehyde by a similar process. However, only a black-brown tar resulted from adduct hydrolysis, and no recognizable product was obtained from this material despite attempts to separate possible components by chromatography. The infrared spectrum did show absorptions characteristic of an aromatic aldehyde with carbonyl stretching bands at 1700 and 1780 cm⁻¹. Attempted characterization of these components via their 2,4-dinitrophenylhydrazine derivatives was not successful, though a small amount of a derivative of ill-defined melting point was obtained.

Mass spectral evidence suggested that the brown tar was largely polymeric.

The hydrolysis of the 2,4,6-tri-*t*-butylphenol-chromyl chloride complex yielded the ortho-quinone, 3,5-di-*t*-butyl-1,2-benzoquinone together with a red-brown oil which could not be crystallized but whose infrared spectrum showed many features common to that of the pure ortho-quinone.

The reactions of the naphthols were rather different from those of the alkylated phenols. Because of their low solubility in carbon tetrachloride the reactions with the naphthols were conducted using suspensions of these compounds in the solvent.

However, reaction was rapid, leading to the formation of black insoluble complexes.

Hydrolysis of the 1-naphthol complex gave a brown insoluble solid. Continuous extraction by pentane yielded 1,4-naphthoquinone, leaving a black insoluble residue. This solid had a poorly defined infrared spectrum, but an examination of the mass spectrum suggested the presence of dimeric compounds of molecular weights 300 and 318 (molecular weight of 1-naphthol is 144), as well as compounds of higher molecular weight.

No recognizable products could be isolated from the hydrolysis products of the 2-naphthol-chromyl chloride complex. A brown amorphous solid was precipitated in the hydrolysis reaction. Thin layer chromatography of the chloroform extract of this solid showed the presence of small quantities of at least four components, but the major component was a dark tar. Column chromatography failed to resolve the mixture, most of which rapidly darkened on the column, from which it could not be eluted, even by using relatively polar solvents.

6.2.9 The Reaction of Nitrophenols with Chromyl Chloride

Complexes were prepared from ortho, meta and para nitrophenols but under different conditions to those employed for the oxidation of the alkylphenols.

All the nitrophenols were visibly slower to react with chromyl chloride, and in each case the yield of solid complex was much lower than that expected for the quantitative oxidation of the phenol.

In order to increase the yield of each complex each nitrophenol was dissolved in a mixture of chromyl chloride and carbon tetrachloride, and the resulting solution heated under reflux. The adducts which resulted were similar in appearance to those formed, for example, from the alkylphenols.

Hydrolysis of the complexes gave brown resinous materials and in the case of m-nitrophenol some phenol was recovered.

Most of the products of oxidation remained in aqueous solution and could not be extracted by organic solvents.

Reaction of 2,6-dinitrophenol with chromyl chloride was achieved in a similar manner, although a larger reflux time was required to produce even a moderate yield of solid product. Hydrolysis of the complex led to the recovery of the starting material in a yield of 66%.

6.2.10 The Formation of Soluble Coloured Intermediates

Significant exceptions to the above general reaction pattern were observed when a small quantity of a dilute solution of chromyl chloride was added to a solution of a phenol in the same solvent. An immediate deep blue or green colouration was observed, but no precipitate was formed. On addition of more oxidant, the colour faded and aggregates of the brown complex were formed.

Attempts to isolate these intermediates were not successful, although spectroscopic measurements were made on the solutions.

The e.s.r. spectra of these solutions failed to show the presence of paramagnetic species, although on standing some solutions did give e.s.r. absorptions. The strength of the signal appeared to be related to the degree of solid formation.

Similarly the electronic absorption spectra of the blue solutions was not consistent with the presence of organic free radicals.

The significance of these observations is discussed in Chapter 9.

6.3 The Reductive Hydrolysis of the Complexes

In certain oxidations by chromyl chloride, the yields of products can be increased by conducting the hydrolysis of the intermediate complex in the presence of a reducing agent (see Chapter 3, section 5.7).

The most successful method of reductive hydrolysis employed in the Etard reaction is that introduced by Freeman and his co-workers¹⁰⁷. They subjected the Etard complex to hydrolysis, without prior filtration, in the presence of fine zinc dust^{69,107}.

This method was used to hydrolyse certain phenol-chromyl chloride complexes to see if there was any change in the nature and yield of the products.

The results are listed in Table 10. It can be seen that there is an increase in the yield of methylquinones, but even so this technique does not lead to the quantitative formation of these products.

TABLE 10

Products of Reductive Hydrolysis of Phenol-Chromyl Chloride

Complexes

| Phenol | Mole Ratio CrO_2Cl_2 : ArOH | % Substituted p-benzoquinone | Other Products |
|-----------------------------------|--|---------------------------------|---|
| Phenol | 2:1 | Trace | Brown tar |
| 2-t-Butylphenol | 2:1 | 0 (5) | 2-t-Butylhydroquinone (about 5%) and brown tar |
| 2,5-Dimethylphenol | 2:1 | 23 (14.5) | Yellow-brown tar |
| 2,5-Di-isopropylphenol | 2:1 | 54 (42) | " " " |
| 2,4-Di-t-butylphenol | 2:1 | 0 (1) | Brown tar |
| 2,3,5-Trimethylphenol | 2:1 | 58 (10) | Some 2,3,5-trimethyl- hydroquinone (about 5%) |
| 2,3,6-Trimethylphenol | 2:1 | 68 (10) | Yellow resin |
| 2,6-Di-t-butyl-4- methylphenol | 2:1 | 2 (2) | 3,5-Di-t-butyl-4- hydroxybenzaldehyde (8%) |
| 2,4-Di-t-butyl-6- methylphenol | 2:1 | 0 (0) | Brown tar |
| 2,4,6-Tri-t-butylphenol | 2:1 | 0 (0) | Some 3,5-di-t-butyl- 1,2-benzoquinone and a red paramagnetic resin |
| 3,5-Di-t-butyl- catechol | 2:1 | 0 (0) | Red paramagnetic resin |

The figures in brackets refer to the yields obtained using non-reductive hydrolysis.

With 2,4,6-trimethyl and 2,4,6-tri-*t*-butylphenol there was no improvement over the comparable non-reductive hydrolysis of the complexes. Again, no identifiable product was obtained from the trimethylphenol. Some ortho-quinone was formed from 2,4,6-tri-*t*-butylphenol, but the main product was a paramagnetic, red, resinous material which was soluble in organic solvents, but not in water. The spectroscopic properties of this substance were similar to those of the product of oxidation of 3,5-di-*t*-butylcatechol.

6.4. The Oxidation by Chromyl Acetate

The oxidations of phenols with chromyl acetate were carried out in a similar manner to those of chromyl chloride.

The products of oxidation were obtained directly from the reaction solution after removal of the reduced oxidant by filtration.

The only exceptions to this were to be found in the oxidation of the 2,6-dialkylphenols. The limited solubility of the diphenoquinones, which are formed in the reactions, in carbon tetrachloride, resulted in a proportion of these compounds being precipitated with the solid containing the reduced chromium. Continual treatment of the solid with hot solvent, resulted in the removal of the diphenoquinones from the chromium complex.

The products and their yields are summarized in Table 11 and a comparison is made with the corresponding oxidations by chromyl chloride.

TABLE 11

The Products of Oxidation by Chromyl Acetate

| Phenol | Mole Ratio $\text{CrO}_2(\text{OAc})_2$: ArOH | % substituted p-benzoquinone | Other Products |
|--------------------------------|--|---------------------------------|--|
| 2,5-Dimethylphenol | 2:1 | 31 (14.5) | Brown resin |
| 2,6-Dimethylphenol | 2:1 | 90 (48) | 3,3',5,5'-Tetra- methyldiphen- quinone (3%) |
| 2,3,5,6-Tetramethyl- phenol | 2:1 | 82 (10) | Yellow resin |
| 2,5-Di-isopropyl- phenol | 2:1 | 54 (42) | Yellow-brown resin |
| 2,6-Di-isopropyl- phenol | 2:1 | 60 (56) | 3,3',5,5'-tetra- isopropyldiphen- quinone (5%) |
| 2,5-Di-t-butylphenol | 2:1 | 86 (83) | |
| 2,6-Di-t-butyl- phenol | 2:1 | 70 (68.5) | Some 3,3',5,5'- tetra-t-butyl- diphenquinone |

The figures in brackets refer to the corresponding oxidations by chromyl chloride

In all cases, the major products were identical to those obtained from the comparable oxidations by chromyl chloride.

In most cases however, the yields of *p*-benzoquinone were much improved and the amount of resinous material was much reduced compared to the equivalent oxidations with chromyl chloride.

The results are listed in Table 11.

CHAPTER 7

THE REACTION OF PHENOLS WITH VANADIUM (V) OXYTRICHLORIDE AND

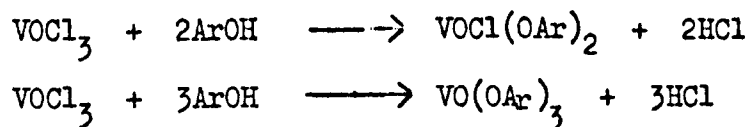
CHROMIUM (V) OXYTRICHLORIDE

In part 1 of this chapter, the results of the interactions of certain phenols with vanadium (V) oxytrichloride (VOCl_3) are discussed.

Part 2 is concerned with the reactions of chromium (V) oxytrichloride (CrOCl_3) with phenols.

7.1. The Products of Reaction of Phenols with Vanadium (V) Oxytrichloride

The reports on this topic indicate that several different types of reaction may take place between vanadium (V) oxytrichloride and phenols. Funk, Weiss and Zeising¹⁵³ have described the formation of esters with, for example, phenol and p-chlorophenol:



The phenyl vanadates are deeply coloured solids which are very susceptible to hydrolysis, on which they regenerate the original phenol in quantitative yield. However, the treatment of other phenols, for example the cresols and naphthols, with vanadium (V) oxytrichloride under identical conditions, results in rapid oxidation with no ester formation.

Other workers¹⁵⁴ prepared phenyl vanadates with all these phenols, and under conditions more vigorous than those employed by Funk et al. No cases of oxidation were reported. The only published

evidence for the structure of these compounds was the elemental analysis. In the few cases where the analysis figures for specific phenyl vanadates were the same in each paper, the reported physical and chemical properties of the compounds differed considerably. No spectroscopic or other techniques were used by either group of workers to substantiate the classification of these compounds.

In order to clarify this situation, the interaction of some alkylphenols and vanadium (V) oxytrichloride was investigated.

The initial investigation, with phenol itself, and with di- and tri-substituted t-butyl-phenols, suggested that, substitution, rather than oxidation, occurred. Phenyl vanadates similar to those reported by Funk and his co-workers were prepared.

7.1.1 Reaction Products

On addition of the phenols to vanadium (V) oxytrichloride (both in carbon tetrachloride) deep red or violet solutions developed and evolution of hydrogen chloride was observed. There was no precipitation of a solid product analogous to that formed in the Etard reaction.

Removal of the solvent and excess vanadium (V) oxytrichloride under reduced pressure at room temperature yielded black or blue-black residues. On hydrolysis of these solids, the original phenol was recovered in high yield.

Evidence for the formation of phenyl vanadates was obtained from infrared spectroscopy, nuclear magnetic resonance spectrometry and mass spectrometry.

All the phenols studied showed a 'free' O-H stretching frequency at about 3600 cm^{-1} when the infrared spectra of their dilute solutions in carbon tetrachloride were observed. Shortly after addition of vanadium (V) oxytrichloride, in the same solvent, the O-H band was observed to decrease as the reaction proceeded, until it was very small indeed. Another change in the spectra which accompanied this diminution, was a shifting of the band at 1035 cm^{-1} attributed to V=O stretch in vanadium (V) oxytrichloride, to a slightly lower wavenumber. The V=O stretch in vanadium (V) oxytrichloride is reported to occur at 1035 cm^{-1} in the vapour phase¹⁵⁵. It was found that, when the spectra were observed for the compound in carbon tetrachloride solution, there was only a very slight difference in this value.

Other changes in the infrared spectra of these reaction mixtures were all small and of less significance than those mentioned above.

The n.m.r. spectra of the reaction mixtures likewise suggested the formation of phenyl vanadates.

The spectra were obtained after the mixtures had been allowed to stand for twenty four hours. In all cases well resolved n.m.r. bands were observed with no apparent line broadening. Thus there is no evidence for the presence of paramagnetic species, as even small amounts of such species cause significant line broadening, with reduced resolution¹⁵⁶.

This evidence suggests that no oxidation reaction occurs: vanadium (V), with a d^0 electronic configuration, has no unpaired electrons. Vanadium (IV) and vanadium (III), d^1 and d^2 respectively, have unpaired electrons and are strongly paramagnetic.

The reactions with each phenol were very similar to each other. In every case, the experimental evidence for formation of phenylvanadates followed the same pattern and thus a reasoned argument is presented for one typical example only, that of 2,5-di-*t*-butylphenol.

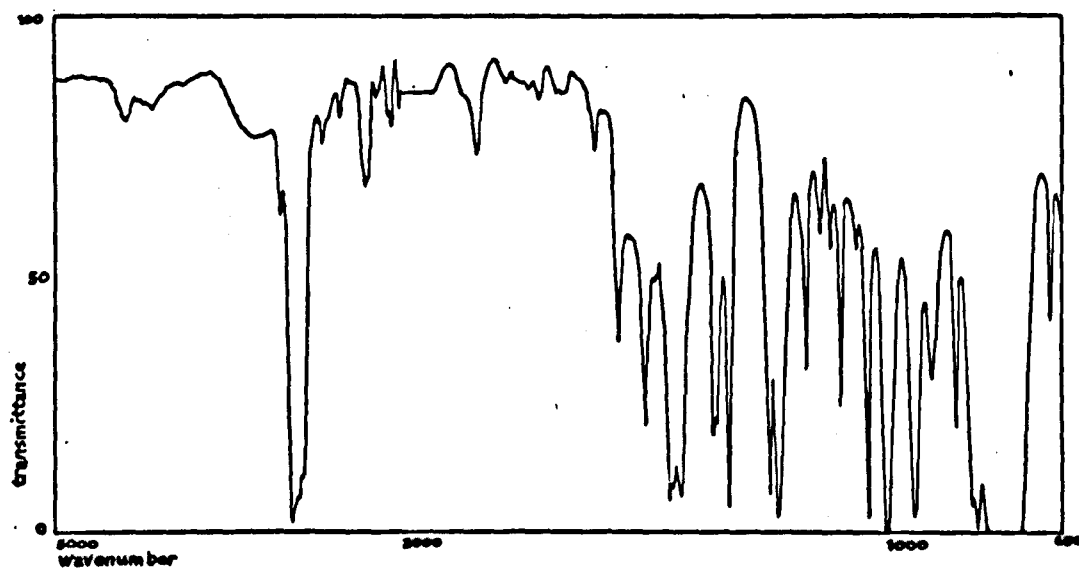
The reaction of 2,5-di-*t*-butylphenol with vanadium (V) oxytrichloride, in carbon tetrachloride, results in the evolution of hydrogen chloride and formation of a deep blue-violet solution.

The infrared spectrum of this solution, after concentration (Fig 3), shows no absorption which can be assigned to O-H stretching. The spectrum of the parent phenol shows a sharp absorption, of medium intensity at 3580 cm^{-1} .

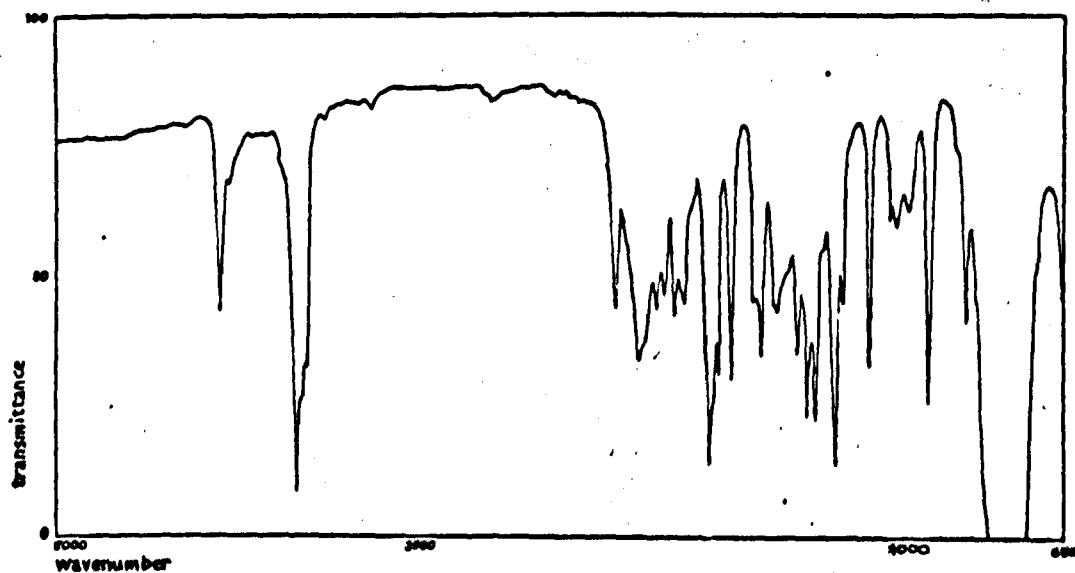
The absorption at 975 cm^{-1} can be assigned to the V=O stretch in the phenylvanadate; the absorption at 1035 cm^{-1} is due to a similar stretching frequency in the excess vanadium oxytrichloride present. Very similar shifts in these stretching modes have been observed in the spectra of complexes between vanadium (V) oxytrichloride and carbonyl compounds¹⁵⁷.

The n.m.r. spectrum of 2,5-di-*t*-butylphenol and its vanadate are shown in Fig 4 . The data for the two compounds are listed in Table 22 .

It can be seen that the phenolic proton is completely absent in the case of the vanadate, and, whilst there is only a small change in the chemical shift of the *t*-butyl groups, the resonances of the aromatic protons have been considerably modified; the complex pattern appearing at about 3.05τ for the phenol is



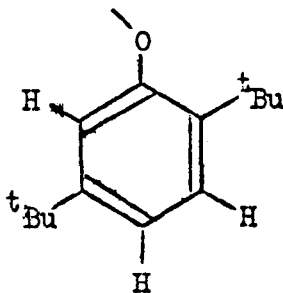
(a)



(b)

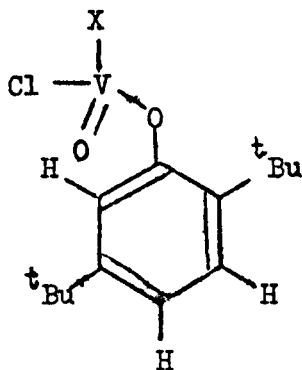
Fig.3. The infrared spectra of (a) bis(2,5-di-t-butylphenyl) chlorovanadate (V), and (b) 2,5-di-t-butylphenol. Both as solutions in carbon tetrachloride.

replaced by two singlet peaks. An inspection of the integrated areas of these absorptions indicates that the peak at 1.91 τ is due to the resonance of the proton ortho to the phenolic position, whilst that at 2.70 τ is due to the other aromatic protons:



If one assumes that the compound under discussion is either the monoester ArO-VOCl_2 or the diester $(\text{ArO})_2\text{VOCl}$, the resolution of these bands and the large chemical shift associated with one of them are readily explained.

Electron withdrawing substituents on an aromatic ring tend to shift the resonance position of the ring protons to lower field due to enhancement of the diamagnetic deshielding effect. The downfield shift observed for both the positions of resonance of the ring protons and the t-butyl protons is a comparable effect, brought about by the electron withdrawal of the vanadate group. The large size of the shift for the resonance of the ortho proton can be explained by the natural tendency of the vanadate and t-butyl groups to take up the following configuration due to their bulkiness:



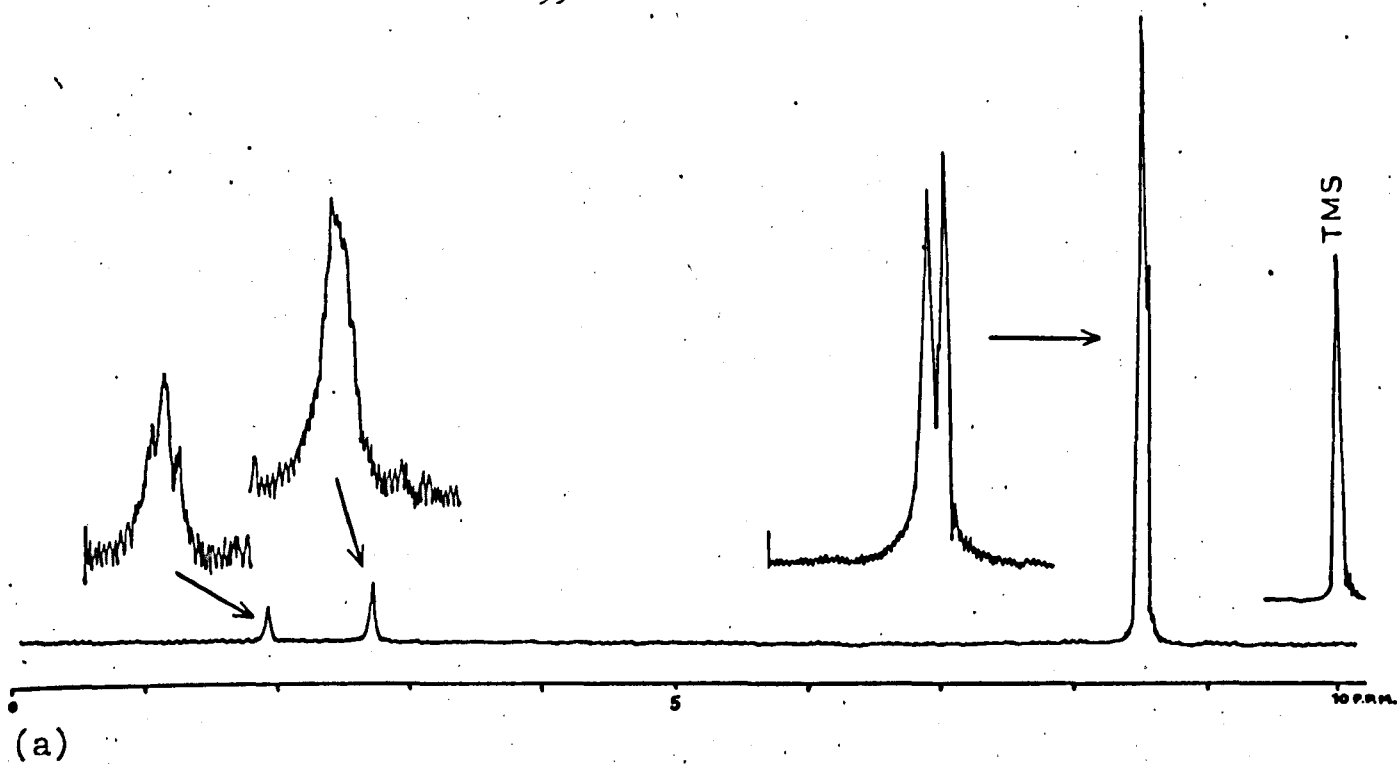


Fig.4. The n.m.r. spectra of (a) bis(2,5-di-t-butylphenyl) chlorovanadate (V), and (b) 2,5-di-t-butylphenol.

The ortho proton would thus lie within range of the deshielding effect of the V=O group and hence its resonance would experience a further chemical shift downfield, in comparison to the other ring protons. The exact shift of the resonances of all the ring protons is not easy to determine without a proper analysis of their absorptions in the parent phenol. The general trend, however, is quite clear. The small shifts of the meta and para proton resonances and those of the t-butyl protons are consistent with their being affected only by the electron withdrawing effect of the vanadate group.

(The chemical shifts were all measured using tetramethyl silane as an external standard, as this compound appeared to react with the vanadates).

Finally, the molecular weight of the compound was established by mass spectrometry. The mass spectrum of the blue-black solid compound, obtained by the method described earlier, is illustrated as a line diagram, in Figure 5 , and the pertinent data is listed in Table 64 .

The ion having a mass:charge ratio of 512 was identified as the molecular ion (M).

The ratio of the intensities of $M:(M + 2)$ was found to be approximately 3:1. A molecule with one chlorine atom would show a similar ratio because the relative isotopic abundances, $^{35}\text{Cl}:^{37}\text{Cl}$, is 3:1.

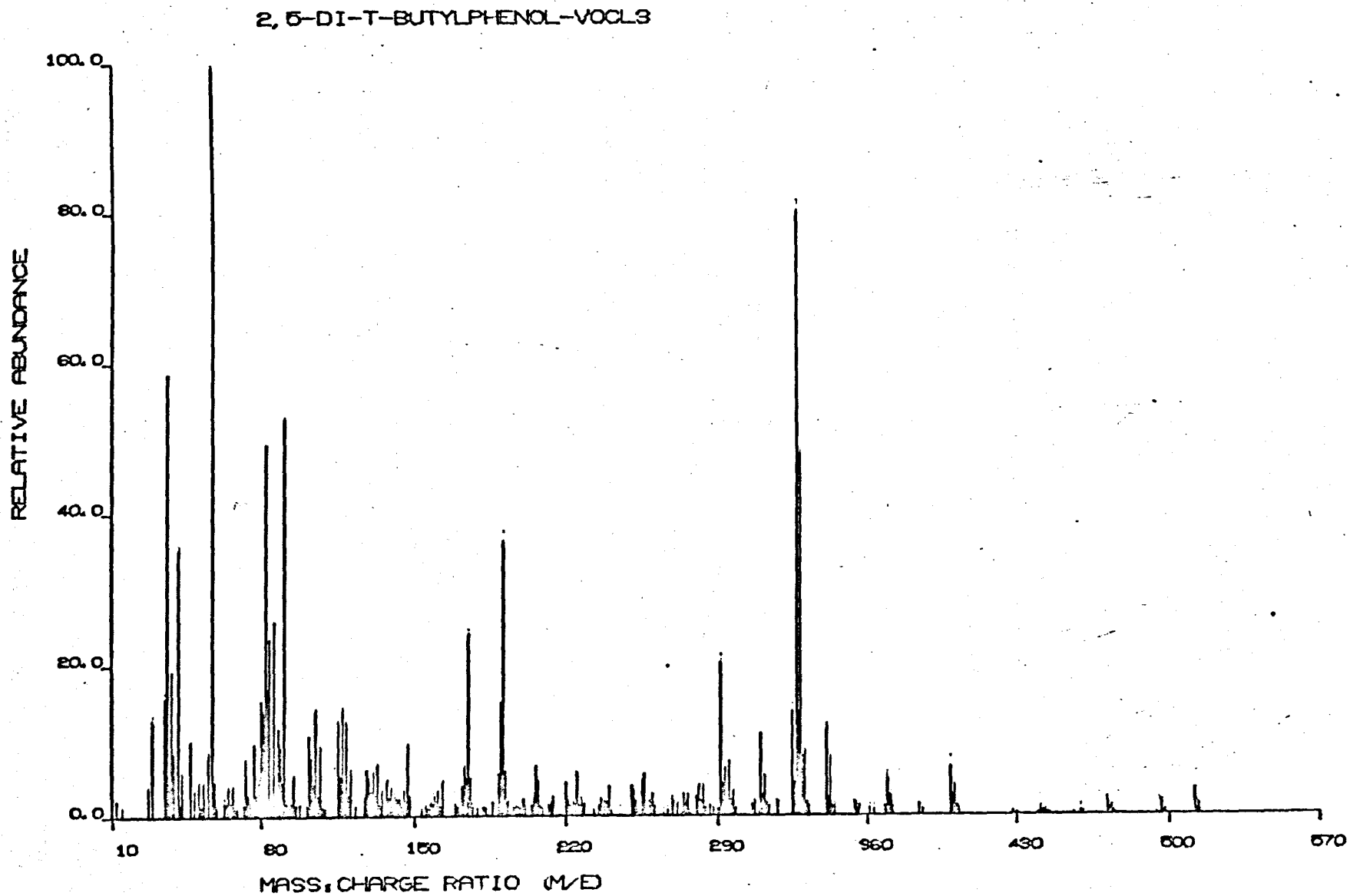
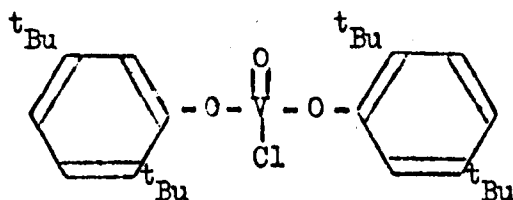


Fig.5. The mass spectrum of bis(2,5-di-t-butylphenyl)chlorovanadate(V).

Two chlorine atoms per molecule would require a series of m/e values $M:(M+2):(M+4)$ corresponding to a ratio of 9:6:1 and, likewise, three chlorine atoms (as in vanadium (V) oxytrichloride) would require a ratio $M:(M+2):(M+4):(M+6)$ of 27:27:9:1.

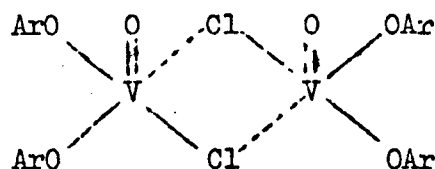
The relative abundance of the isotopes of vanadium is of no use for analysis in low resolution mass spectrometry, the natural abundance of ^{50}V being 0.24% and that of ^{51}V being 99.76%.¹⁵⁸

The conclusion reached from these results is that the reaction between 2,5-di-*t*-butylphenol and vanadium (V) oxytrichloride gives a high yield of bis (2,5-di-*t*-butylphenyl) chlorovanadate (V) which has the following structure:-



From a consideration of the mass spectral data (Table 64) it is apparent that some of the monoester, ArOVOCl_2 may also have been present. However, there is evidence that phenylvanadates of this type exist as dimers, linked by chlorooxygen bridges¹⁵⁹. This is comparable to the situation found with methyl vanadate, $(\text{MeO})_3\text{VO}$, which has been shown to be dimeric, by X-ray diffraction methods¹⁶⁰.

Such a bridged system would result in the close proximity of the chlorine atoms:



Subsequent fragmentation of the dimer would thus result in the formation of ions containing two chlorine atoms, as well as ions derived from the breakdown of the molecular ion $(\text{ArO})_2\text{VOCl}^+$.

The electronic spectrum of the vanadate was also recorded. A comparison of this spectrum with that of the parent phenol shows only slight changes in the region 265 - 290 nm. Both the parent phenol and the vanadate show two distinct bands in this region, which may be assigned to $\pi \rightarrow \pi^*$ transitions of the ring electrons. The vanadium system is obviously not near enough to the ring to cause much alteration of these bands.

The other significant band is that which occurs only in the visible region of the spectrum of the bis (2,5-di-*t*-butylphenyl) chlorovanadate itself. This band ($\lambda_{\text{max}} = 510 \text{ nm}$) is intense ($\epsilon \approx 3000$) and broad and this absorption gives rise to the colour of the compound.

The intensity of the band suggests that it arises from a charge-transfer transition, as vanadium (V) has a d^0 configuration, no d-d transitions can occur.

The details of these spectra are listed in Table 23 .

7.1.2 Recent Developments

Whilst this investigation was being carried out, two new reports concerning the reaction of phenols with vanadium (V) oxytrichloride were published.

The first paper¹⁶¹, in agreement with the findings of Funk, Weiss and Zeising¹⁵³, describes the oxidation of the cresols and naphthols by vanadium (V) oxytrichloride. A thorough study showed that the products of these reactions are dimeric phenols. Other phenols e.g. 2,6-dimethylphenol were also reported to undergo similar oxidative dimerization. The failure to oxidize phenol under similar conditions to those used for the above reactions, shows agreement with the earlier work.

Schwartz, Holton and Scott¹⁶² reported the oxidative coupling of a phenol, but considered that the first stage in the reaction was the formation of a substitution compound, akin to those previously described.

The method used by these workers was to mix the phenol with the oxytrichloride at low temperature and then to reflux the mixture for a considerable time. Extraction with water gave the coupled product in high yield. If, however, the mixture was hydrolysed prior to being heated under reflux, the original phenol was recovered quantitatively. This shows that the oxidative coupling only occurs after prolonged heating. It is significant that, after this prolonged heating, the colour of the reaction

mixture was green, compared to the initial deep blue. The bis(2,5-di-t-butylphenyl) chlorovanadate is also a deep blue-violet in solution. The other phenylvanadates similarly are either deep red or blue in solution.

As a consequence of the publication of these reports, especially the one which stated that further work on the topic was to be reported in due course, the general study of phenol-vanadium (V) oxytrichloride systems was not continued.

One further experiment which was conducted to determine if oxidation occurred under reflux conditions was to react 2,5-di-t-butylphenol with vanadium oxytrichloride.

Ether was chosen as a solvent, this being the solvent used by Schwartz and his coworkers¹⁶². Addition of the phenol to the vanadium (V) oxytrichloride in ether caused the solution to turn blue-violet; it also led to the evolution of hydrogen chloride. The mixture was heated under reflux for twelve hours, but no further colour change was observed. Hydrolysis of the reaction mixture gave a quantitative yield of the original phenol.

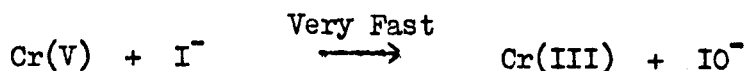
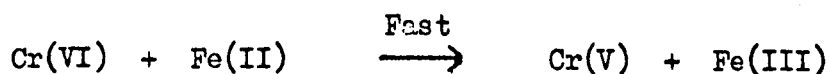
The reaction was repeated using toluene as a solvent, so that a higher reflux temperature could be obtained. Again no colour change was observed during heating. Hydrolysis of the reaction mixture yielded a small quantity of 2,5-di-t-butyl-1,4-benzoquinone, a small amount of a chlorinated di-t-butylphenol and recovered starting material. Analysis of the products by gas-liquid chromatography showed the presence of small amounts (<10%) of a compound having a molecular weight much higher than that of the phenol. This suggested that some coupling does occur under these more rigorous conditions.

7.2 The Reaction of Chromium (V) Oxytrichloride with Phenols

7.2.1 Introduction - Oxidations by Chromium (V)

Oxidations by chromium (V) compounds have not been reported³¹, but there are numerous references in the literature to the formation of chromium (V) and chromium (IV) species as intermediates in both organic and inorganic redox reactions. That these chromium species function as oxidants in their own right is now also established. Much of the evidence for this comes from the phenomenon of induced oxidation^{137,163}.

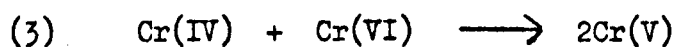
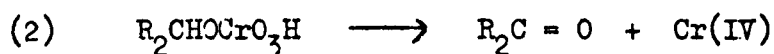
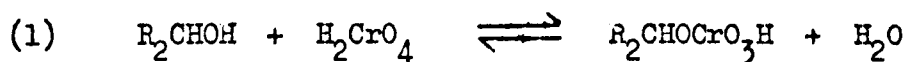
An example of this phenomenon is found in the oxidation of iodide ion by chromium (VI) in dilute acid. Whilst, at low concentration, the reaction is extremely slow, the addition of ferrous ion causes a rapid reaction to occur, leading to the formation of iodine¹⁶⁴. The reaction of iodide ion with ferric ion is slow under these conditions, hence the iodide must be oxidized by a species other than chromium (VI) or iron (III). The explanatory reaction scheme is as follows:



Similar processes have been suggested for the oxidation of organic compounds by chromium (VI). For example the oxidation of cyclohexanone by chromic acid yields adipic acid as the main product, together with smaller amounts of glutaric and succinic acids.

The simplest explanation for the formation of these minor products is by the further oxidation of adipic acid. However, adipic acid is quite unreactive towards chromic acid under the reaction conditions employed. The conclusion reached is that the oxidation to glutaric and succinic acids is caused by Cr(V); this has been confirmed by quantitative experiments on this and other systems¹⁶⁵.

More recently, the presence of chromium (V) species as oxidation intermediates has been confirmed by the direct observation of their ultraviolet and electron spin resonance spectra, during chromic acid oxidations of secondary alcohols^{166,167}. The reaction of chromium (V) with the alcohols is an important stage in the formation of products, as illustrated by the following scheme:



There is recent evidence that, in certain oxidations,¹⁶⁸ chromium (IV) plays a greater part than previously believed. For example, oxidative cleavage reactions which occur in similar systems are now considered likely to be caused by chromium (IV), rather than chromium (V)^{169,170}. Similarly, further research^{167,168} in this field has shown discrepancies in the relative rates of oxidation by

chromium (VI), (V) and (IV) previously reported^{137,165}.

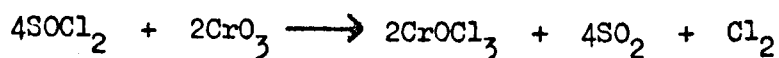
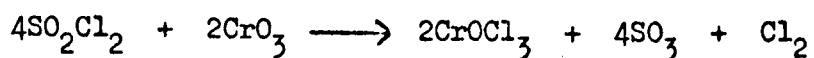
It seems probable that the ease of oxidation or oxidative cleavage is not only dependent on the oxidation state of the chromium but is also dependent on the type of compound undergoing oxidation^{167,168}.

The comparison of the oxidation of an organic compound by chromium (VI) with a similar oxidation by a chromium (V) or chromium (IV) compound would furnish useful information concerning the role of these various oxidants.

As outlined in Chapter 4, section 3, various compounds of chromium (V) and (IV) have been prepared but very few can be used for oxidations in organic chemistry because of their low solubility in suitable solvents. Chromium (V) oxytrichloride which is readily soluble in carbon disulphide and nitrobenzene¹⁷¹, has properties which suggest it may be an exception in this respect.

7.2.2. Chromium (V) Oxytrichloride

Chromium (V) oxytrichloride was first prepared by Krauss and Muenster¹⁵¹, as a red-black crystalline solid, by treating chromium (VI) trioxide with either sulphuryl or thionyl chloride:



The yields of the product were very low but later attempts to prepare this compound, by the reduction of chromyl chloride by various chlorides and oxychlorides, were more successful¹⁷². Thus the reaction between chromyl chloride and boron trichloride gave chromium (V) oxytrichloride in 50% yield.



Although very few of the properties of this compound have been investigated, it is known to decompose readily in the presence of light and to disproportionate into chromyl chloride and solid chromium (III) derivatives at temperatures above 0°.¹⁵¹

It undergoes hydrolysis very rapidly.

The physical properties of the oxychloride are somewhat better documented than the chemical ones. Cryoscopy in nitrobenzene solution has shown that the compound is monomeric; the results of magnetic measurements on the solid are consistent with it being a chromium (V) compound: the chromium has an effective magnetic moment of 1.80 B.M.^{151,171} (cf 1.7 - 1.8 B.M. for metal ions with d¹ configuration, calculated by the 'spin only' formula).

7.2.3 The Reaction of Chromium (V) Oxytrichloride with Phenols

Chromium (V) oxytrichloride was prepared by the method of Krauss and Muenster¹⁵¹, as described in Chapter 10.

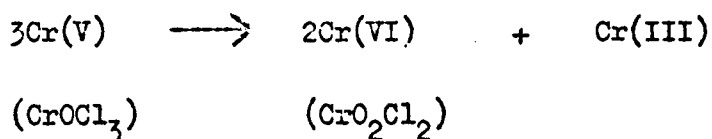
The solubility of the compound in carbon disulphide, appeared to be rather less than that reported¹⁷¹ but, nevertheless, a red solution was obtained.

Addition of a dilute solution of a phenol (3,5-di-t-butylphenol, 2,5-di-t-butylphenol, 2,4,6-tri-t-butylphenol or 2,3,5,6-tetramethylphenol) in carbon disulphide, at 0°, to the solution of chromium (V) oxychloride resulted in the solution turning to a deep blue-green colour. No precipitate was formed at this stage, but continued addition of phenol solution resulted in the reduction in the intensity of the colouration and in precipitate formation. Filtration yielded a small amount of a brown solid, very similar to the chromyl chloride phenol complexes in appearance, together with a small quantity of green solid. The filtrate was a deep brown colour. Where the two di-alkyl-substituted phenols and the tetramethylphenol were used, hydrolysis of both the solid and filtrate yielded small amounts of the corresponding p-benzoquinone. Hydrolysis of the solid derived from 2,4,6-tri-t-butylphenol yielded only a trace of brown resinous material.

Some of the green solid was separated from a suspension of the brown complex by filtration through a coarse filter - the green material was found to exist in relatively large aggregates. It was found to be readily soluble in water and its spectrum in the visible region showed absorptions almost identical to those of an aqueous solution of chromium (III) chloride. Addition of the green substance to an acidic solution of potassium iodide failed to liberate iodine, confirming the absence of chromium in valence states (IV) to (VI).

These results suggest that some of the reduced chromium formed when the phenol is oxidized remains in solution and that it does not form an insoluble complex in an analagous way to the reduced chromium in chromyl chloride oxidations; this also suggests that some disproportionation of the chromium (V) compound occurs.

If disproportionation takes place, chromyl chloride could be formed¹⁵¹ and would itself oxidize phenols:



The possibility that such disproportionation occurs was investigated; the visible spectrum of the solution of chromium (V) oxytrichloride in carbon disulphide was observed prior to addition of a phenol. Very great care was taken to ensure the solvent and apparatus were thoroughly dried and to keep the temperature of the solution at 0°. Exposure of the solution to light was avoided as far as possible.

The resultant spectrum showed a strong, broad band with a maximum at 415 nm. This absorption can be assigned to chromyl chloride (CrO_2Cl_2 $\lambda_{\text{max}} = 416 \text{ nm}$)¹⁷³. Less intense bands, with maxima at 524 nm (broad) and 392 nm (shoulder) can be attributed to the presence of chromium (V) oxytrichloride which has absorption maxima at 522 nm and 390 nm¹⁵¹.

It is thus apparent that some disproportionation occurs. Close inspection shows that some solid material, probably due to chromium (III) compounds, precipitated from the solution of chromium (V) oxytrichloride on standing.

The possibility that the disproportionation had been caused inside the spectrometer by the scanning radiation itself was discounted. Although Krauss and his coworkers had reported the compound to be

light sensitive, they apparently had no difficulty in obtaining the spectrum over the range 300 - 600 nm.

The reaction of chromium (V) oxytrichloride with 2,5-di-*t*-butylphenol was then repeated, in a similar manner as previously, but at -30° in the hope that disproportionation would be minimized. Difficulty was experienced in keeping the phenol in solution at this temperature; thus the phenol was added, partly in suspension, to the solution of oxidant.

The course of the reaction was largely as before. Initially a blue colouration was observed, followed by formation of a brown precipitate - a sequence identical to that observed during the reaction of this phenol with chromyl chloride. The mixture was kept at -30° for six hours and then allowed to warm to room temperature. Filtration gave a yellow-brown filtrate and a solid residue which was a mixture of a green crystalline solid and a brown amorphous complex. Hydrolysis of the solid yielded only a small amount of 2,5-di-*t*-butyl-1,4-benzoquinone. Extraction of the filtrate with water left a yellow organic layer, which, on evaporation, gave a similar product.

Due to the impracticability of observing the spectrum of the solution of chromium (V) oxytrichloride at -30° , no evidence for the presence of chromyl chloride at this temperature is available. It does seem likely, however, that some chromyl chloride was present.

The infrared spectra of the brown precipitates formed in these reactions showed marked similarity to those of the equivalent chromyl chloride-phenol complexes (see Fig. 19); this again suggests oxidation by chromyl chloride. However, although the elemental analyses were not consistent and showed that the complexes were non-stoichiometric, there was a higher proportion of chlorine than that found in the equivalent chromyl chloride complexes, implying that some interaction between the oxytrichloride and phenols occurred.

The analyses of four complexes are presented in Table 12, a comparison is made with those of the similar compounds between chromyl chloride and the same phenols.

7.2.4 Conclusion

From the results discussed above, it is apparent that some disproportionation must occur in each of the reactions with chromium (V) oxytrichloride.

It is probable that the addition of the phenol to the solution of oxychloride accelerates the disproportionation. As the reaction of chromyl chloride with the phenol has been established as a very rapid one, the removal of the former by such a process would tend to favour the disproportionation.

It is also possible that the reaction of the chromium (V) compound with phenols is a slow one in comparison to that of chromyl chloride, despite the reports of rapid oxidations by chromium (V) species in induced oxidations.

TABLE 12

Analyses of Complexes from Chromium (V) Oxychloride Reactions

| Phenol | Found | | | | Calculated for $\text{ArOH} \cdot \text{CrOCl}_3$ | | | | Calculated for $\text{ArOH} \cdot 2\text{CrOCl}_3$ | | | |
|---------------------------|-------|-----|------|------|---|-----|------|------|--|-----|------|------|
| | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% |
| 2,5-Di-t-butylphenol | 23.8 | 4.4 | 32.8 | 18.8 | 44.2 | 5.8 | 28.0 | 13.6 | 30.2 | 4.0 | 38.3 | 18.7 |
| 2,5-Di-t-butylphenol | 24.7 | 3.9 | 34.0 | 19.5 | " | " | " | " | " | " | " | " |
| 2,3,5,6-Tetramethylphenol | 18.6 | 3.5 | 35.6 | 19.6 | 36.9 | 4.3 | 32.8 | 16.0 | 24.1 | 2.8 | 42.8 | 20.9 |
| 2,3,5,6-Tetramethylphenol | 21.1 | 3.9 | 36.9 | 20.8 | " | " | " | " | " | " | " | " |

Analyses of Corresponding Chromyl Chloride Complexes

| Phenol | Found | | | |
|---------------------------|-------|-----|------|------|
| | C% | H% | Cl% | Cr% |
| 2,5-Di-t-butylphenol | 29.7 | 4.4 | 28.8 | 18.7 |
| 2,3,5,6-Tetramethylphenol | 20.1 | 2.8 | 33.2 | 24.5 |

Evidence for this can be deduced from the comparative stabilities of the two chromium compounds in various solvents. For example, chromium (V) oxychloride is reported¹⁵¹ to be only slightly less stable in acetone than in carbon disulphide; the addition of chromyl chloride to acetone results in a vigorous reaction, often accompanied by ignition⁴⁷.

CHAPTER 8

THE PROPERTIES OF THE SOLID COMPLEXES

8.1 The Phenol-Chromyl Chloride Complexes

The reaction of chromyl chloride with the phenols, whose oxidation products have been described in the previous Chapter, yields coloured, amorphous solids, analogous to the Etard adducts.

The difficulties associated with the elucidation of the structure of the Etard adducts have been outlined in Chapter 4, part 3; the principle problems are the complete insolubility of the adducts in non-polar solvents, and the irreversible reaction of the adducts with polar solvents.

It has been found, in this study, that the same problems exist for the phenol-chromyl chloride complexes: the complexes are completely insoluble in carbon tetrachloride, carbon disulphide and other non-polar solvents. However, in polar donor solvents, the complexes are completely decomposed. Thus, subsequent removal of the polar solvent fails to give back the original complex and hence purification by recrystallization is not possible.

The lack of a suitable solvent for the complexes makes the use of techniques such as nuclear magnetic resonance and ultra-violet spectroscopy of little value in the elucidation of their structure.

Because these compounds have a distinctive colour, which varies with the phenol oxidized, an attempt was made to examine the visible/ultra-violet absorption spectra by a reflectance method. A similar technique has yielded pertinent information in the case of other insoluble complexes⁸⁴.

The spectra of these phenol-chromyl chloride complexes consisted of very broad, ill-defined bands and no interpretation of them was made.

Physical techniques which were used successfully to study these complexes in the solid state included infrared and electron spin resonance spectroscopy, and the measurement of magnetic susceptibility.

Elemental analyses were obtained for the complexes, and the reaction of one of the complexes with donor solvents was investigated in detail.

The results of this investigation are presented below.

8.1.1 Elemental Analyses

The phenol-chromyl chloride complexes were analysed for carbon, hydrogen, chlorine and chromium. For the complexes derived from the nitrophenols, nitrogen was determined also.

The analytical results are listed in Tables 13,14 and 15. A comparison has been made with the values calculated for both 1:1 and 1:2 complexes ($\text{ArOH}:\text{CrO}_2\text{Cl}_2$ and $\text{ArOH} \cdot 2\text{CrO}_2\text{Cl}_2$ respectively).

It can be seen that the experimental figures correspond more closely to those calculated for a 1:2 complex than those for a 1:1 complex. However, in most cases there is an absence of simple stoichiometry.

There are a number of exceptions to this general rule. For example, the complex obtained from the interaction of chromyl chloride and 2,6-dinitrophenol had an approximate 1:1 stoichiometry; by comparison the 3,5-di-t-butyl catechol complex had a composition corresponding to the 1:2 complex, $\text{C}_{14}\text{H}_{22}\text{O}_2 \cdot 2\text{CrO}_2\text{Cl}_2$.

Analysis of those complexes which yielded an oxidation product resulting from side-chain attack (e.g. the complexes derived from 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butyl-4-methylphenol) showed stoichiometries which differed considerably from those required for either 1:1 or 1:2 complexes.

One significant feature of the analytical results is that the chromium to chlorine ratio is very close to 1:2 in most of the complexes*. The implication of this is that chlorination does not occur in these oxidations to any great extent. By comparison, oxidation of hydrocarbons by chromyl chloride often results in the formation of chlorinated products^{5,79}, which do not readily form chromyl chloride 'adducts'. Thus, these chlorinated compounds are generally found in the filtrates obtained from the isolation of the Etard complexes. For this reason, analysis of the latter often shows an inexact chromium to chlorine ratio.

The elemental analyses of the phenol-chromyl chloride complexes were found to vary with the mode of preparation of the complex, and also with the solvent used for the reaction. Thus complexes prepared in carbon tetrachloride had a high chlorine content with low analyses for other elements, compared to the complexes prepared in carbon disulphide. This trend is illustrated below for the complex derived from 2,6-di-*t*-butylphenol.

| Solvent | C% | H% | Cl% | Cr% |
|----------------------|------|-----|------|------|
| Carbon Tetrachloride | 23.7 | 2.4 | 30.2 | 13.5 |
| Carbon Disulphide | 29.4 | 4.3 | 27.9 | 20.8 |

The experimental procedures employed for the preparation of the complexes are described in Chapter 10.

* See Table 16.

TABLE 13

Analyses of Phenol-Chromyl Chloride Complexes

| Phenol | Found | | | | Calculated for $\text{ArOH} \cdot \text{CrO}_2\text{Cl}_2$ | | | | Calculated for $\text{ArOH} \cdot 2\text{CrO}_2\text{Cl}_2$ | | | |
|-------------------------------|-------|------|------|------|--|-----|------|------|---|-----|------|------|
| | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% |
| Phenol | 22.8 | 3.9 | 28.5 | 18.1 | 28.9 | 2.4 | 28.5 | 20.9 | 17.8 | 1.5 | 35.1 | 25.7 |
| 2-t-Butylphenol | 24.7 | 4.0 | 30.1 | 20.6 | 39.3 | 4.6 | 23.3 | 17.0 | 26.1 | 3.0 | 30.9 | 22.6 |
| 4-t-Butylphenol | 22.5 | 3.35 | 30.4 | 19.3 | 39.3 | 4.6 | 23.3 | 17.0 | 26.1 | 3.0 | 30.9 | 22.6 |
| 2,5-Dimethylphenol | 20.9 | 3.2 | 31.6 | 23.4 | 34.7 | 4.7 | 25.6 | 18.8 | 22.2 | 3.0 | 32.9 | 24.1 |
| 2,5-Di-isopropylphenol | 28.6 | 3.6 | 28.9 | 21.0 | 43.2 | 5.4 | 21.3 | 15.6 | 29.5 | 3.7 | 29.1 | 21.3 |
| 2,6-Di-isopropylphenol | 28.0 | 4.0 | 28.6 | 21.4 | 43.2 | 5.4 | 21.3 | 15.6 | 29.5 | 3.7 | 29.1 | 21.3 |
| 2,3,5-Trimethylphenol | 23.3 | 3.1 | 30.9 | 21.4 | 37.1 | 4.1 | 24.4 | 17.9 | 24.2 | 2.7 | 31.8 | 23.3 |
| 2,3,6-Trimethylphenol | 23.9 | 3.2 | 30.6 | 21.3 | 37.1 | 4.1 | 24.4 | 17.9 | 24.2 | 2.7 | 31.8 | 23.3 |
| 2,3,5,6-Tetramethylphenol | 20.1 | 2.8 | 33.2 | 24.3 | 39.3 | 4.6 | 23.3 | 17.0 | 26.1 | 3.0 | 30.9 | 22.6 |
| 2,5-Di-t-butylphenol | 29.7 | 4.4 | 28.8 | 18.7 | 46.5 | 6.1 | 19.7 | 14.4 | 32.6 | 4.3 | 27.5 | 20.6 |
| 2,6-Di-t-butylphenol | 29.4 | 4.3 | 27.9 | 20.8 | 46.5 | 6.1 | 19.7 | 14.4 | 32.6 | 4.3 | 27.5 | 20.2 |
| 3,5-Di-t-butylphenol | 29.3 | 4.2 | 28.4 | 20.6 | 46.5 | 6.1 | 19.7 | 14.4 | 32.6 | 4.3 | 27.5 | 20.2 |
| 2,4-Di-t-butylphenol | 26.6 | 4.2 | 28.4 | 19.0 | 46.5 | 6.1 | 19.7 | 14.4 | 32.6 | 4.3 | 27.5 | 20.2 |
| 2,4,6-Tri-t-butylphenol | 26.75 | 4.4 | 24.7 | 21.4 | 51.8 | 7.2 | 17.0 | 12.5 | 37.8 | 5.2 | 24.8 | 18.2 |
| 2,6-Di-t-butyl-4-methylphenol | 27.4 | 4.1 | 29.8 | 22.2 | 48.0 | 6.4 | 18.9 | 13.9 | 34.0 | 4.5 | 26.8 | 19.6 |

TABLE 14

Analyses of Phenol - Chromyl Chloride Complexes (Contd.)

| Phenol | Found | | | | Calculated for $\text{ArOH} \cdot \text{CrO}_2\text{Cl}_2$ | | | | Calculated for $\text{ArOH} \cdot 2\text{CrO}_2\text{Cl}_2$ | | | |
|--------------------------------|-------|-----|------|------|--|-----|------|------|---|-----|------|------|
| | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% | C% | H% | Cl% | Cr% |
| 2,4-Di-t-butyl-6-methyl-phenol | 28.1 | 4.4 | 27.4 | 17.0 | 48.0 | 6.4 | 18.9 | 13.9 | 34.0 | 4.5 | 26.8 | 19.6 |
| 3,5-Di-t-butylcatechol | 31.4 | 4.1 | 26.5 | 19.3 | 44.6 | 5.8 | 18.8 | 13.8 | 31.6 | 4.1 | 26.7 | 19.5 |
| 4,6-Di-t-butylpyrogallol | 25.5 | 4.2 | 27.4 | 17.4 | 42.7 | 5.6 | 18.1 | 13.2 | 30.7 | 4.0 | 25.9 | 19.0 |
| 1-Naphthol | 30.8 | 1.0 | 28.3 | 20.2 | 40.1 | 2.3 | 23.7 | 17.4 | 26.4 | 1.8 | 33.3 | 22.9 |

TABLE 15

Analyses of Nitrophenol-Chromyl Chloride Complexes

| Phenol | Found | | | | | Calculated for $\text{ArOH} \cdot \text{CrO}_2\text{Cl}_2$ | | | | | Calculated for $\text{ArOH} \cdot 2\text{CrO}_2\text{Cl}_2$ | | | | |
|-------------------|-------|-----|------|------|-----|--|-----|------|------|-----|---|-----|------|------|-----|
| | C% | H% | Cl% | Cr% | N% | C% | H% | Cl% | Cr% | N% | C% | H% | Cl% | Cr% | N% |
| 2-Nitrophenol | 13.5 | 2.0 | 25.2 | 19.2 | 3.6 | 24.5 | 1.7 | 24.1 | 17.7 | 4.8 | 16.1 | 1.1 | 31.6 | 23.2 | 3.7 |
| 3-Nitrophenol | 16.0 | 2.6 | 26.9 | 20.2 | 2.7 | 24.5 | 1.7 | 24.1 | 17.7 | 4.8 | 16.1 | 1.1 | 31.6 | 23.2 | 3.1 |
| 4-Nitrophenol | 12.0 | 2.5 | 30.5 | 21.1 | 1.2 | 24.5 | 1.7 | 24.1 | 17.7 | 4.8 | 16.1 | 1.1 | 31.6 | 23.2 | 3.1 |
| 2,6-Dinitrophenol | 21.3 | 1.4 | 20.6 | 16.4 | 7.6 | 21.2 | 1.2 | 20.9 | 15.3 | 8.3 | 14.5 | 0.8 | 28.8 | 21.1 | 5.7 |

TABLE 16

The Ratio of Chromium to Chlorine in the Complexes

| Phenol | Ratio of Chromium to Chlorine in the Complex |
|-------------------------------|---|
| Phenol | 1 : 2.3 |
| 2-t-Butylphenol | 1 : 2.1 |
| 4-t-Butylphenol | 1 : 2.3 |
| 2,5-Dimethylphenol | 1 : 2.0 |
| 2,5-Di-isopropylphenol | 1 : 2.0 |
| 2,6-Di-isopropylphenol | 1 : 1.95 |
| 2,3,5-Trimethylphenol | 1 : 2.1 |
| 2,3,6-Trimethylphenol | 1 : 2.1 |
| 2,3,5,6-Tetramethylphenol | 1 : 2.0 |
| 2,5-Di-t-butylphenol | 1 : 2.2 |
| 2,6-Di-t-butylphenol | 1 : 1.95 |
| 3,5-Di-t-butylphenol | 1 : 2.0 |
| 2,4-Di-t-butylphenol | 1 : 2.2 |
| 2,4,6-Tri-t-butylphenol | 1 : 1.7 |
| 2,6-Di-t-butyl-4-methylphenol | 1 : 2.0 |
| 2,4-Di-t-butyl-6-methylphenol | 1 : 2.4 |
| 3,5-Di-t-butylcatechol | 1 : 2.0 |
| 4,6-Di-t-butylpyrogallol | 1 : 2.3 |
| 1-Naphthol | 1 : 2.05 |
| 2-Nitrophenol | 1 : 1.9 |
| 3-Nitrophenol | 1 : 1.95 |
| 4-Nitrophenol | 1 : 2.1 |
| 2,6-Dinitrophenol | 1 : 1.9 |

8.1.2 The Magnetic Properties of the Complexes

The magnetic susceptibilities of the phenol-chromyl chloride complexes were measured over a wide range of temperature, using the Gouy method.

In each case, the susceptibility was determined at two different field strengths in order to observe the dependence on field strength that might accompany a temperature dependence.

From these measurements, the magnetic moments of the complexes were calculated. These results are listed in Tables 24 to 36, and are presented graphically in Figures 6 to 11.

All the complexes were found to be paramagnetic; the molar susceptibility per g. atom of chromium (χ_M) was found to be inversely proportional to the absolute temperature. This temperature dependence of the susceptibility indicates that the Curie-Weiss Law is obeyed:

$$M = \frac{C}{T + \Theta}$$

χ_M = the molar susceptibility, calculated per g. atom of chromium

C = the Curie constant

Θ = the Curie-Weiss constant

T = the absolute temperature

The values of the Curie-Weiss constants were found to be small and negative ($< 30^\circ$).

The graphs of χ_M vs T are all smooth curves with no points of inflexion or any discontinuities (Figs. 6 and 7).

From these results it may be concluded that, over the temperature range studied, the complexes all show simple

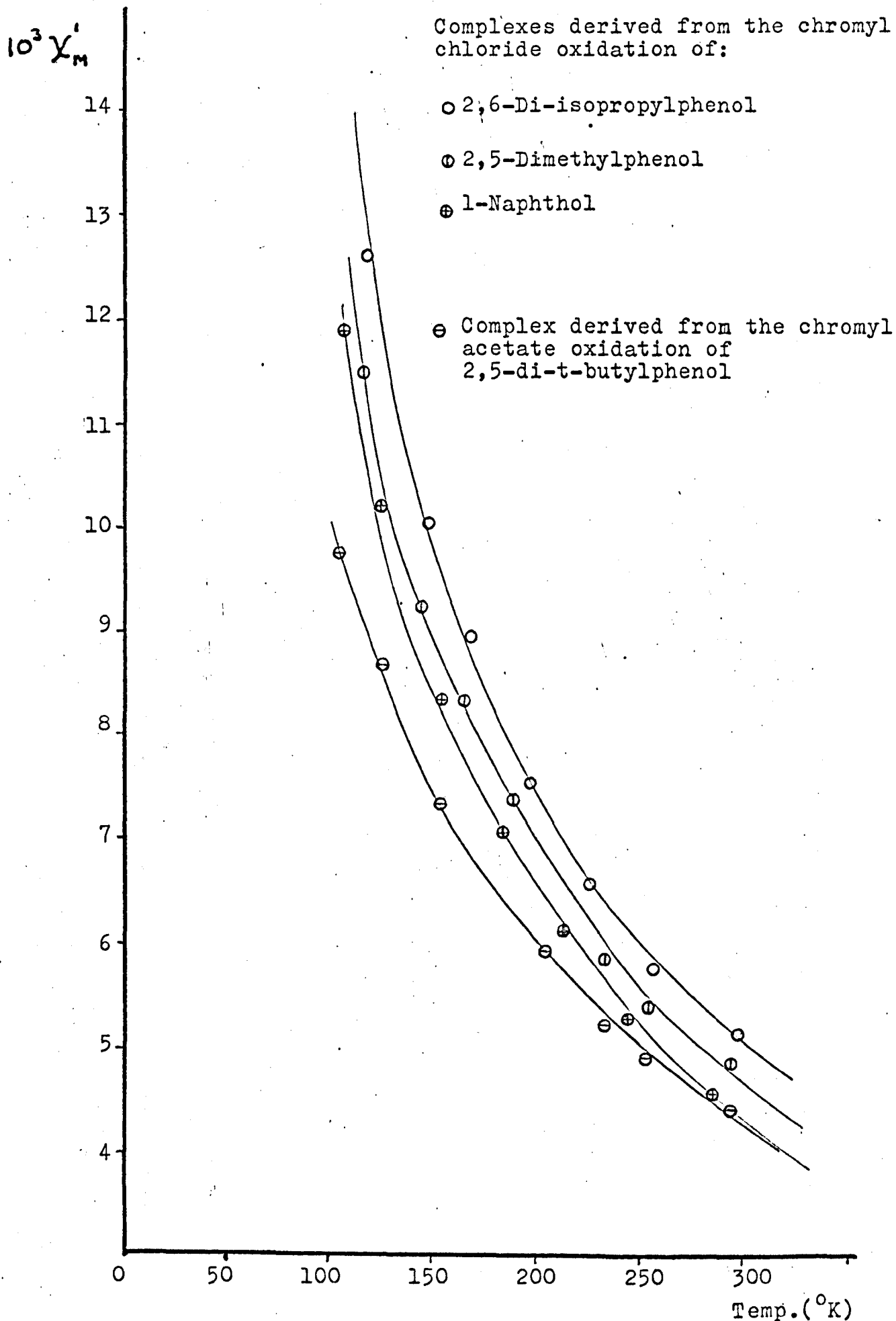


Fig.6. Corrected molar susceptibility vs temperature.

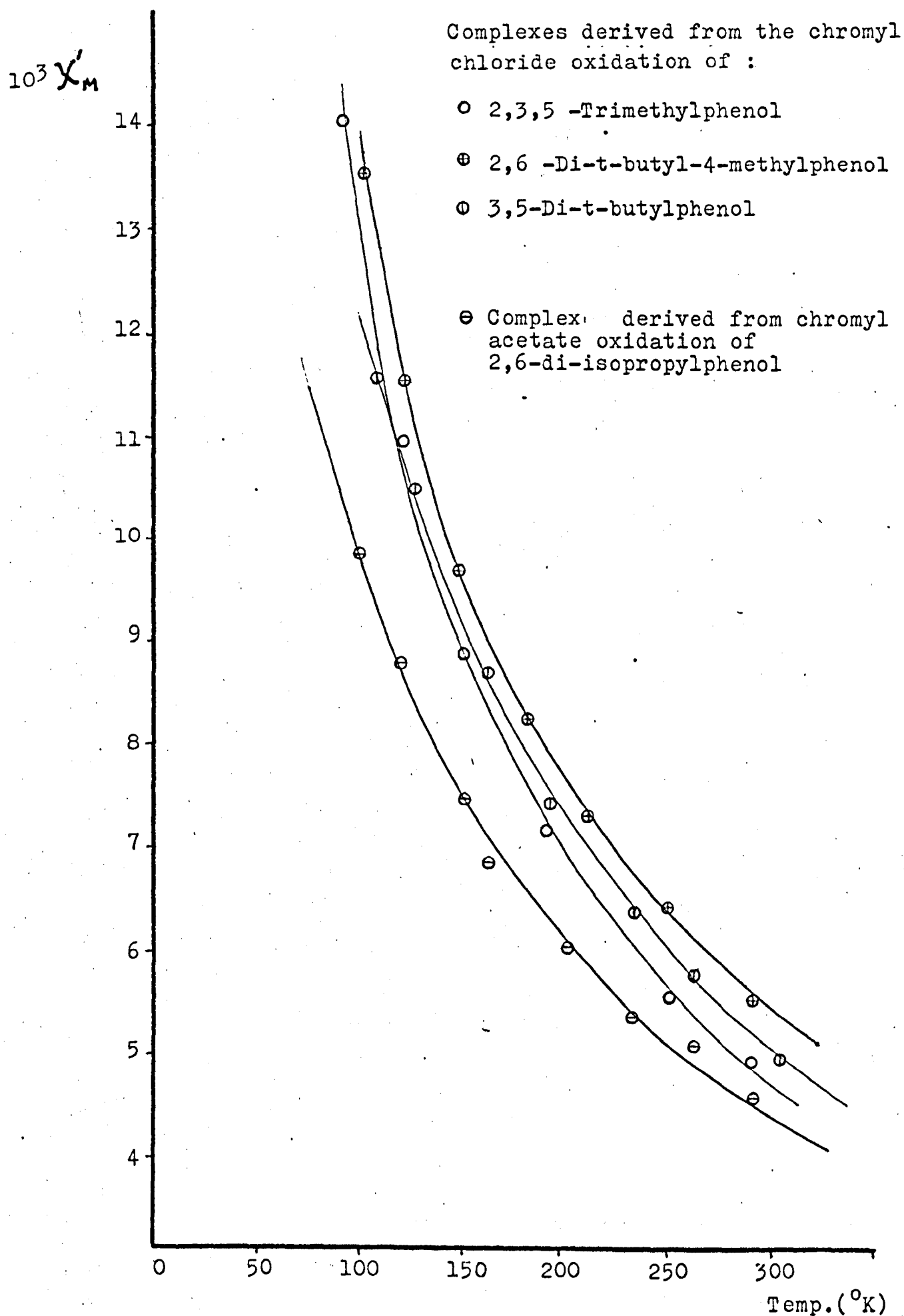


Fig.7. Corrected molar susceptibility vs temperature.

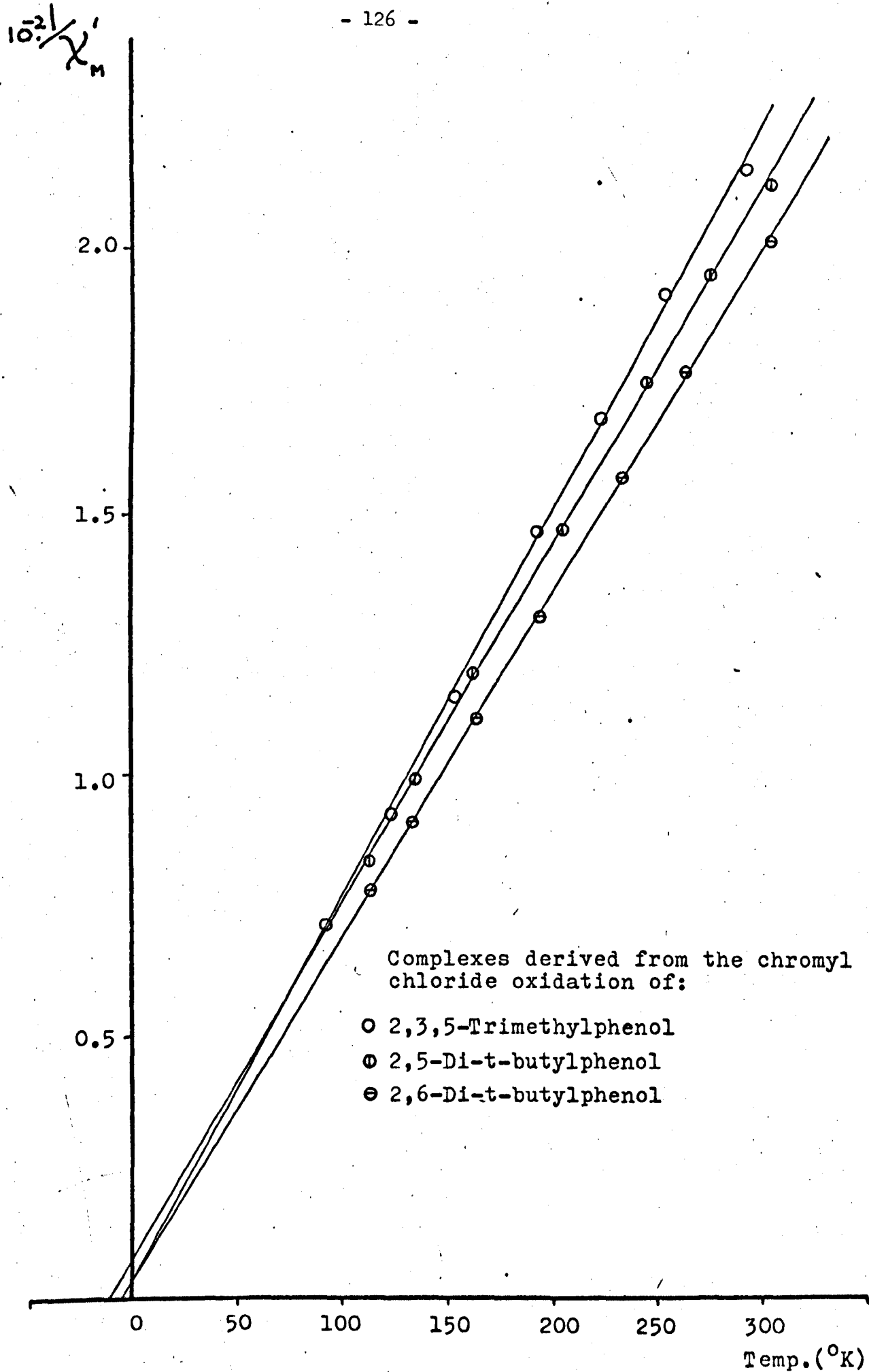


Fig.8. Inverse corrected molar susceptibility vs temperature.

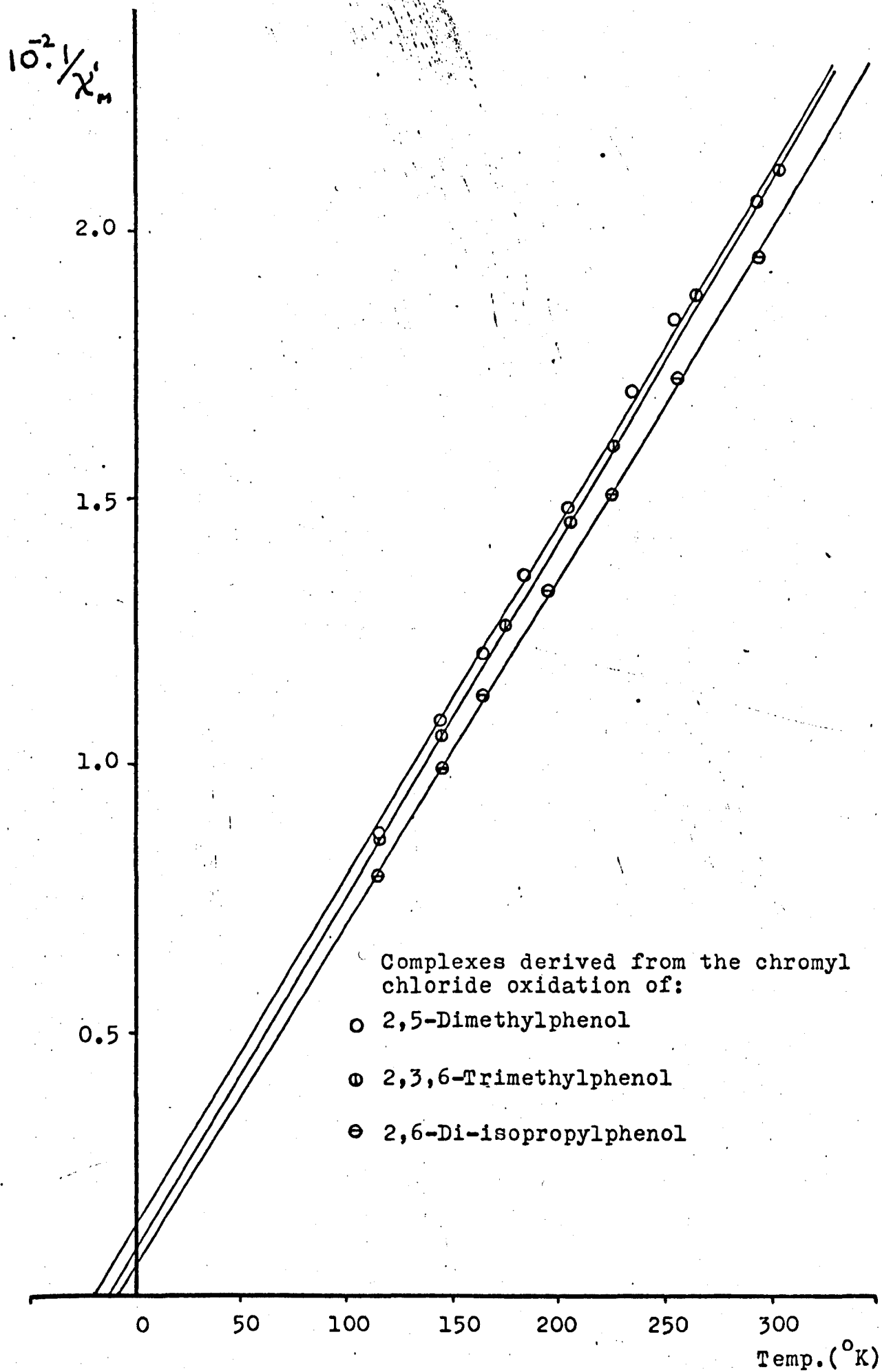


Fig.9. Inverse corrected molar susceptibility vs temperature

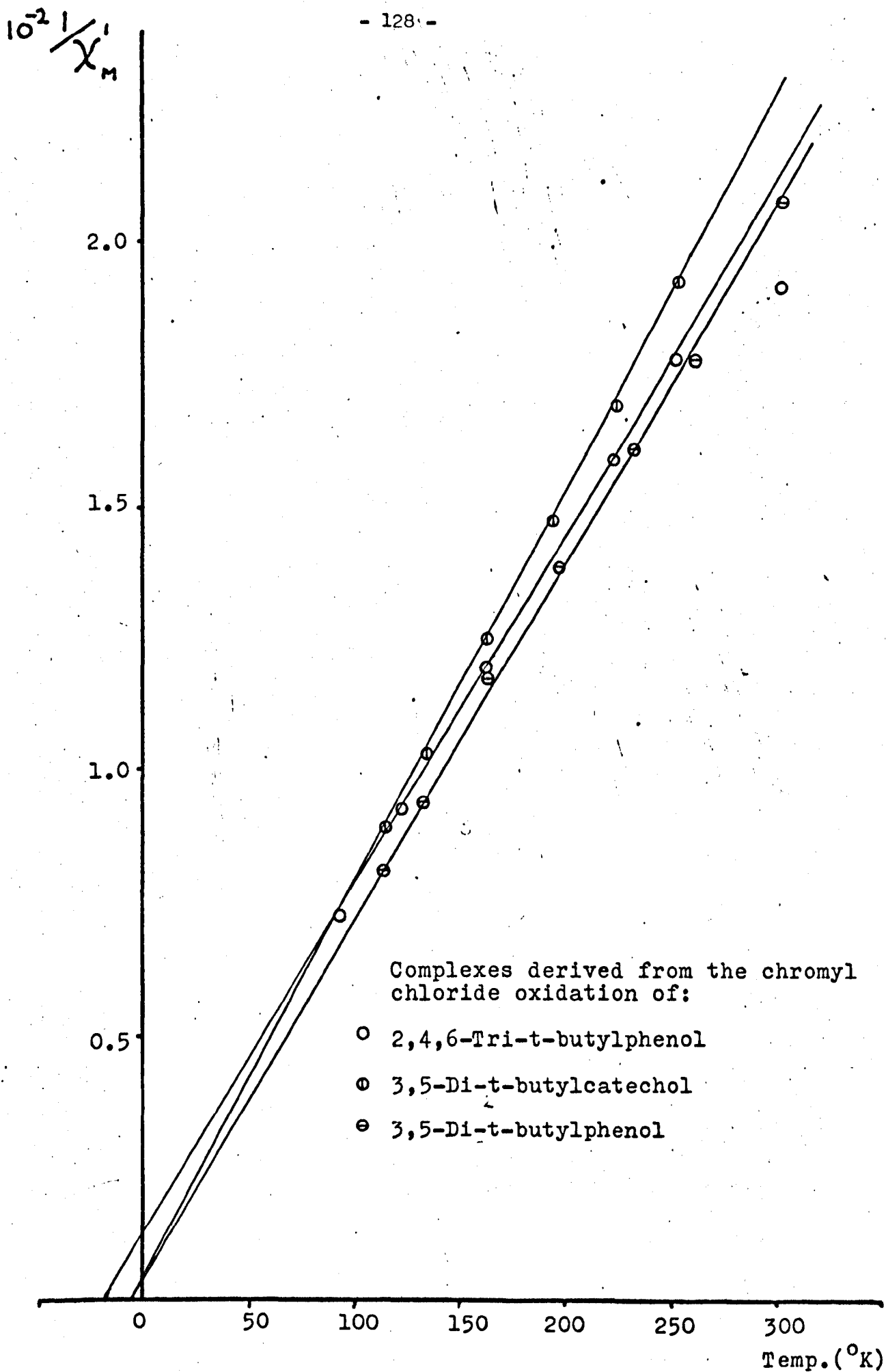


Fig.10. Inverse corrected molar susceptibility vs temperature

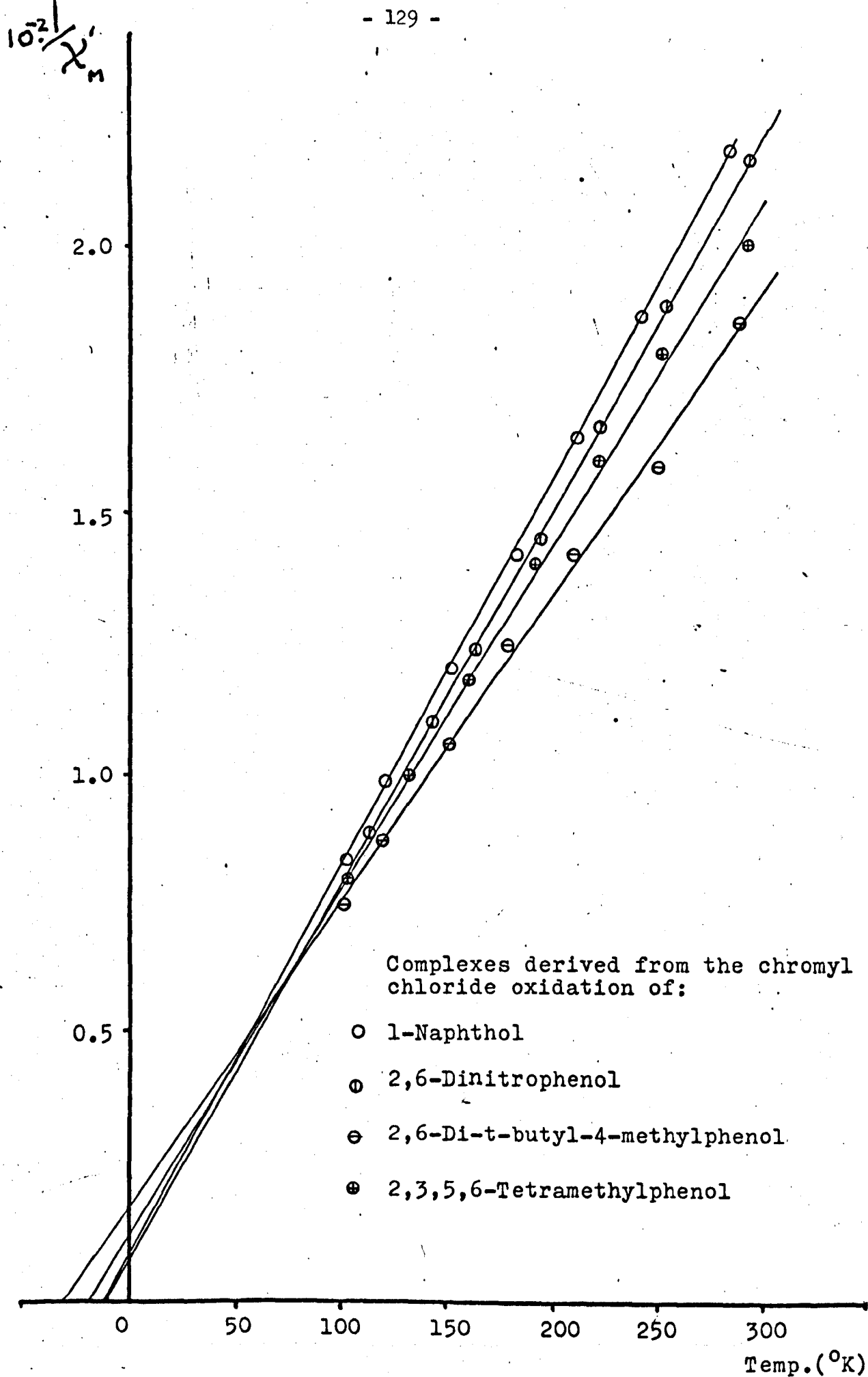


Fig.11. Inverse corrected molar susceptibility vs temperature.

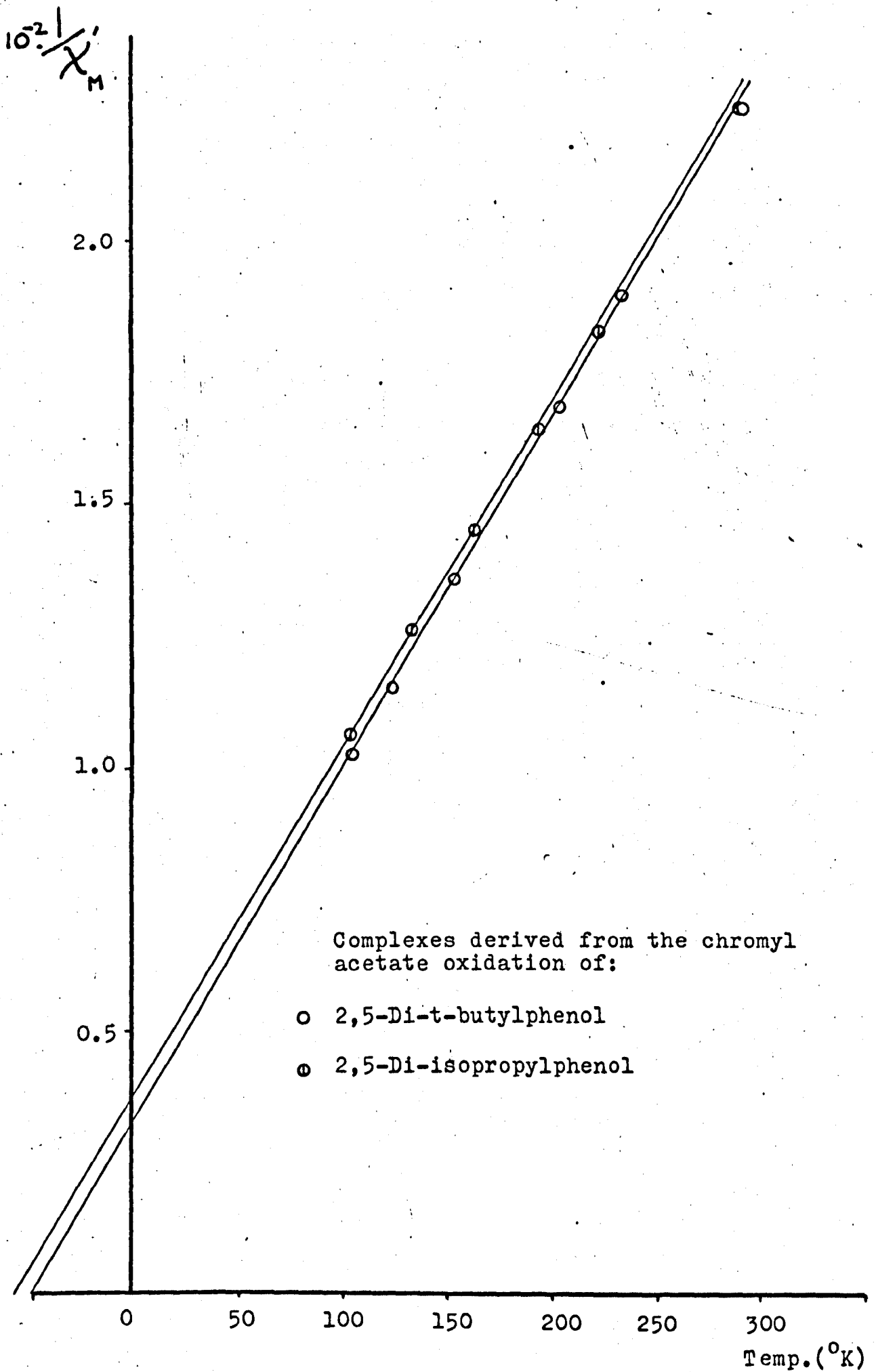


Fig.12. Inverse corrected molar susceptibility vs temperature.

paramagnetism with no evidence for ferromagnetism or anti-ferromagnetism.

However, it is possible that these effects could be observed at lower temperature.

The average values of the effective magnetic moments of the chromium in these complexes are listed in Table 17, it can be seen that they vary between 3.23 B.M. and 3.46 B.M. These values have been corrected as far as possible for the diamagnetism of the groups or atoms present with the chromium in the solids.

The values of the effective magnetic moment which have been obtained for simple, magnetically dilute, chromium compounds, are tabulated below¹⁷⁴ :

| Valency State | Calculated Value* of Effective Magnetic Moment (B.M.) | Observed Value of the Moment (B.M.) |
|---------------|--|---|
| Cr (VI) | 0 | Diamagnetic |
| Cr (V) | 1.73 | 1.7 → 1.8 |
| Cr (IV) | 2.83 | 2.8 → 3.1 |
| Cr (III) | 3.87 | 3.85 → 3.9 |

The experimental values do not fall within the limits given for any one oxidation state but come between the values expected for chromium (III) and chromium (IV).

However, it has been reported¹⁷⁵ that, when bridging groups are present in binuclear complexes of chromium (III) and iron (III),

* The calculated values are those obtained from the 'spin-only' formula.

TABLE 17

Collected Data from Magnetic Susceptibility Measurements for
Phenol-Chromyl Chloride Complexes

| Phenol from which complex is derived | Average Effective Magnetic Moment (B.M.) | Weiss constant (Θ°) |
|--------------------------------------|--|---|
| 2,5-Dimethylphenol | 3.31 | 20 |
| 2,3,5-Trimethylphenol | 3.29 | 7 |
| 2,3,6-Trimethylphenol | 3.31 | 16 |
| 2,3,5,6-Tetramethylphenol | 3.33 | 16 |
| 2,6-Di-isopropylphenol | 3.42 | 9 |
| 2,5-Di-t-butylphenol | 3.33 | 12 |
| 2,6-Di-t-butylphenol | 3.44 | 8 |
| 3,5-Di-t-butylphenol | 3.24 | 9 |
| 2,6-Di-t-butyl-4-methylphenol | 3.45 | 30 |
| 2,4,6-Tri-t-butylphenol | 3.33 | 18 |
| 3,5-Di-t-butylcatechol | 3.24 | 5 |
| 1-Naphthol | 3.20 | 13 |
| 2,6-Dinitrophenol | 3.27 | 13 |

interactions occur between the magnetic centres. This results in values of effective magnetic moment which differ from those calculated by use of the 'spin-only' formula.

For example, the value of effective magnetic moment of the complex $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4\text{H}_2\text{O}] \text{Br}_5$ varies linearly from 2.75 B.M. at 100.4°K to 3.52 B.M. at 293.7°K, whilst that of a similar complex varies from 2.73 B.M. at 99.0°K to 3.44 B.M. at 294.5°K¹⁷⁵.

The values of effective magnetic moment for chromium complexes with two or more bridging groups, whether chloro or hydroxy are very little different from those of the 'spin-only' value, at room temperature, but tend to fall below this value at lower temperature¹⁷⁵.

It is significant that, if there is only one bridging group in the complex, the Weiss constant is large, usually greater than 70°, Since the Weiss constants for the chromyl chloride-phenol complexes are all much smaller than the values for the bridged complexes described above, it is unlikely that an interaction of this type is the explanation of the experimental results.

The most likely consideration is that both chromium (III) and chromium (IV) are present in these complexes. The presence of chromium species with a large number of chloro or hydroxy bridges between chromium atoms cannot be ruled out, as such systems appear to lead to only minor deviations from the 'spin-only' formula.

Confirmation of the oxidation state by titrimetric methods proved to be impractical because hydrolysis of the complexes liberates p-benzoquinones which are themselves oxidants which interfere with the analytical methods used.

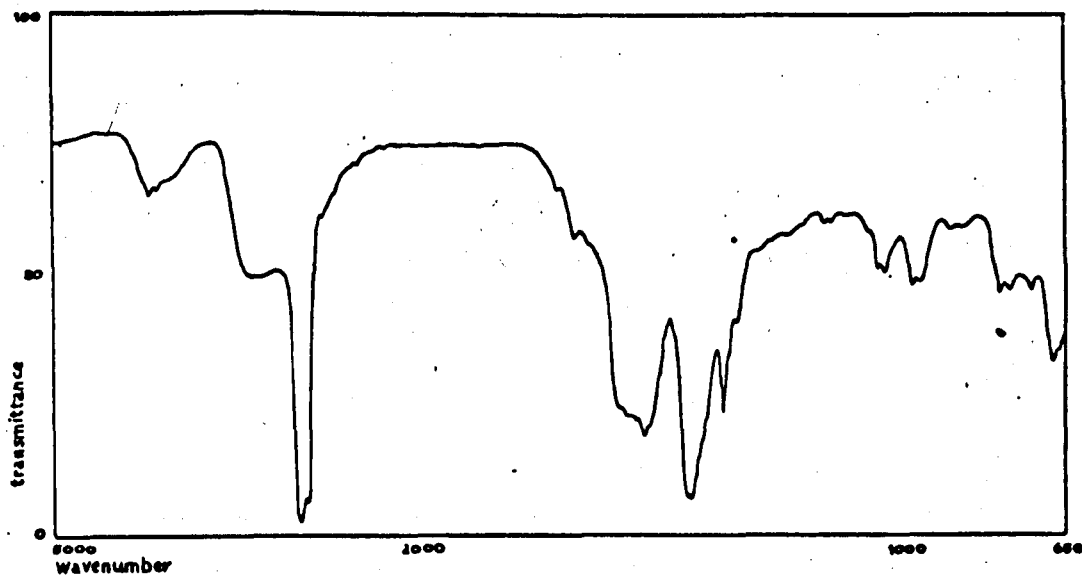
From a consideration of the magnetic measurements it can be seen quite clearly that the formation of the complex has been accompanied by a reduction in the oxidation state of the chromium. It is not possible, however, to come to positive conclusions regarding the structure of these solids on the basis of these results. Some of the possible structures of the phenol-chromyl chloride complexes are discussed in Chapter 9.

8.1.3 The Infrared Spectra of the Phenol-Chromyl Chloride Complexes

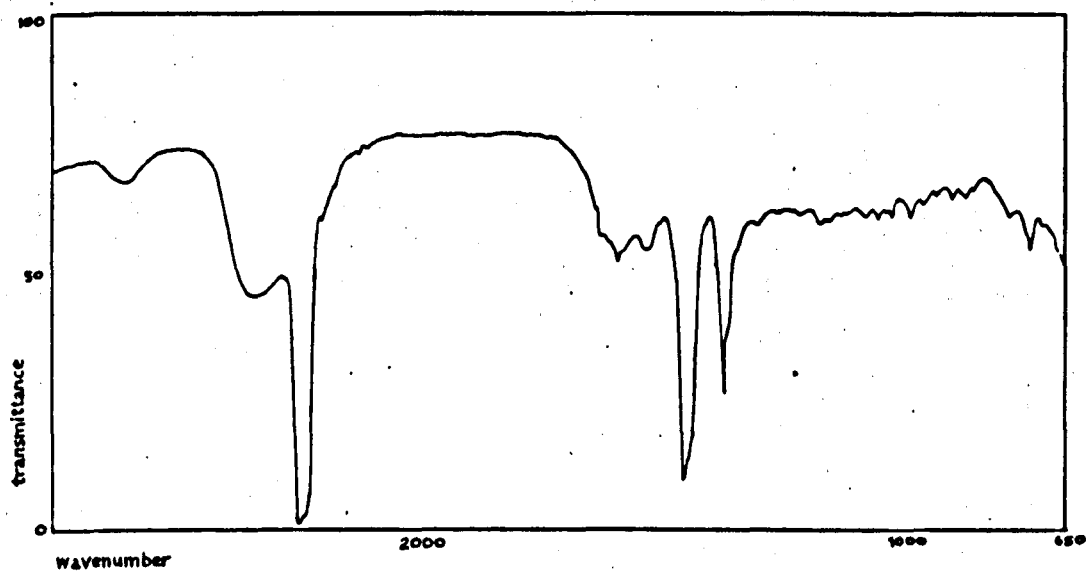
Only the infrared spectra of the complexes in the solid state were obtained; the insolubility of the complexes in non-polar solvents prevented an examination of the solution spectra.

The infrared spectra of the complexes are presented in Tables 39 to 58, and certain of these are illustrated in Figs. 13-19. In the tables, details of the spectra of the phenols, from which the complexes have been derived, and their oxidation products have been included for the sake of comparison.

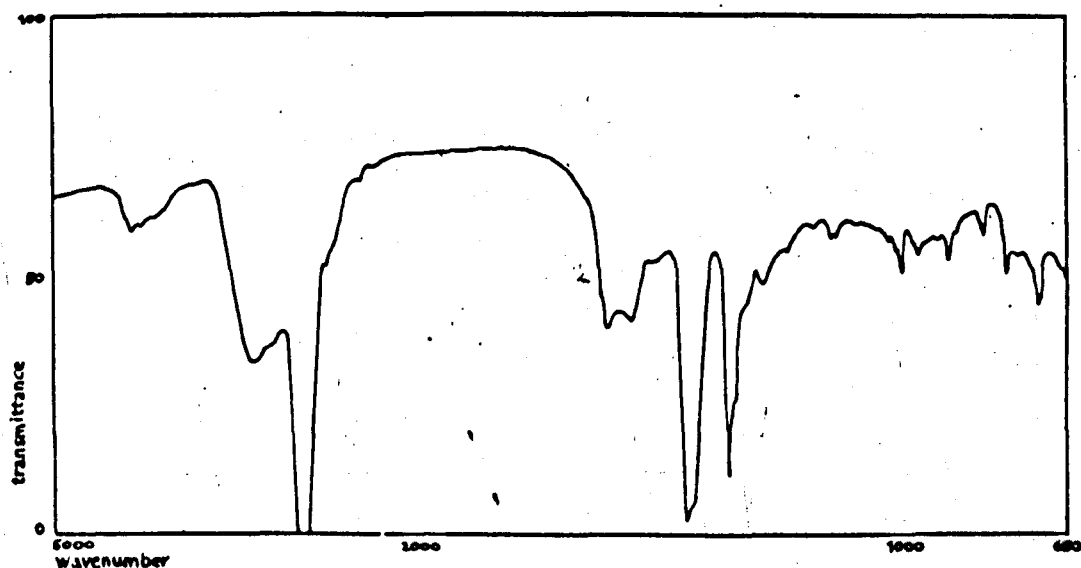
It can be seen that, apart from a very broad band of strong intensity between 3000 and 3500 cm^{-1} , there are few bands common to all the spectra. However, a comparison with the spectra of the phenol-oxidation products often shows considerable similarity between the spectra. It is significant, that the spectra of the complexes, which on hydrolysis give high yields of a discrete organic product, are better defined, with sharper absorptions, than those of complexes which yield mainly resinous material. The spectra of the latter are poorly defined, with broad and indistinct absorptions, indicating the absence of a high concentration of any single organic species in the complexes.



Complex derived from the oxidation
of phenols by chromyl acetate.

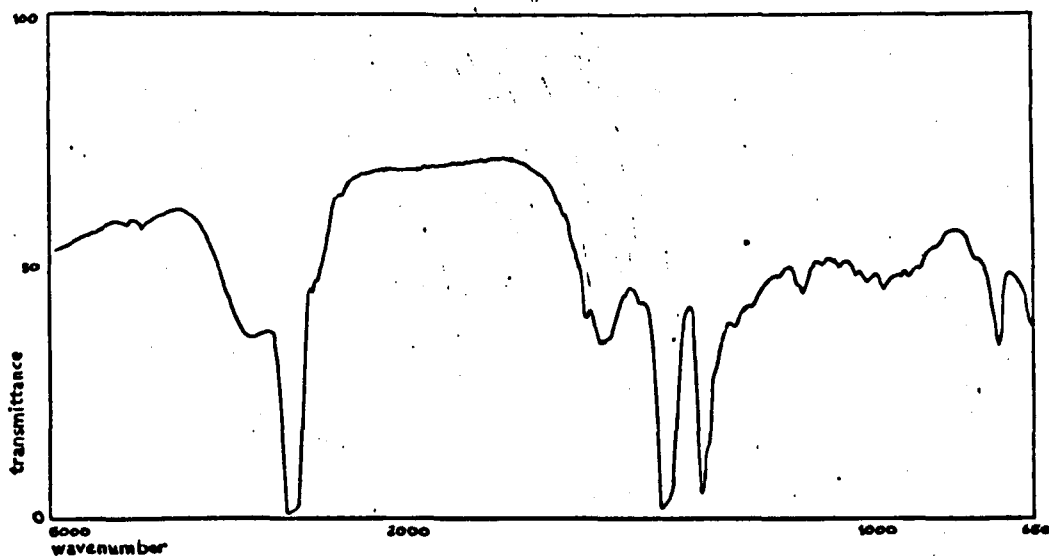


Phenol—chromyl chloride complex.

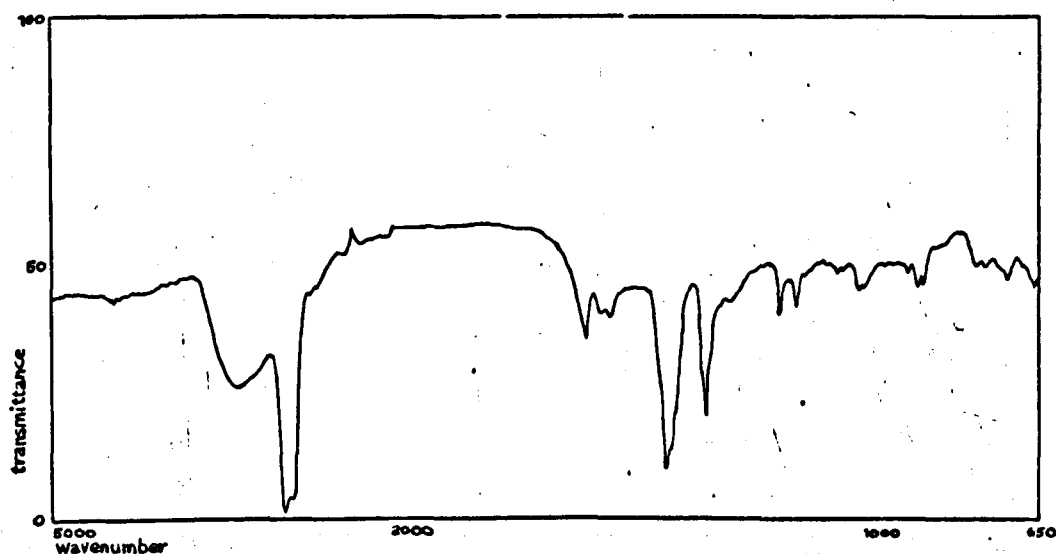


2-t-Butylphenol - chromyl chloride complex.

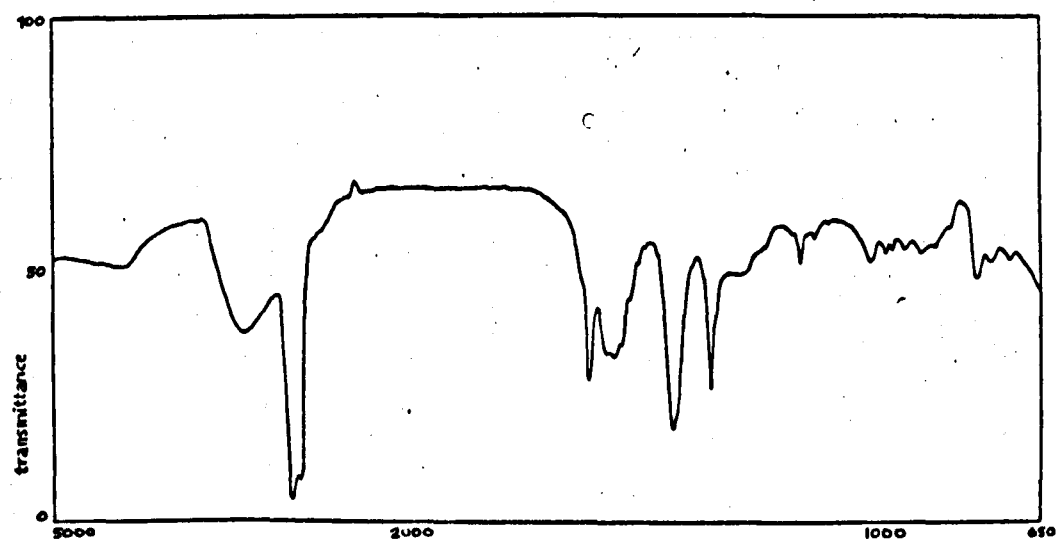
Fig.13. Infrared spectra of complexes derived from chromyl acetate and chromyl chloride oxidation of phenols.



2,5-Dimethylphenol - chromyl chloride complex.

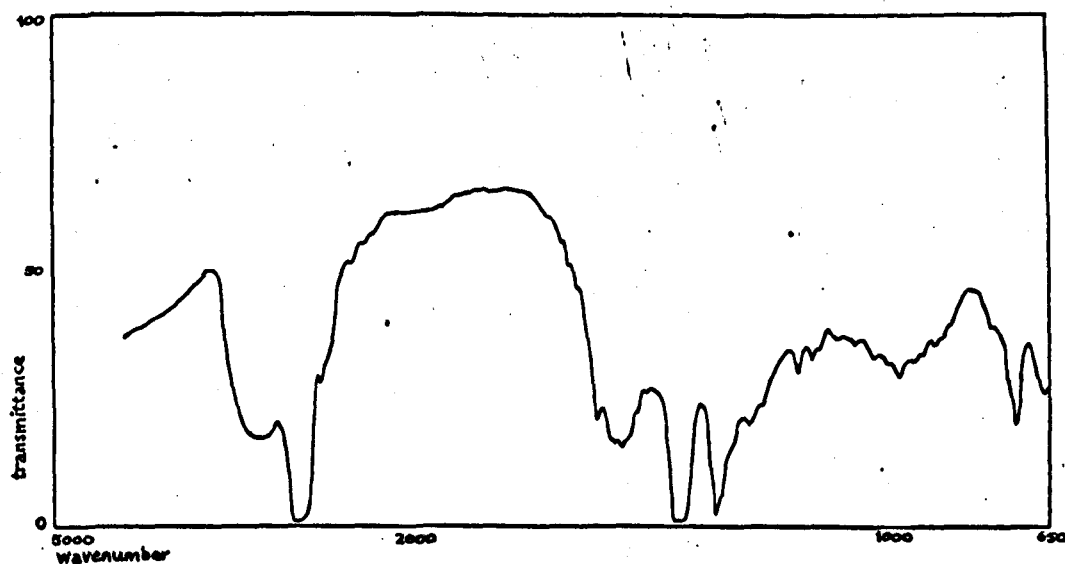


2,6-Dimethylphenol - chromyl chloride complex.

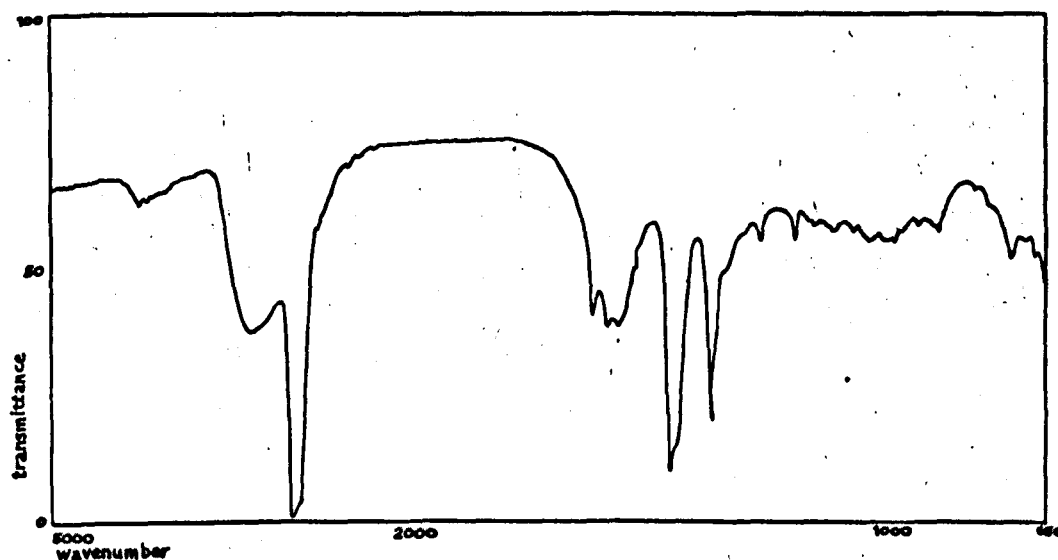


3,5-Dimethylphenol - chromyl chloride complex.

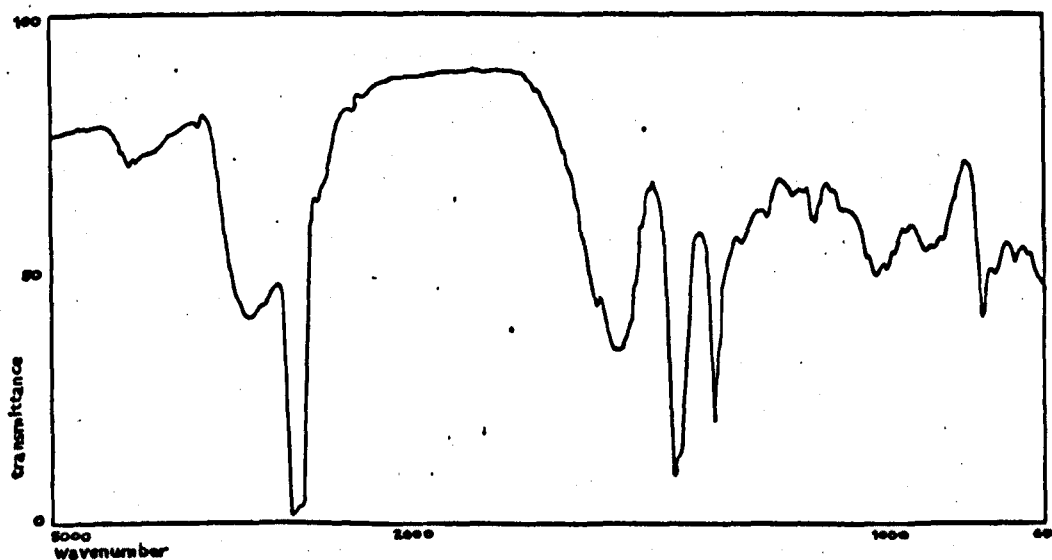
Fig.14. Infrared spectra of phenol - chromyl chloride complexes



2,3,6-Trimethylphenol - chromyl chloride complex.

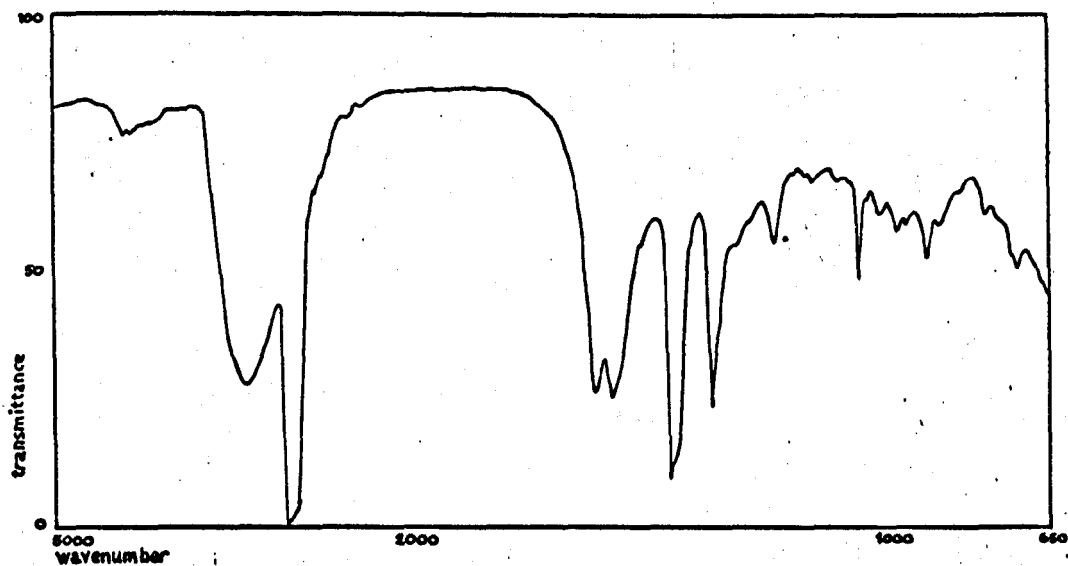


2,3,5-Trimethylphenol - chromyl chloride complex.

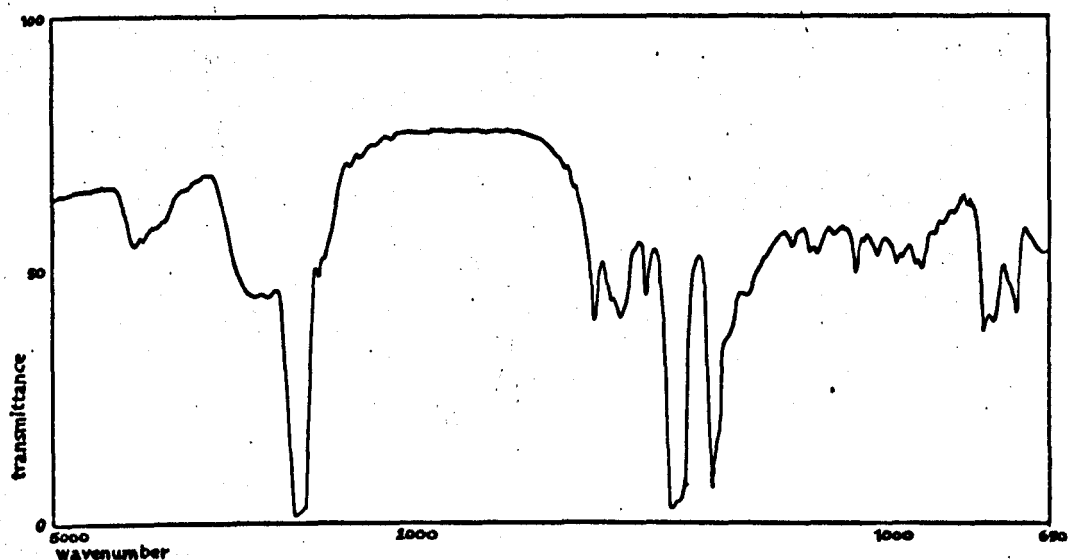


2,4,6-Trimethylphenol - chromyl chloride complex.

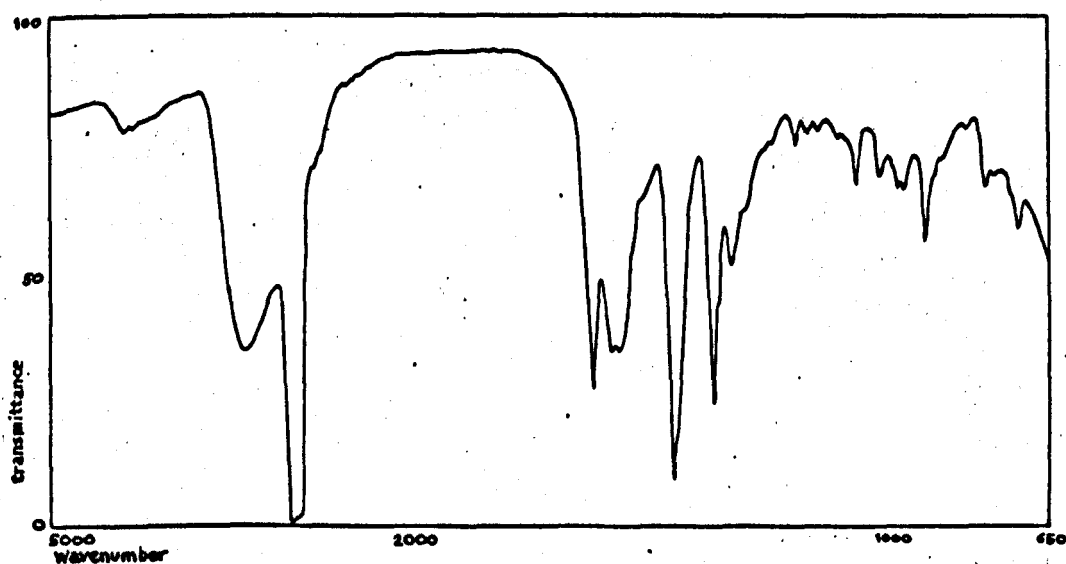
Fig.15. Infrared spectra of phenol - chromyl chloride complexes.



2,5-Di-isopropylphenol. - chromyl chloride complex.

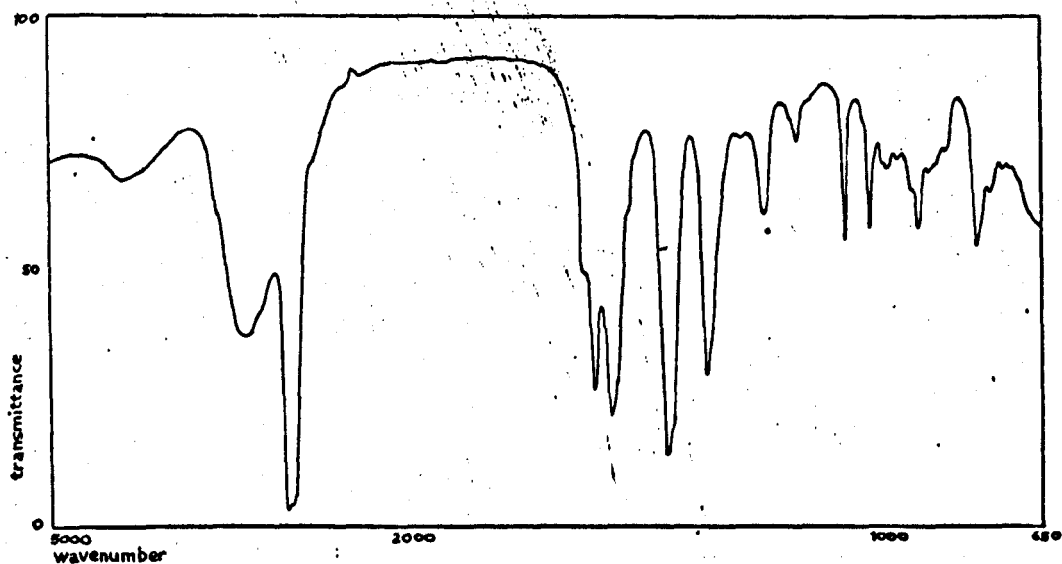


2,6-Di-isopropylphenol - chromyl chloride complex.

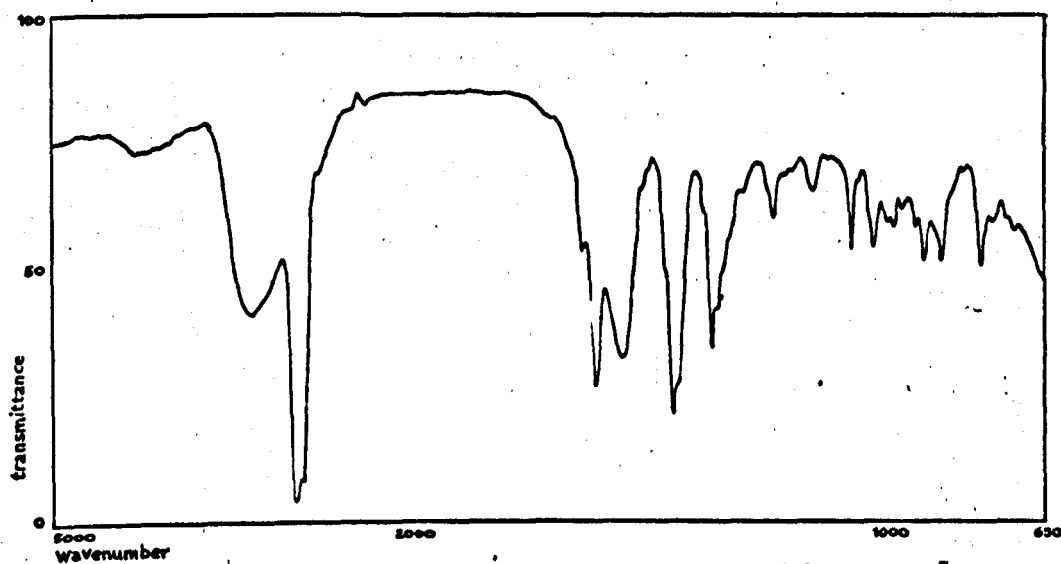


2,6-Di-secbutylphenol - chromyl chloride complex.

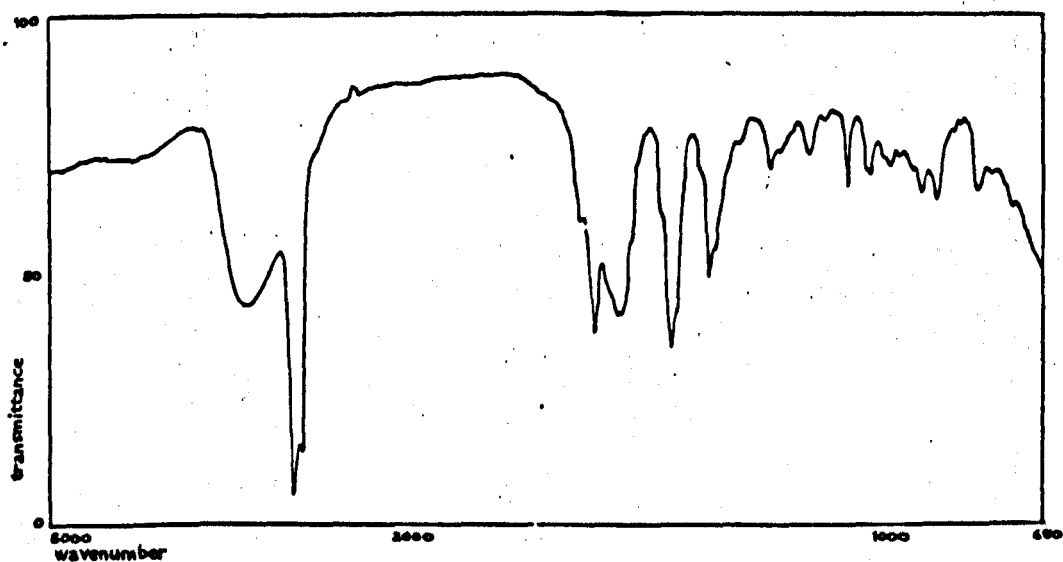
Fig.16. Infrared spectra of phenol - chromyl chloride complexes.



2,5-Di-t-butylphenol - chromyl chloride complex.

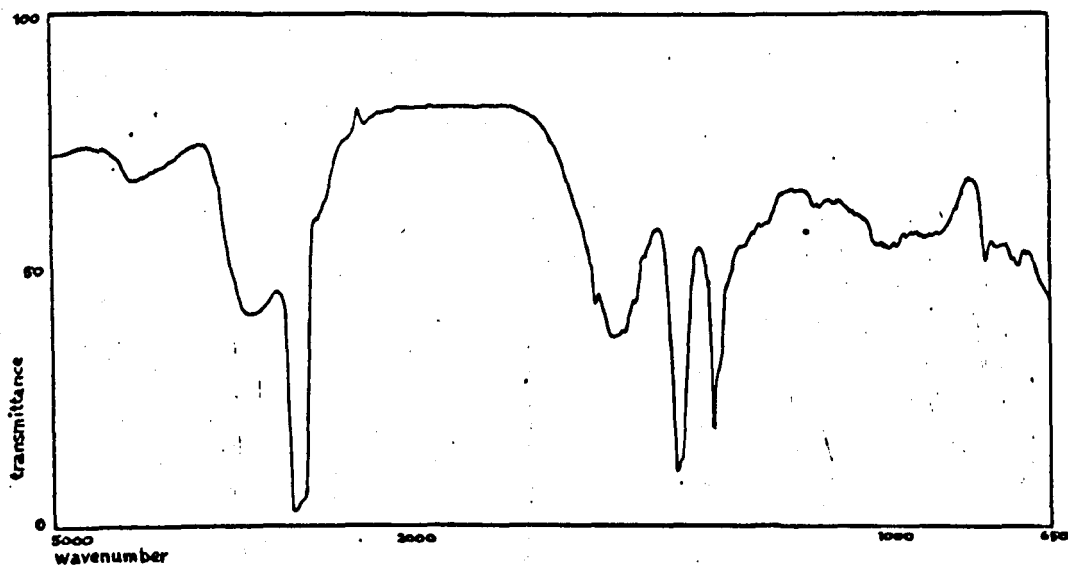


2,6-Di-t-butylphenol - chromyl chloride complex.

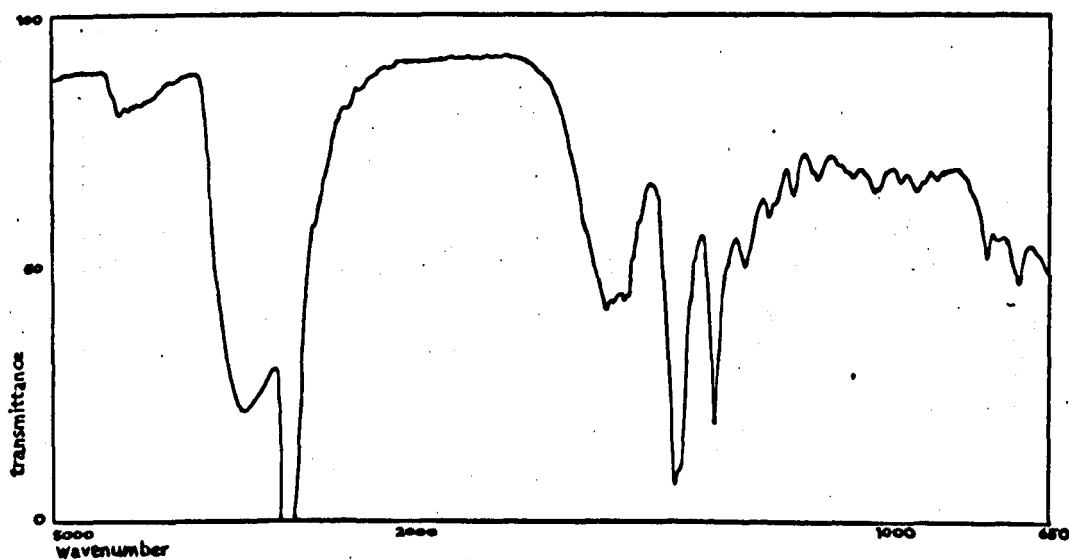


3,5-Di-t-butylphenol - chromyl chloride complex.

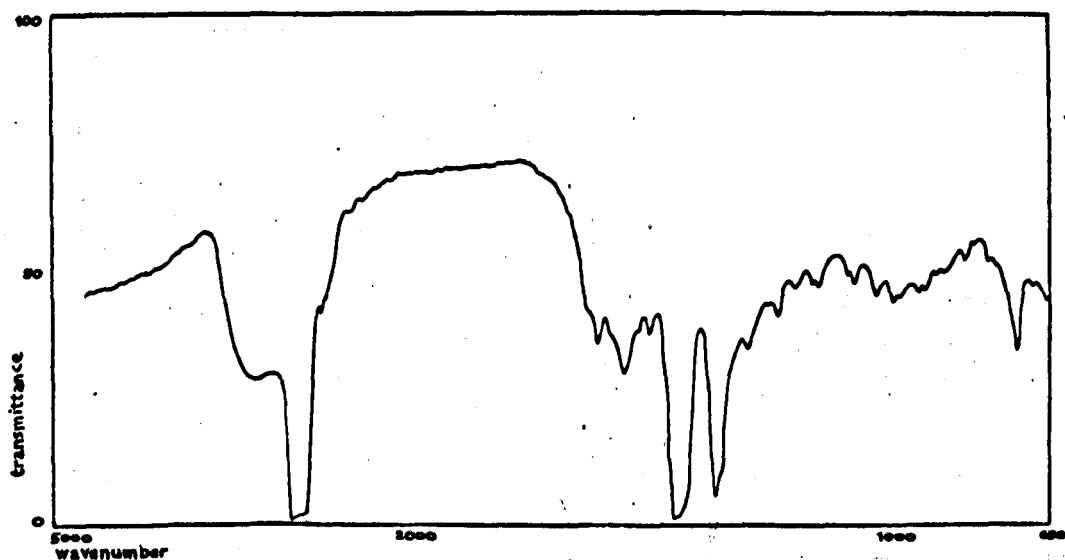
Fig.17. Infrared spectra of phenol - chromyl chloride complexes.



2,3,5,6-Tetramethylphenol - chromyl chloride complex.

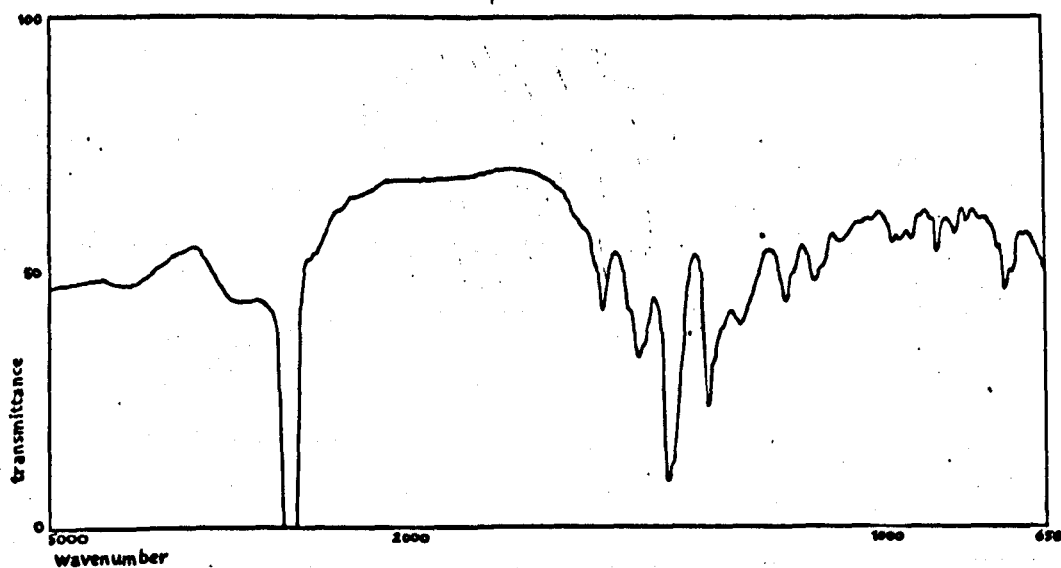


2,6-Di-t-butyl-4-methylphenol - chromyl chloride complex.

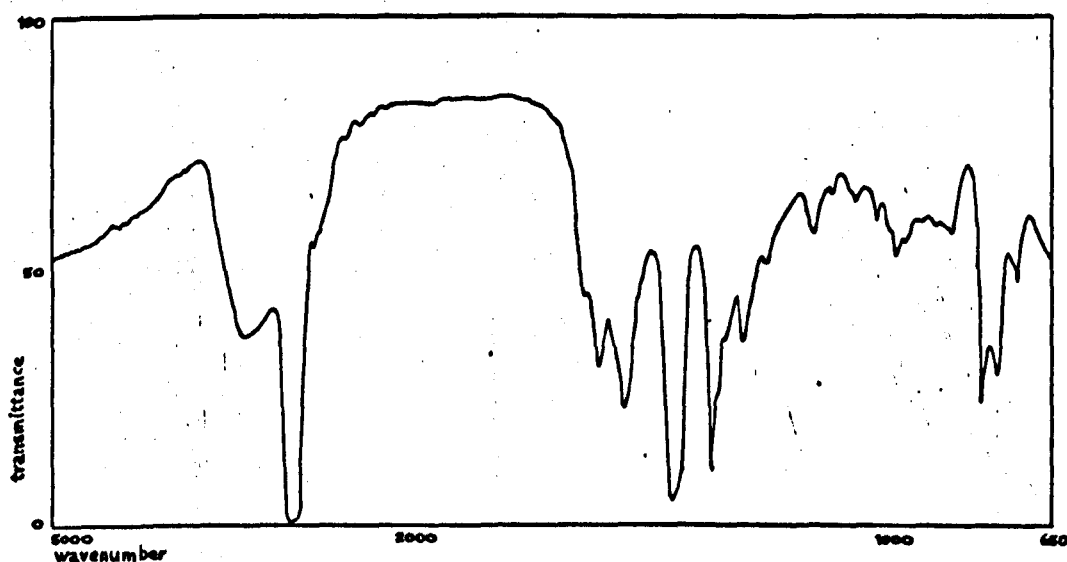


2,4,6-Tri-t-butylphenol - chromyl chloride complex.

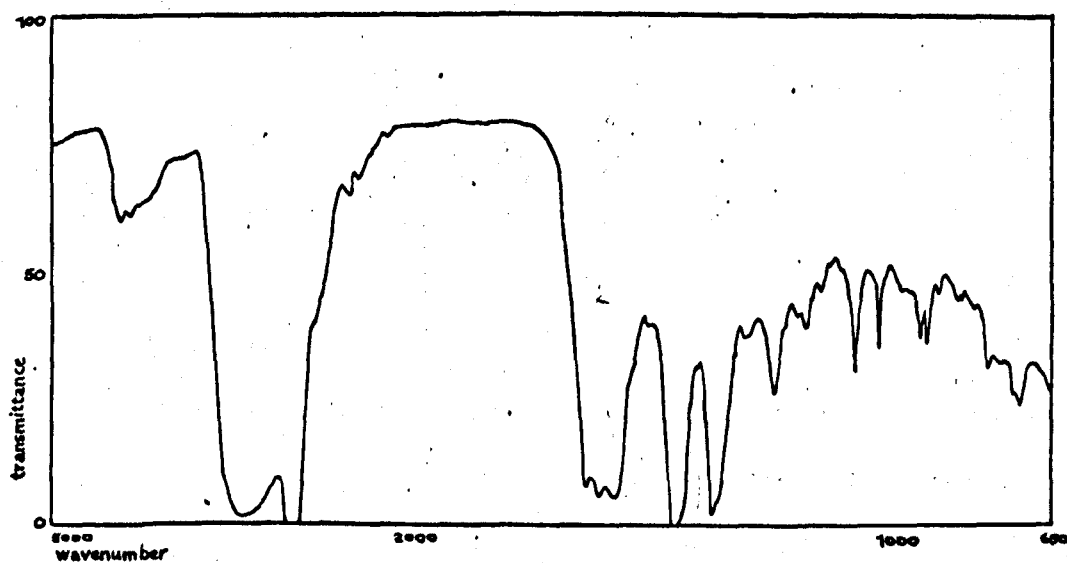
Fig.18. Infrared spectra of phenol - chromyl chloride complexes.



2,6-Dinitrophenol - chromyl chloride complex.



1-Naphthol - chromyl chloride complex.



Complex derived from the reaction of CrOCl_3 with
2,5-di-t-butylphenol.

Fig.19. Infrared spectra of phenol - chromyl chloride complexes and the complex derived from the attempted oxidation of 2,5-di-t-butylphenol with chromium (V) oxytrichloride.

All the complexes which gave *p*-benzoquinones in good yield show the presence of a band between 1600 and 1650 cm^{-1} ; a comparison with the spectra of the quinones suggests that these absorptions are due to quinone carbonyl absorptions, shifted to lower frequency by coordination to chromium.

The presence of oxidation products coordinated to chromium has been deduced by other workers^{98,114} from an examination of the spectra of the toluene-chromyl chloride and triphenylphosphine complexes (see Chapter 3, section 5.12, and Chapter 4, section 3.)

The regions of the spectra between 650 and 300 cm^{-1} were remarkably similar: there were two broad absorptions of medium intensity present in the spectra of the complexes, one between 500 and 600 cm^{-1} and the other between 300 and 400 cm^{-1} . These bands can be assigned to Cr-O and Cr-Cl vibrational modes¹¹⁷ respectively; these common features suggest that there are similarities in the structures of all of the phenol-chromyl chloride complexes.

8.1.4 The Reaction of a Phenol-Chromyl Chloride Complex with Donor Solvents

During the course of the preliminary investigation of the properties of the phenol-chromyl chloride complexes, it was observed that these solids were irreversibly dissolved by many organic solvents.

This dissolution process was investigated with one particular complex. The complex chosen for this purpose was that derived from 2,5-di-*t*-butylphenol, because this is the complex which gives, on hydrolysis, the highest yield of *p*-benzoquinone and the lowest yield of resinous material.

The complex was prepared in the usual manner. Samples of the complex were treated with small quantities of the following carefully dried organic solvents, pyridine, piperidine, diethyl ether, acetone, 1,4-dioxan and tetrahydrofuran. In all cases, with the exception of diethyl ether, the complex was found to be completely soluble in the solvent. When treated with diethyl ether, a small proportion of the complex failed to go into solution.

The resulting solutions were deep brown; their infrared and ultraviolet/visible spectra were very complex. One noticeable feature of the infrared spectra was a carbonyl band of strong intensity at about 1650 cm^{-1} .

The presence of this band suggested that free 2,5-di-*t*-butyl-1,4-benzoquinone might be present in these solutions. Further examination of the spectra showed the presence of other bands which could be attributed to the benzoquinone.

Removal of the solvents under reduced pressure did not result in recovery of the original complex from any of the solutions. Brown, or greenish-brown, non-crystalline solids remained. together with small quantities of yellow needle-shaped crystals.

By washing the residual solids with a suitable solvent (e.g. light petroleum), followed by evaporation of the solvent from the extract, pure 2,5-di-*t*-butyl-1,4-benzoquinone was obtained.

The elemental analyses of the solids remaining after removal of the quinone, were found to vary slightly, depending on the length of time which elapsed between dissolution of the phenol complex and removal of the excess solvent. Typical analysis results are listed in Table 18.

TABLE 18

Analyses of Solids resulting from the Treatment of the 2,5-Di-t-butylphenol-

Chromyl Chloride Complex with Donor Solvents

| Solvent | Found | | | | | Nearest Complex or nearest Empirical Formula | Calculated for Given Complex | | | | |
|-----------------|-------|-----|------|------|-----|---|------------------------------|-----|------|-------|-----|
| | C% | H% | Cl% | Cr% | N% | | C% | H% | Cl% | Cr% | N% |
| 1,4-Dioxan | 26.9 | 5.2 | 22.5 | 16.4 | - | $\text{Cr}(\text{dioxan})_2\text{Cl}_2\text{OH}$ | 30.4 | 5.4 | 22.5 | 16.5 | - |
| Tetrahydrofuran | 24.1 | 5.2 | 25.9 | 19.0 | - | $\text{C}_{11}\text{H}_{20}\text{Cl}_4\text{Cr}_2\text{O}_7$ | 24.0 | 5.1 | 25.8 | 18.9 | - |
| Diethylether | 13.8 | 4.5 | 31.6 | 23.6 | - | $\text{C}_5\text{H}_{10}\text{Cl}_4\text{Cr}_2\text{O}_7$ | 13.7 | 4.6 | 32.4 | 23.7 | - |
| Acetonitrile | 15.2 | 2.6 | 45.4 | 19.2 | 1.8 | $\text{C}_7\text{H}_{14}\text{Cl}_7\text{Cr}_2\text{NO}_5$ | 15.4 | 2.6 | 45.5 | 19.1 | 2.5 |
| Pyridine | 39.3 | 4.1 | 23.9 | 16.0 | 8.2 | $\text{Cr}(\text{py})_2\text{Cl}_2\text{OH}\cdot\text{H}_2\text{O}$ | 38.0 | 4.1 | 22.5 | 16.45 | 8.9 |
| Piperidine | 44.4 | 8.9 | 21.7 | 9.1 | 9.5 | $\text{Cr}_2(\text{pip})_8\text{Cl}_7(\text{H}_2\text{O})_8$ | 42.6 | 5.7 | 22.0 | 7.8 | 9.9 |
| Acetone | 33.3 | 5.9 | 21.4 | 15.7 | - | $\text{Cr}(\text{ac})_3\text{ClOH}\cdot\text{H}_2\text{O}$ | 32.5 | 6.3 | 21.4 | 15.7 | - |

It is apparent from these figures that, in each case, new complexes were present which contained molecules of the organic liquids; the infrared spectra of these complexes indicate that the solvent molecules are present as ligands.

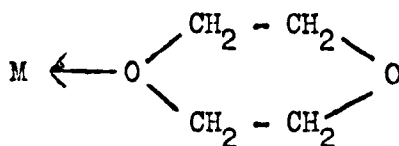
The properties of each of the new complex species are discussed separately below.

(a) The complex obtained from 1,4-dioxan

The treatment of the 2,5-di-*t*-butylphenol complex with dry dioxan, followed by removal of the excess solvent and washing with light petroleum, gives a yellow-brown solid which analysed as $C_7H_{16}Cl_2CrO_6$ (see Table 18). The chromium-chlorine ratio is exactly 1:2, indicating that the oxidation process and the solvation reaction are not accompanied by loss of chlorine from the chromium.

The infrared spectrum of the solid (Table 59; Fig. 20) is consistent with the presence of dioxan coordinated to chromium.

The similarity between the spectra of the complex and of pure dioxan, plus the presence of certain new bands in the spectrum of the complex, has been observed in other transition metal-dioxan complexes e.g. $MoCl_5$ (dioxan)¹⁷⁷. The spectrum of this complex has been interpreted in terms of coordinated and uncoordinated oxygen atoms in dioxan i.e. the dioxan acts as a unidentate ligand:



In other complexes e.g. $Cr(CO)_6$ (dioxan)¹⁷⁸ and the adducts¹⁷⁹ of dioxan and divalent metal halides (e.g. cobalt, iron and nickel (II) halides), the spectra show the presence of coordinated

oxygen only, suggesting that the dioxan is acting as a bridging group, both oxygen atoms being involved as ligands.

The infrared spectrum of the solid obtained from the phenol-chromyl chloride complex shows bands in the region associated with the C-O-C group ($1257 \sim 879 \text{ cm}^{-1}$) which may be assigned to both free and coordinated oxygen in dioxan.

Further evidence for the presence of dioxan ligands has been obtained by treating these complexes with solvents more polar than dioxan. For example, treatment of the dioxan — chromium carbonyl complex with acetone liberates the cyclic ether¹⁷⁸. This compound is not a particularly strong ligand and its release in the presence of more powerful electron donating ligands such as a ketone, is to be expected.

Similar behaviour was shown by the complex derived from the 2,5-di-*t*-butylphenol-chromyl chloride solid: treatment with water liberated dioxan.

(b) The complex obtained from pyridine

The 2,5-di-*t*-butylphenol-chromyl chloride complex was dissolved in dry pyridine. Removal of the excess solvent, followed by washing with light petroleum yielded a green-brown amorphous solid. 2,5-di-*t*-butyl-1,4-benzoquinone was obtained by evaporating the petrol solution.

Elemental analysis gave the empirical formula of the green-brown complex as $\text{C}_{10}\text{H}_{13}\text{Cl}_2\text{CrN}_2\text{O}_2$ which corresponds to $\text{Cr}(\text{py})_2\text{Cl}_2\text{OH}\cdot\text{H}_2\text{O}$, a hydrated pyridine complex of chromium. As in the case of the dioxan-containing complex, the Cr:Cl ratio was exactly 1:2.

The infrared spectrum of the complex (Table 62, Fig. 21) is consistent with such a formulation,

Gill and his co-workers¹⁸⁰ have shown that the infrared spectra of many complexes, which contain pyridine coordinated to a metal, differ only slightly from the spectrum of pyridine itself; because of 'back-coordination', the bonding in the heterocyclic molecule is little changed by its attachment to the metal centre. However, small shifts in the position of absorptions are observed in the spectra of these complexes and may be used to discriminate between free and coordinated pyridine.

Thus the band at 1580 cm^{-1} (C-N stretching vibration of free pyridine) is shifted to about 1600 cm^{-1} (C=N stretching of coordinated pyridine). The presence of a weak band between 1235 and 1250 cm^{-1} is also indicative of coordinated pyridine.

The spectrum of the complex obtained by treating the phenol-chromyl chloride compound with pyridine shows both of these features. The spectrum shows marked similarities to that of pyridine, but there are small shifts in the position of many bands similar to those found by Gill and his coworkers¹⁸⁰.

It was also found that if the solution of phenol-chromyl chloride complex in pyridine was allowed to stand in the presence of air for some length of time, a green precipitate formed. This also had a composition corresponding closely to $\text{Cr}(\text{py})_2\text{Cl}_2\text{OH}\cdot\text{H}_2\text{O}$. The infrared spectrum of this complex showed it to be very similar to that of the brown complex previously described.

(C) The Complex obtained from Piperidine

The complex from piperidine is a green-brown solid. Elemental analysis, after removal of the benzoquinone, showed that the complex did not have a simple stoichiometry.

The infrared spectrum of the complex (Table 62, Fig.21) can again be interpreted in terms of a coordination complex.

The broad band at 3290 cm^{-1} , of medium intensity (N-H stretch), in piperidine, is more intense in the spectrum of the complex, although it is partly obscured by the broad band in this region assigned to an O-H stretch. Furthermore, the band shows a shift to lower frequency of about 50 wavenumbers; an exact shift cannot be accurately measured because the frequency of this absorption is very dependent on the nature of the medium in which the spectrum is obtained¹⁸¹.

Greenwood and Wade¹⁸² studied the infrared spectrum of the 1:1 complex formed between boron trichloride and piperidine; they found a shift in the N-H stretching frequency comparable to that described above. They also found similarities in the ring vibrations and C-C twisting modes in both the spectrum of the complex and that of piperidine.

Other bands compatible with the presence of coordinated piperidine can be seen in the spectrum of the chromium complex, but assignments of these have not been made.

(d) The Complex obtained from Tetrahydrofuran

This complex is a yellow-brown solid. Elemental analysis showed that the complex was non-stoichiometric although, as in the previous complexes, the chromium:chlorine ratio was found to be 1:2.

The infrared spectrum of the complex (Table 59, Fig. 20) shows a situation similar to that of the dioxan complex.

In the region where the absorptions assigned to the C-O-C stretching frequency would be expected to occur, there are a series of bands which differ from those in the spectrum of pure tetrahydrofuran. The strong absorption at 1076 cm^{-1} in the spectrum of tetrahydrofuran is much reduced in that of the complex, as is the band at 909 cm^{-1} . New bands at 1020, 980, 963 and 865 cm^{-1} are apparent in the spectrum of the complex.

Just as in the case of dioxan-containing complexes, these changes in the spectra indicate coordination through the oxygen of the ether to the metal centre¹⁸³.

The spectrum of the complex showed a degree of similarity to that of the complex $\text{CrCl}_3(\text{THF})_3$ obtained by Kern¹⁸⁴, especially in the region cited above. The C-O-C stretching absorptions of tetrahydrofuran (1076 and 909 cm^{-1}) are shifted to lower frequency by 57 and 54 cm^{-1} respectively, in Kern's complex. This shows a good correlation with the bands at 1020 and 862 cm^{-1} in the spectrum of the chromium complex obtained in this study.

Infrared spectroscopy was also used to show the presence of free tetrahydrofuran in the mixture obtained by treating the complex with water.

The compound $\text{CrCl}_3(\text{THF})_3$ was found to have similar properties; the only solvent in which it dissolved without decomposition was tetrahydrofuran itself. The use of more polar solvents resulted in ligand exchange and thus decomposition of the original complex¹⁸⁴.

(e) The Complex obtained from Acetonitrile

This complex was obtained as a light brown powder, after removal of solvent and benzoquinone from the solution of the 2,5-di-*t*-butylphenol complex in dry acetonitrile.

Elemental analysis showed a complex composition, confirming the presence of a small amount of nitrogen.

The outstanding feature of the infrared spectrum of the nitrogen containing complex (Table 61, Fig. 21) was the presence of a doublet with absorption maxima at 2290 and $2320 \pm 10 \text{ cm}^{-1}$. This compares with bands at 2256 and 2294 cm^{-1} in pure acetonitrile¹⁸⁵. Such a shift to a high frequency is typical of a band due to a coordinated $\text{C}\equiv\text{N}$ stretching vibration¹⁸⁶. The positive shift, as opposed to the more usual shift to lower frequency, on coordination, may be explained in terms of ionic resonance structures of the nitrile groups, which strengthen the bond¹⁸⁶.

An example of a compound which shows such a shift is trichlorotriacetatonitriletitanium (III). In this case¹⁸⁷, the band due to $\text{C}\equiv\text{N}$ stretching occurs at 35 cm^{-1} above that of the equivalent band in free acetonitrile. Similar effects have been observed in complexes of group (IV) metals with other alkyl cyanides¹⁸⁸, and cyanoacetamide, $\text{NH}_2\text{COCH}_2\text{CN}$ ¹⁸⁹.

(f) The Complex obtained from Acetone

The new complex, obtained from the acetone solution of the 2,5-di-*t*-butylphenol-chromyl chloride compound, was a lustrous green solid.

Elemental analysis suggested that the complex contained acetone. This was confirmed on hydrolysis of the complex, when acetone was liberated.

The presence of some residual 2,5-di-t-butyl-1,4-benzoquinone from the phenol oxidation, was also apparent in the hydrolysis mixture. This would account for the absence of simple stoichiometry for the complex, as shown by the analysis results.

The infrared spectrum of the complex (Table 60, Fig. 20) shows only a few strong, well-defined bands. A strong, but rather broad absorption at 1651 cm^{-1} (with a shoulder at 1688 cm^{-1}) is evident; this can be assigned to a coordinated carbonyl stretching frequency. Shifts to lower frequency of a similar order have been observed for complexes such as $\text{TiCl}_3 \cdot 3\text{R}_2\text{CO}$ ¹⁹⁰ and adducts between titanium (IV) chloride and aromatic ketones¹⁹¹.

(g) The Solid obtained from Diethyl Ether

On treatment with diethyl ether, only a proportion of the 2,5-di-t-butylphenol complex was found to be soluble. Evaporation of the supernatant liquor after filtration showed that it contained mainly 2,5-di-t-butyl-1,4-benzoquinone.

Elemental analysis of the residual solid showed that it had a complicated stoichiometry. The chromium to chlorine ratio was, however, 1:2.

Hydrolysis of this solid and subsequent analysis of the carbon tetrachloride extract showed that ether had been liberated.

The infrared spectrum (Table 60) showed only poorly defined bands. One at 1126 cm^{-1} can be assigned to the C-O-C stretching frequency of diethyl ether but further assignments are difficult to make.

Similar results were obtained by Tucker⁷⁹ when he attempted to dissolve the Etard toluene adduct in diethyl ether. The adduct was only partially soluble, and the residual solid did not have a simple stoichiometry.

8.1.4.1 The Infrared Spectra of the Complexes in the Region 650 - 300 cm⁻¹

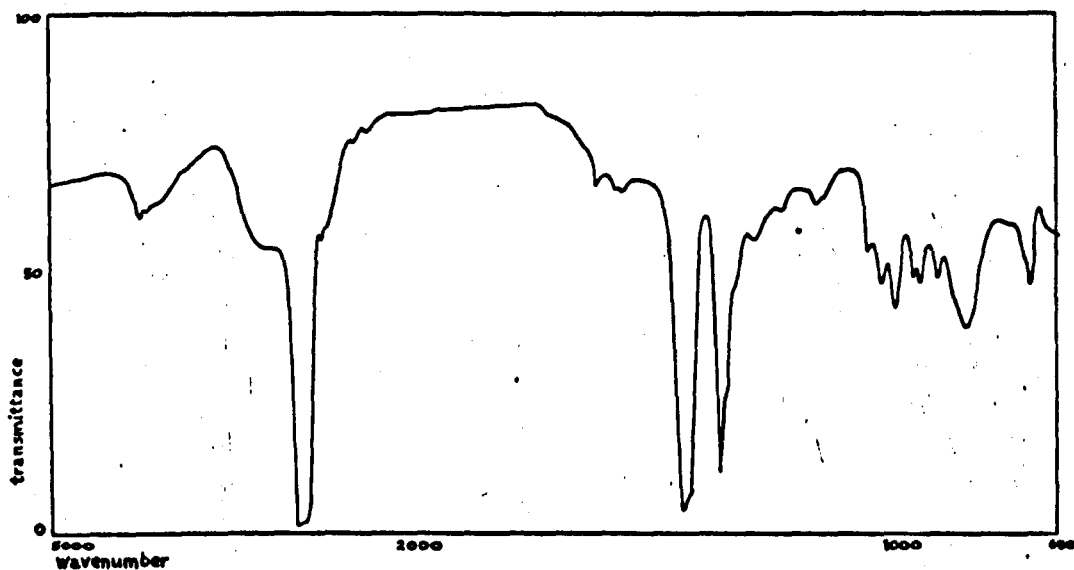
The infrared spectra of the complexes obtained from the organic solvents, in the region 650 - 300 cm⁻¹ have not been discussed hitherto as they have little bearing on the coordination of the ligand molecules. However, absorptions were recorded in this region for some of the complexes. Most of the absorption bands observed could be assigned to Cr-O stretching frequencies.

Thus in both the piperidine and pyridine complexes, there were medium intensity bands at 440 cm⁻¹. This compares with a value of 410 - 450 cm⁻¹ observed by Makhija and Stairs¹¹⁷ in the spectra of the ternary Etard complexes (see page 64)

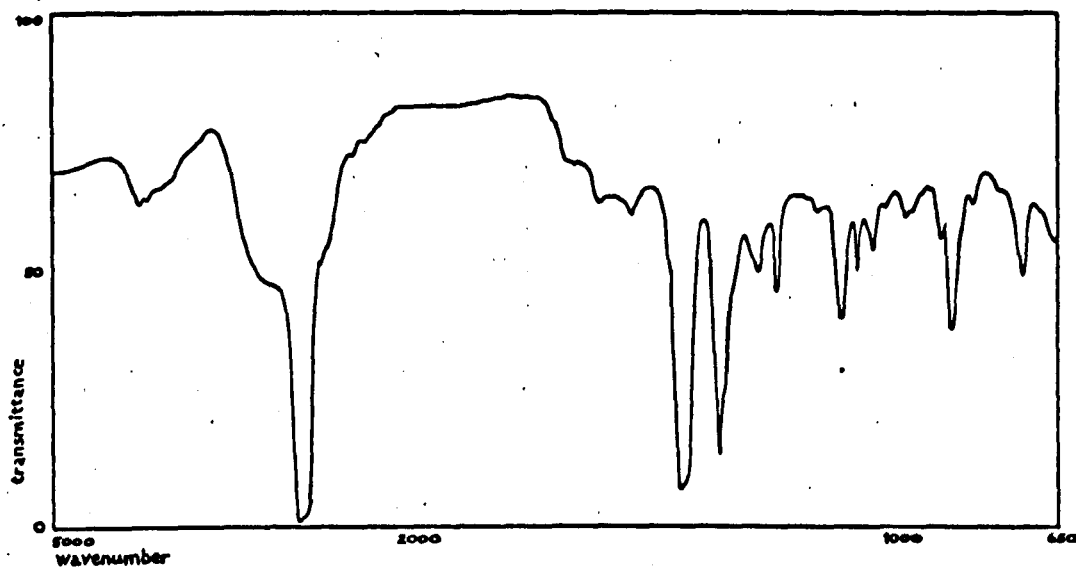
Both the spectra of the dioxan and tetrahydrofuran complexes showed a broad band of weak intensity in the region 530 - 500 cm⁻¹. A similar band can be seen in the spectra of the acetonitrile and pyridine complexes. The comparable band in the spectrum of the piperidine complex was, by contrast, of relatively strong intensity.

No absorptions which could be assigned to Cr-N or Cr-Cl stretching frequencies were observed in the spectra, though some weak intensity bands between 350 and 280 cm⁻¹ may have been due to these modes.

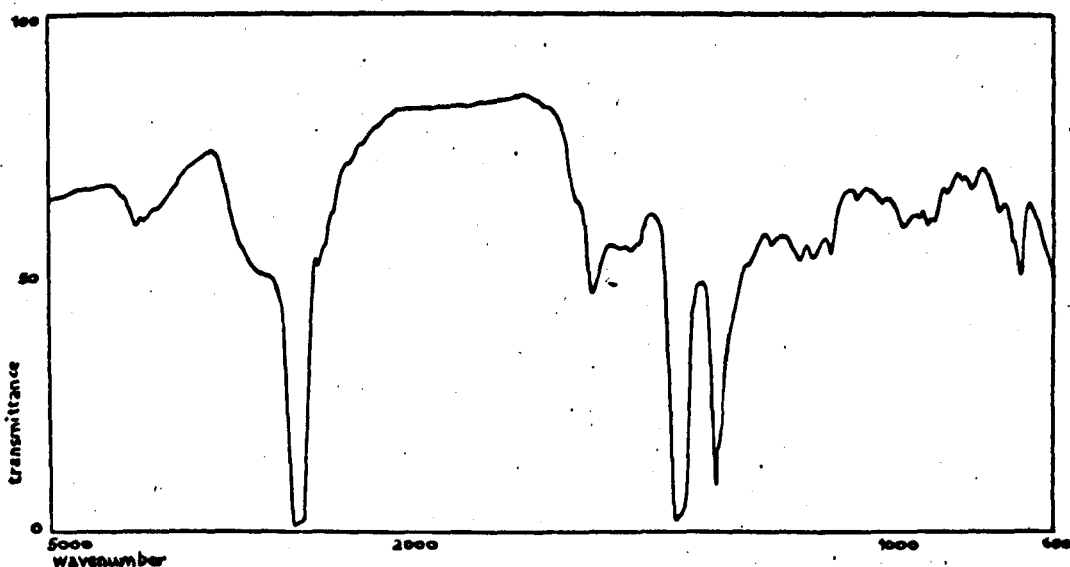
Makhija and Stairs¹¹⁷, in their study of the spectra of similar compounds, stated that only tentative assignments can be made in this region, and also that not all the expected bands are observed.



The complex obtained from tetrahydrofuran.

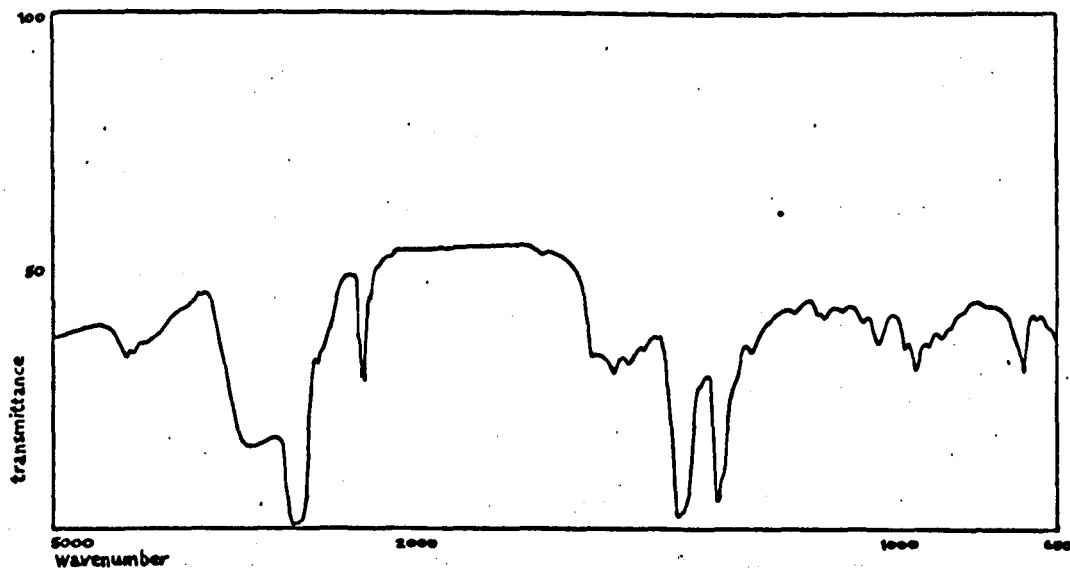


The complex obtained from dioxan.

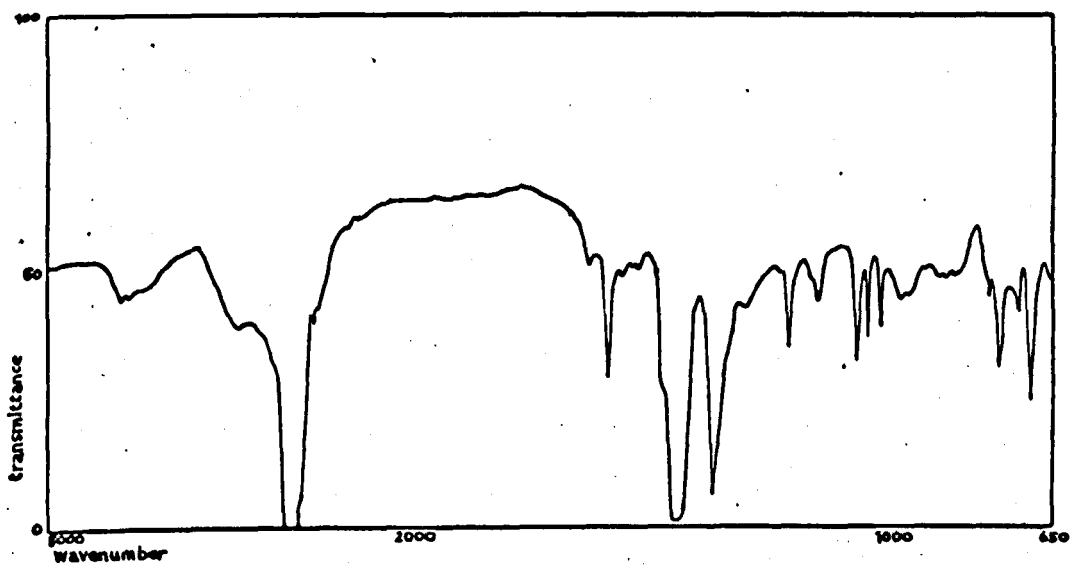


The complex obtained from acetone.

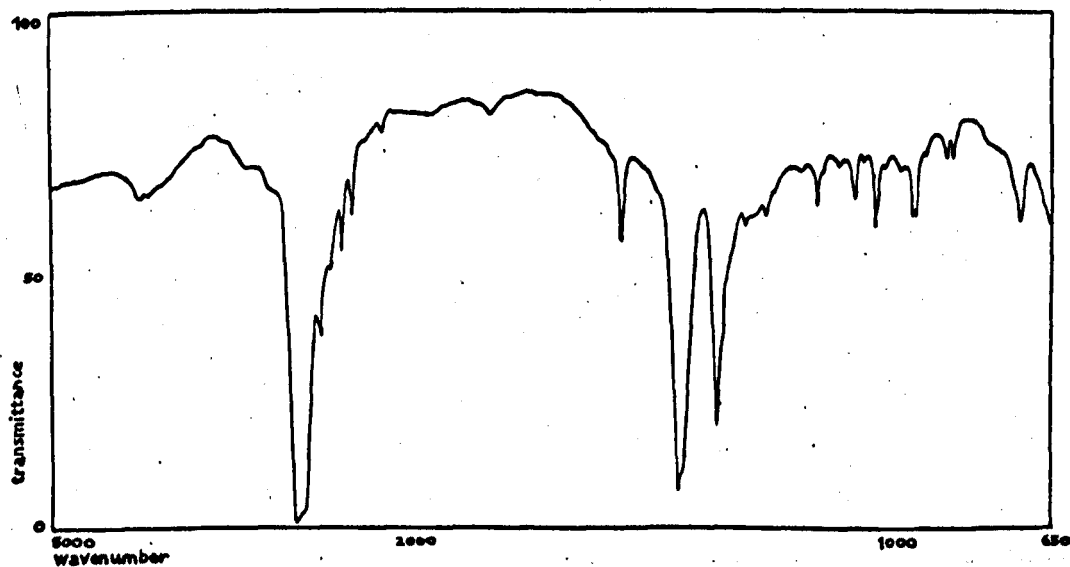
Fig.20. Infrared spectra of the solids resulting from the treatment of the 2,5-di-*t*-butylphenol chromyl chloride complex with donor solvents.



The complex obtained from acetonitrile.



The complex obtained from pyridine.



The complex obtained from piperidine.

Fig.21. Infrared spectra of the solids resulting from the treatment of the 2,5-di-t-butylphenol - chromyl

8.2 The Solid Product from Chromyl Acetate Oxidations

The solid products obtained from the oxidations of phenols with chromyl acetate in carbon tetrachloride were green-brown solids which appeared to be stable in moist air (unlike typical Etard complexes). It was shown by infrared spectroscopy and elemental analysis, that, with only very minor variations, the solid products were very similar, that is the properties of the solid products are independent of the phenol being oxidized.

Attempted purification by recrystallization failed. The complexes were insoluble in non-polar solvents, insoluble in cold glacial acetic acid, but irreversibly soluble in the boiling acid, and irreversibly soluble in water. Attempted purification by vacuum sublimation resulted in the decomposition of the complex.

Magnetic measurements were carried out on samples of the solid products in the same manner as for the phenol-chromyl chloride complexes, and the residual oxidizing power i.e. the percentage of chromium in oxidation state greater than (III) was obtained for a number of the solid products of different oxidation reactions.

The results of these studies confirm that the solid formed in chromyl acetate oxidations is derived solely from the oxidant and is a reduced form of the oxidant.

The experimental results are discussed in detail below.

8.2.1 Elemental Analysis

The elemental analyses for the solid products derived from the oxidation of various phenols by chromyl acetate are listed in Table 19. It can be seen that although there is a

TABLE 19

Analyses of Solids Derived from Chromyl Acetate Oxidations

| Phenol Oxidized | Cr% | C% | H% |
|---------------------------|------|------|-----|
| 2,6-Di-methylphenol | 25.8 | 23.8 | 3.9 |
| 2,5-Di-methylphenol | 25.0 | 22.8 | 4.0 |
| 2,6-Di-isopropylphenol | 25.6 | 23.7 | 3.9 |
| 2,5-Di-isopropylphenol | 27.2 | 23.1 | 3.7 |
| 2,3,5,6-Tetramethylphenol | 25.0 | 24.3 | 4.0 |
| 2,6-Di-t-butylphenol | 25.6 | 23.7 | 3.7 |
| 2,5-Di-t-butylphenol | 26.3 | 24.6 | 4.0 |
| 3,5-Di-t-butylphenol | 25.4 | 23.8 | 3.9 |

certain minor variation between the figures, the analyses are very similar for each product.

By taking the average of these figures; (C, 23.7; H, 3.8; Cr, 25.7%) and assuming oxygen to be the only other element present, the empirical formula is $C_4H_8CrO_6$. The probable structure of this compound is discussed in the next Chapter.

8.2.2 The Oxidation State of the Chromium

The magnetic susceptibilities of two samples of the reduced chromium acetate were measured (see Tables 21,37,38; Fig.12) In both cases the results obtained were very similar. As in the case of the phenol-chromyl chloride complexes, the Curie-Weiss Law was obeyed and there was no variation of magnetic susceptibility with magnetic field strength.

The average values of the effective magnetic moment were 3.04 B.M. in each case (the solids were derived from 2,5-di-t-butylphenol and 2,6-di-t-butylphenol oxidations).

The average oxidation state of the chromium was also estimated titrimetrically, for the compounds derived from each oxidation.

The oxidizing power of the reduced chromyl acetate was measured using a redox method, which effectively measured the proportion of chromium (VI) in the compound. The results are listed in Table 20.

From the results of the magnetic susceptibility measurements, it can be seen that the values of the effective magnetic moment are similar to those obtained for the chromyl chloride complexes, although somewhat closer to the 'spin-only' value for chromium (IV) (2.83 B.M., see page 131.)

TABLE 20

The Oxidizing Power of Solids derived from Chromyl

Acetate Oxidations

| Phenol Oxidized | Total Cr% | Total Oxidizing Cr% | Oxidizing Power % |
|---------------------------|--------------|---------------------------|-------------------------|
| 2,5-Dimethylphenol | 26.1 | 5.8 | 22.2 |
| 2,6-Dimethylphenol | 25.8 | 5.9 | 22.9 |
| 2,3,5,6-Tetramethylphenol | 25.0 | 5.6 | 22.3 |
| 2,5-Di-isopropylphenol | 27.2 | 7.4 | 27.2 |
| 2,6-Di-isopropylphenol | 25.6 | 3.9 | 15.1 |
| 2,6-Di-t-butylphenol | 25.6 | 5.3 | 20.9 |
| 2,5-Di-t-butylphenol | 26.3 | 6.0 | 22.7 |
| 3,5-Di-t-butylphenol | 25.4 | 6.7 | 26.5 |

The 'oxidizing power' is the percentage of chromium (VI) in the complex; assuming that chromium (IV) or (V) species which may be present in the complex disproportionate into chromium (III) and chromium (VI) in aqueous solution.

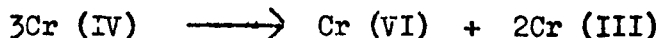
TABLE 21

Magnetic Susceptibility Data for Solids derived from

Chronyl Acetate Oxidations

| Phenol Oxidized | Average Effective Magnetic Moment (B.M.) | Weiss Constant (°) |
|------------------------|--|--------------------------|
| 2,5-Di-t-butylphenol | 3.04 | 48 |
| 2,6-Di-isopropylphenol | 3.04 | 55 |

If it is assumed that chromium (IV) dissociates, in aqueous solution, into chromium (III) and (VI),



the oxidizing power of the reduced chromyl acetate complexes should be 33.3%, i.e. one third of the chromium in the complex may be considered as chromium (VI). In all cases, the experimental figure was found to be below this value.

This situation is not easy to explain, but is very similar to that obtained by Tucker⁷⁹, with the toluene-chromyl chloride adducts. Tucker found that the oxidizing power of the adducts was a maximum for a freshly prepared adduct, decreased with the age of the adduct, and was less than the theoretical value for chromium (IV).

It is probable that the differences between the experimental effective magnetic moments, and the 'spin-only' value is due not to any orbital contributions of chromium-chromium interactions but to the presence of chromium in different oxidation states. This would also explain the results obtained from the determination of oxidizing power of the chromium in the various complexes.

8.2.3 The Infrared Spectra

The infrared spectra of the complexes formed on reduction of chromyl acetate were all very similar. A spectrum is illustrated in Fig. 13 and the bands are listed in Table 63 as are those of chromyl acetate.

The spectrum in the region $3500 - 3000 \text{ cm}^{-1}$ is characteristic of a hydroxy complex, showing a broad band of medium intensity, with two indistinct maxima at 3300 and 3100 cm^{-1} .

The broad band between 1620 and 1530 cm^{-1} is typical of the antisymmetric stretching frequency of the COO group and a similar band with absorption maxima at 1595 cm^{-1} has been observed in the spectrum¹⁹² of hydrated chromium (III) acetate. The absorption assigned to the symmetrical stretching of the COO group in the latter compound has a maximum at 1423 cm^{-1} . A similar band in the spectrum of the reduced chromyl acetate is seen as a shoulder, which appears on the Nujol band, between 1410 and 1430 cm^{-1} .

Other features of the spectrum are a doublet of medium intensity (1042, 1030 cm^{-1}) which may be assigned to a CH_3 rocking mode (cf ref. 192, CH_3 rock 1053, 1032 cm^{-1}) and another doublet at 956 and 972 cm^{-1} . No comparable band occurs in the spectrum of chromium (II) acetate, but bands in the region 1000 - 970 cm^{-1} have been assigned to metal-OH bending frequencies¹⁸⁶ and it is possible that the observed absorptions are due to modes such as these.

The infrared spectrum in the region 650 to 300 cm^{-1} showed only three, rather indistinct bands (see Table 63) and these have not been assigned.

There is little similarity between the spectra of the complexes from chromyl acetate and those from chromyl chloride oxidations, in this region.

8.3 The Electron-Spin Resonance Spectra of the Complexes

Concurrent with the measurement of magnetic susceptibility, the electron spin resonance spectra of the phenol-chromyl chloride complexes were obtained. Each complex gave spectra of very similar line shape (Fig. 22). Most absorptions are broad and intense with half-line widths which vary between 450 and 550 G; the spectrum of the 2,6-dinitrophenol complex has a typical line shape, but is considerably broader, having a half line width of the order of 775 G.

The spectra of the solids derived from chromyl acetate oxidations were all very similar to each other, and to those of the phenol chromyl chloride complexes. The half-widths of the lines obtained from the former were rather closer to 500 G than those derived from chromyl chloride.

The g values of all the complexes were of the order of 2; accurate measurement was not possible because of the width of the lines. For this reason, no correlation could be made between the g values and the Curie constant which can be obtained from the magnetic susceptibility measurements.

Using such a correlation, Hare, Bernal and Gray¹⁹³ have been able to obtain structural information, from a comparison of the values of magnetic susceptibility calculated from e.s.r. measurements, with the experimental values, for a chromium (V) system.

The e.s.r. spectra of the phenol-chromyl chloride complexes are very similar to those reported for the adducts between various phenylmethanes and chromyl chloride⁹⁵, in both their line shape and half-widths.

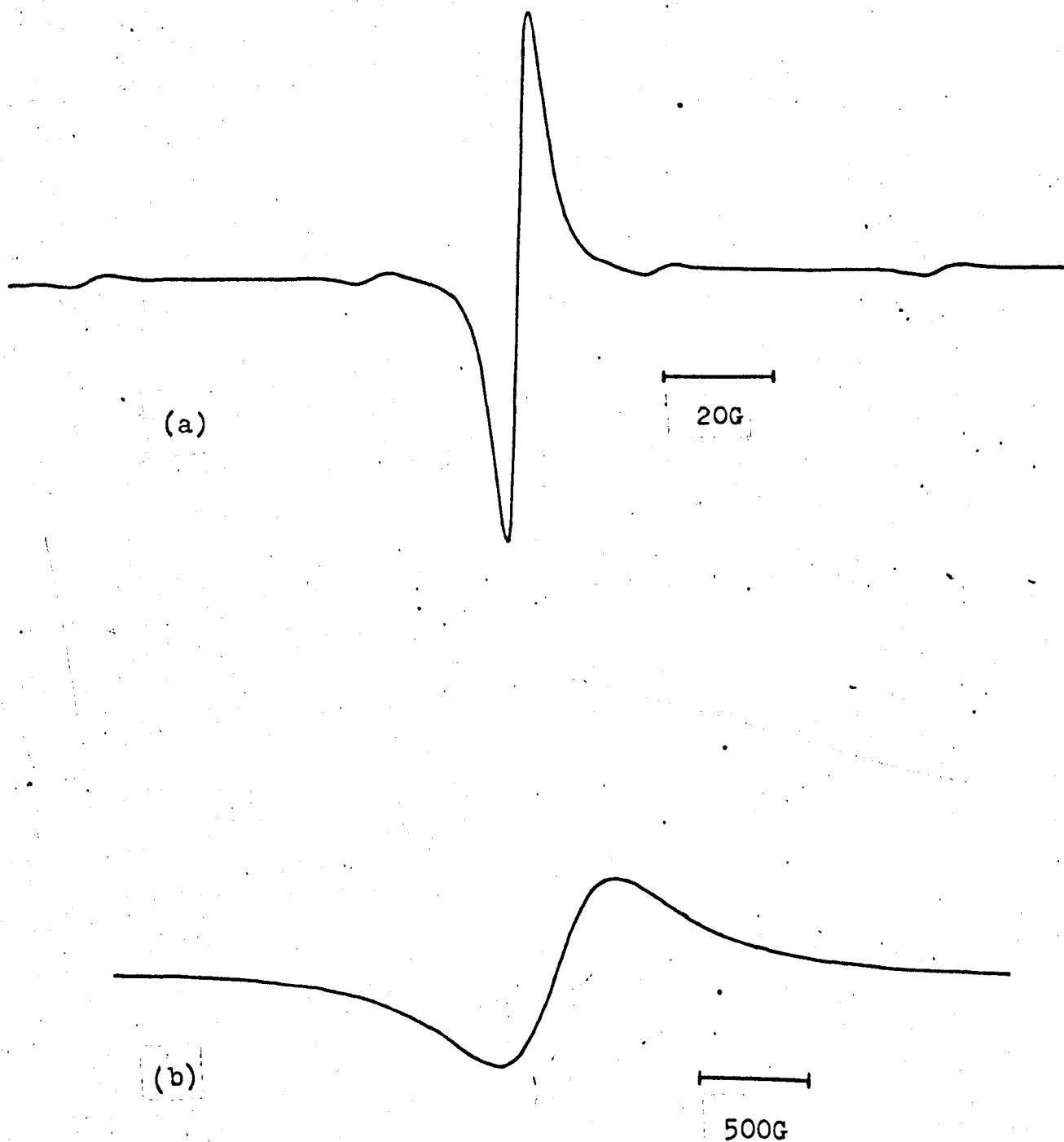


Fig.22. The e.s.r. spectra of (a) the oxidation product of 3,5-di-*t*-butylcatechol, and (b) the 2-*t*-butylphenol - chromyl chloride complex.

As described previously (page 51) these spectra have been interpreted in different ways by various workers and it has not been established exactly what chromium species is responsible for them.

Makhija and Stairs¹¹⁴, who obtained similar spectra from the complexes between chromyl chloride and donor molecules, proposed that they were consistent with chromium in an oxidation state of (IV). It is significant that they also determined the apparent oxidation number of the chromium in the complexes, by titration, and found that the values were less than (IV) in every case.

This is identical to the situation observed with the complexes from the chromyl acetate oxidations and it must be concluded that the assumption of Makhija and Stairs¹¹⁴ is incorrect: an intermediate average oxidation state of between (III) and (IV) for the chromium in these complexes is more consistent with their results and those presented in this thesis.

CHAPTER 9

DISCUSSION OF THE EXPERIMENTAL RESULTS

In part A of this chapter is presented a brief outline of the process of phenol oxidation with reagents other than chromyl chloride or chromyl acetate. In particular, the mechanisms of these phenol oxidations are examined with regard to the type of reaction and the properties of the oxidant.

In the second part of this chapter, part B, the results outlined in the previous chapters of this thesis are discussed with a view to defining the reaction mechanism of the oxidation of phenols by chromyl compounds. Also the experimental results are critically compared to those obtained by other workers, who have used different oxidants.

9.A. The Products and Mechanism of Oxidation of Phenols with Oxidants other than Chromyl Compounds

The reaction of phenols with various oxidizing agents has been described in detail in reviews^{167,194}.

The oxidations may be classified by reference to the number of electron^s removed from the phenol in the first stage of the oxidation process.

The first class of oxidation involves homolytic fission of the phenolic O-H which corresponds to a one electron change and results in the formation of a free phenoxyl radical:



Heterolytic oxidations, by comparison, involve attack by a reagent which can gain control of an electron pair. Attack by heterolytic oxidants may take place either at phenolic oxygen, or

on the aromatic ring, at positions where there is high electron density.

Attack at the phenolic hydroxyl position might be expected to result in the formation of a free phenoxonium ion:



but the free existence of ions such as this is unlikely; more probable is the formation of transient intermediates of this type, between the phenol and electrophile. The loss of the phenolic proton, followed by rearrangement or further oxidation via elimination of the electrophilic moiety would result in the formation of oxidation products.

Attacks at the ortho and para positions of a phenolic ring by electrophilic reagents may also be considered to be oxidations¹⁹³, and as the electrophile gains a pair of electrons in the process, such oxidations are also heterolytic in nature.

Both homolytic and heterolytic oxidations of phenols are discussed fully below.

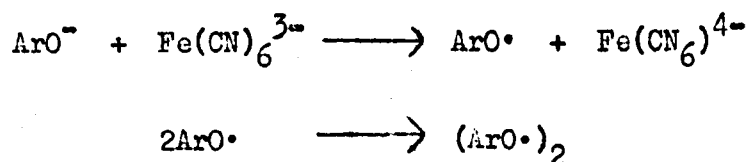
9.A.1. Reactions which involve a One-electron Transfer

It is now well established that many phenol oxidations involve either the homolytic fission of the oxygen-hydrogen bond of the phenol to give an aryloxy free radical, or the removal of one-electron from the phenoxide anion:



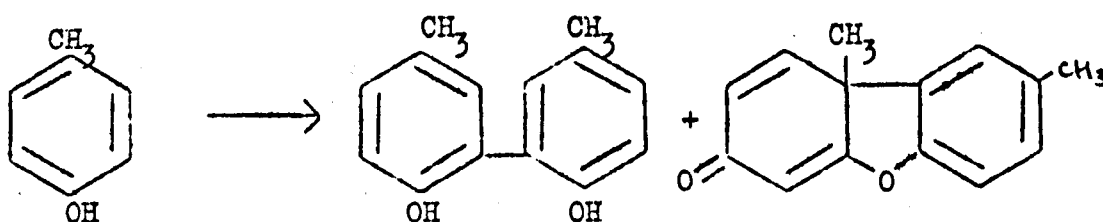
The formation of a free radical as the primary product of oxidation of phenols by certain oxidants was first suggested by Pummerer and his co-workers¹⁹⁶.

They studied the oxidation of many of the simpler phenols by the ferricyanide ion, $\text{Fe}(\text{CN})_6^{3-}$, in alkaline solution, and proposed the initial formation of free radicals to explain the subsequent formation of dimeric products. The reaction scheme may be outlined as follows:



Coupled Products

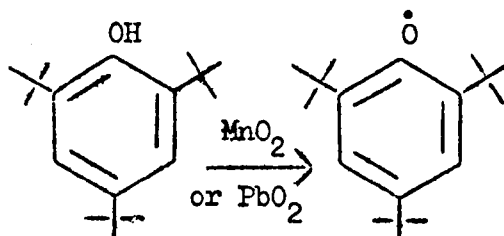
In a typical example, the oxidation of p-cresol yielded the ortho coupled dimer and the ketone shown below:



The coupling at positions other than that of original electron removal was later explained by the contributing structures of the resonance stabilized system.

More recent research has now confirmed the presence of free radicals in many phenol oxidations. In certain cases, the free radicals themselves have been isolated¹⁹⁷. They are intensely coloured paramagnetic solids which react readily with oxygen, nitric oxide and the halogens. An example¹⁹⁸ of such a phenoxyl radical is that obtained by treating 2,4,6-tri-*t*-butylphenol with manganese dioxide or lead dioxide in an inert solvent. The resultant blue solution deposits, at low temperatures, a blue

crystalline solid, the 2,4,6-tri-*t*-butylphenoxyl free radical:



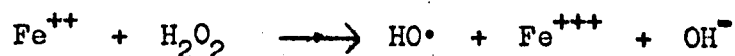
In other cases where the radicals have not been isolated, their presence has been shown by electron spin resonance spectroscopy and electronic absorption spectroscopy.

9.A.1.1 One-Electron Oxidizing Agents

Since the original use of the ferricyanide ion as a one-electron oxidant, many other such oxidants have been reported.

Typical examples are salts of metals in a higher oxidation state, which can readily undergo a unit oxidation-state change to a lower state. Examples of these compounds are ferric salts^{199,200}, and compounds of cobalt (III), cerium (IV), manganese (III), silver (II) and copper (II)²⁰¹. As well as the salts, the oxides of many of these metals in the oxidation states cited have also found considerable use as one-electron oxidants.

Similar one-electron oxidations of phenols have been reported with reagents such as hydrogen peroxide and ferrous ions (Fenton's Reagent) in which the reactive hydroxyl radical, $\cdot\text{OH}$, is liberated:



This radical is an effective hydroxylating agent²⁰² for phenols. Other radicals which have been reported to oxidize phenols are organic and inorganic nitroxides such as diphenylnitroxide²⁰³ and potassium nitrosodisulphonate, $\text{ON}(\text{SO}_3\text{K})_2$ (Fremy's Salt)²⁰⁴.

The autoxidation of phenols⁴ is yet another example of the one-electron oxidation process, in this case, oxygen may be considered a diradical.

9.A.1.2 The Products of Further Reaction of the Radicals

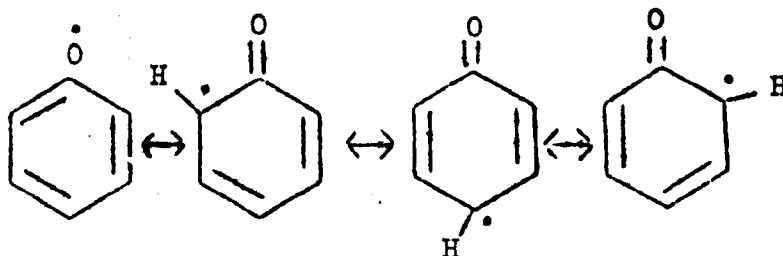
The further reaction of the phenoxyl radical is determined by a number of factors. The most important of which is probably the stability of the radical itself (see section (c)).

Thus if the radical is inherently stable, and only a mild oxidant is used, it is possible that no further reaction need occur, once the radical is formed. Thus the oxidation of 2,4,6-tri-*t*-butylphenol by manganese dioxide or lead dioxide results in a high yield of the 2,4,6-tri-*t*-butylphenoxyl radical and no further reaction takes place, even in the presence of excess oxidant.

Less stable radicals usually react rapidly in either of two ways: they may couple with each other to give dimers, trimers, or higher polymers, or they may react with excess oxidant.

The possible products of radical coupling are dependent on the structure of the phenol. It is apparent that steric factors are important in such a process.

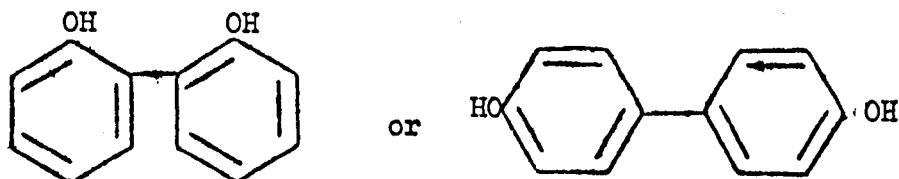
In the simple example of phenol, various canonical forms of the phenoxyl radical may be drawn as follows:



The polymeric products can be explained in terms of coupling at the various positions of high electron density. The possible products of further reaction may be considered as follows:

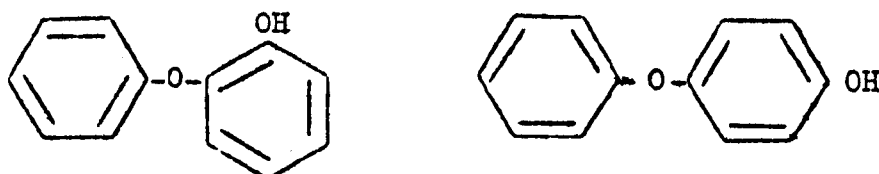
(i) Those derived from carbon-carbon coupling

e.g.

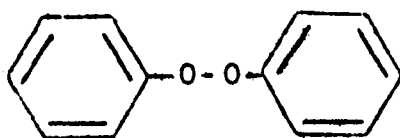


(ii) Those derived from carbon-oxygen coupling

e.g.

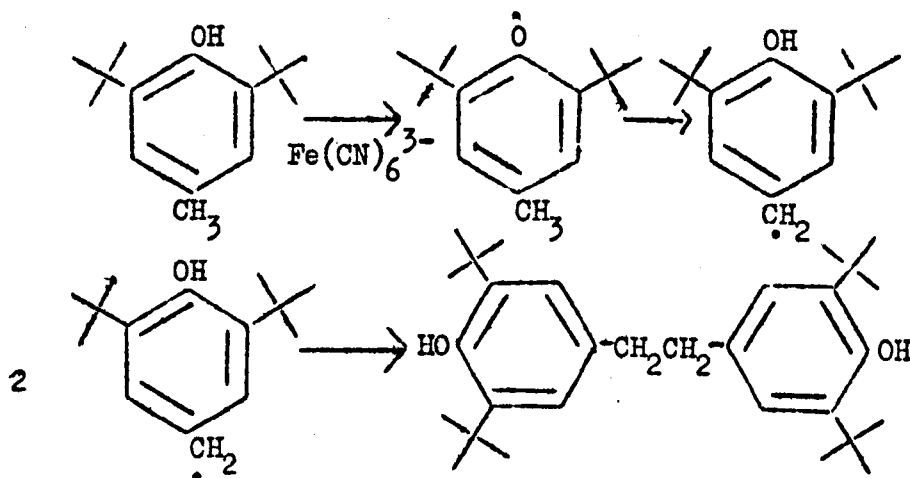


(iii) Those found by oxygen-oxygen coupling to give peroxides



Of these three classes of product, both (i) and (ii) are well substantiated, but no bona-fide examples of 'head-to-head' coupling have been reported²⁰⁵.

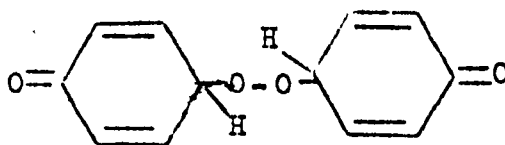
Other reported products, which do not strictly fall into the above classification, are those due to rearrangement of the intermediate radical²⁰⁶ e.g.



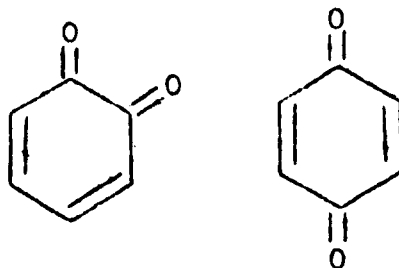
The formation of all the coupled products described above is favoured by the lack of available oxygen, or reactive group. As many of the oxidants commonly used are ionic, and not readily soluble in covalent solvents, the ratio of available oxygen or oxidant to phenol in the reaction mixtures, is often low, and coupling occurs readily.

Further reaction with the oxidant, as opposed to other radicals, will be favoured if oxygenation can easily occur. An obvious requirement for this is the presence of readily available oxygen in the oxidant.

A typical example of this type of process is the formation of peroxides as the products of autoxidation:

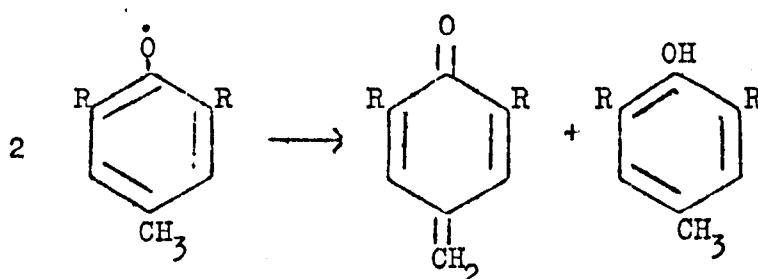


In other oxidations, both the ortho and para quinones may be formed:

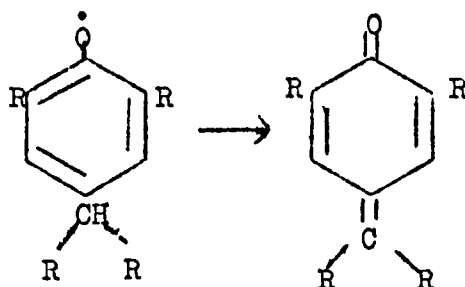


Another factor which must be taken into account when considering the products of oxidation of phenols via a free radical reaction is steric hindrance. The presence of bulky groups, ortho to the phenolic OH, favours coupling at the para-position. The presence of bulky groups in both ortho and para positions may lead to the formation of a complex mixture of products; if however a rearrangement of the intermediate radical can occur, as in the case of 2,6-di-t-butyl-4-methylphenol (see page 170) a straightforward

C-C coupling may occur, though the quinone methide may also result from disproportionation of the primary radical²⁰⁶;

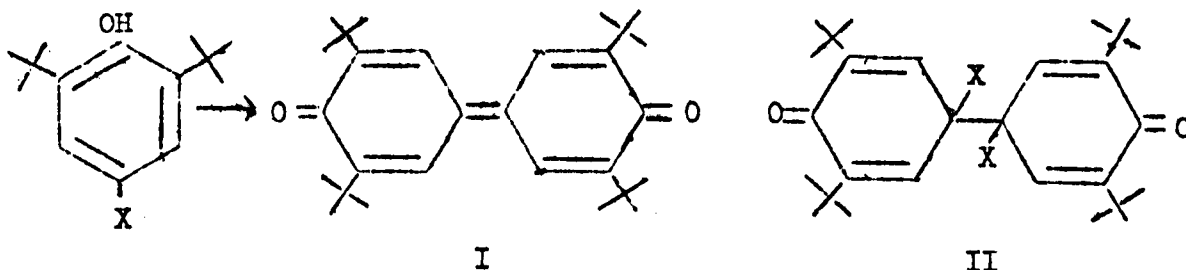


Further reaction of the methide with an excess of radicals may again lead to coupled products²⁰⁷. The formation of methides is favoured by ring substituents with α -hydrogen atoms²⁰⁸; these are readily removed and allow the above disproportionation to occur:



In the case of phenols such as those above, which have groups in both ortho and para positions, the form of coupling is very dependent on the nature of the groups. Thus coupling will occur where the most labile groups are present.

Typical examples of this type of behaviour are the oxidation of 2,6-di-*t*-butyl-4-halogenophenols. Oxidation of the respective chloro, bromo and iodo compounds has been reported²⁰⁹ to give the coupled product containing the halogen and the diphenoquinone in which the halogen has been eliminated. The proportion of non-halogenated product increases as the para group increases in size:

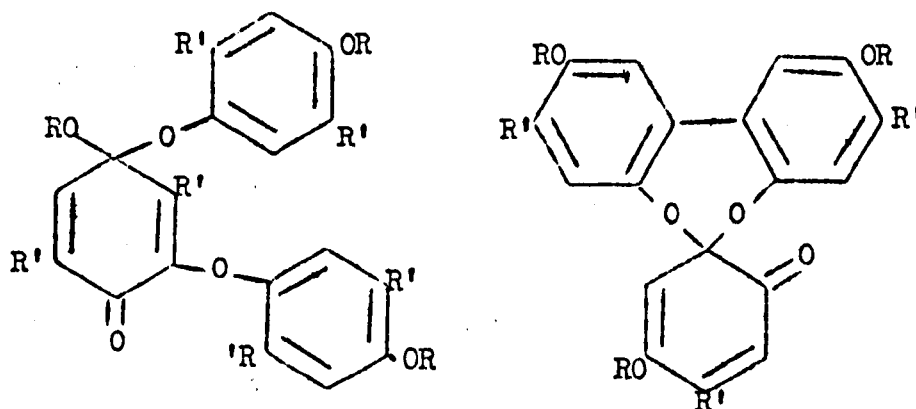


If X = Cl or Br Products I and II are formed

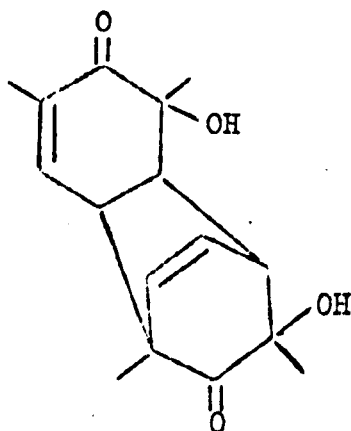
If X = I Product I only is formed

Bulky ortho groups tend to preclude ether formation, via C-O coupling if the para group is a labile one, though their presence may not prevent it entirely.

Until quite recently, only the simple products of oxidative dimerization and trimerization were reported. Modern chromatographic and other analytical techniques have led to the separation and identification of much more complex products resulting from one-electron oxidation of phenols. Typical examples are the keto-ethers and spiro-ketals isolated after the oxidation of 2,5-di-alkyl-4-alkoxyphenols²¹⁰ and 3-alkyl-4-alkoxyphenols²¹¹ respectively, by Hewgill and his co-workers:



Similarly, a novel coupled product has been identified very recently on autoxidation of 2,6-dimethylphenol in the presence of a copper (I) catalyst²¹²,



Other products which are formed in very many oxidations by one-electron abstracting agents are mixtures of phenolic polymers^{195,213}. In most cases these compounds, which consist of aromatic nuclei linked via oxygen, are considered undesirable contaminants of the oxidation product. In some cases, however, controlled polymerization has resulted in good yields of discrete polymers with only a small molecular weight distribution²¹⁴.

9.A.1.3 The Stability of the Free Phenoxyl Radical

The ease of oxidation of a phenol by a one-electron oxidant, depends on a number of factors. Firstly, the redox potential of the oxidant is important; for example *p*-chlorophenol is not oxidized by ferricyanide although phenol is oxidized readily by this reagent. *p*-Chlorophenol requires an oxidant with higher redox potential¹⁹⁵. With the use of non-aqueous, and in particular non-polar solvents, this factor is difficult to evaluate. However, it is clear that electron withdrawing substituents tend to make oxidation more difficult, by reducing the electron density in the region of the phenolic oxygen. In contrast, the alkylated phenols are more readily oxidized to radicals than phenol or halogenated phenols.

Another factor on which the ease of oxidation depends, is the stability of the radical once it is formed; the more stable the free-radical, the more likely it is that one-electron abstraction will occur. Thus di-hydroxybenzenes are more easily oxidized²⁰¹ than monohydric phenols, which in turn are more readily oxidized than enols or alcohols.

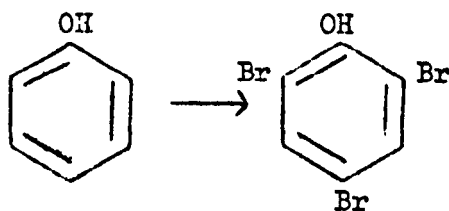
The most stable phenoxyl free radicals are those which have bulky ortho and para groups²⁰⁵; hence it is to be expected that the phenols with such substituents will be oxidized very easily by

one-electron abstractors. This hypothesis is substantiated by the work described in the literature (see refs 167, 209, 210 and 211 etc.).

9.A.2 Reactions which involve a Two-electron Transfer

The heterolytic oxidation of phenols, i.e. oxidation involving a two-electron change, is rather different mechanistically from the homolytic processes described above.

Phenols readily undergo nuclear substitution in the ortho and para positions by electrophilic reagents such as bromine and this type of reaction may be regarded as an oxidation¹⁹⁵.



For the purpose of comparison with the homolytic oxidation of phenols, only heterolytic oxidation by oxygen-containing reagents will be considered.

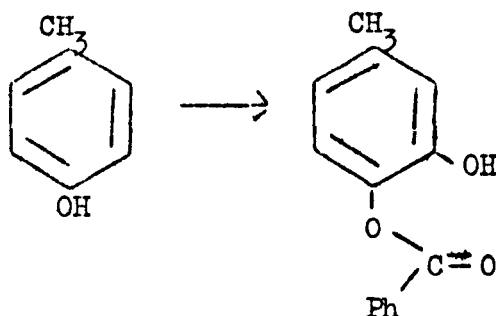
Heterolytic oxidations involve attack on the phenol by an electrophilic reagent which can thus gain a further electron pair. The most likely site for attack by such a reagent is the phenolic oxygen, with its exposed electrons, but the activating influence of OH makes ring attack an important process.

This type of reaction differs from the homolytic reactions previously described, in that the products of oxidation, which are usually stable molecular or ionic species, are formed in one, or perhaps two, consecutive stages. Chain reactions do not readily occur and so polymer formation is not a feature of this type of process, although as will be shown in the examples described later in this section, simple coupling of two rings may occur to give diphenoquinones.

Whilst there are numerous examples of one-electron oxidations of phenols, two-electron oxidations are less common.

A number of examples of this type of oxidation of phenols is described below.

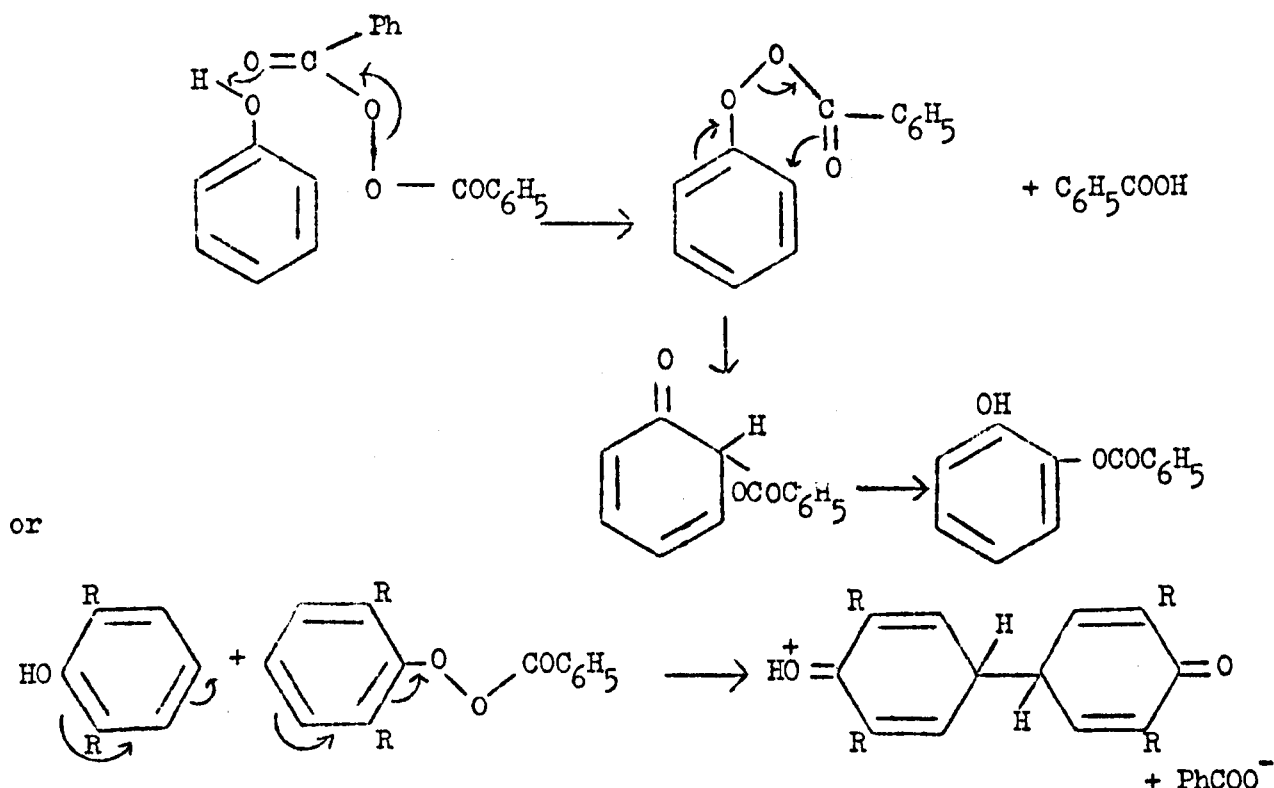
One well substantiated example of a heterolytic oxidation is the reaction of benzoyl peroxide with p-cresol to yield 4-benzoyloxy-3-hydroxytoluene²¹⁵:



No intermolecular coupling occurs unless the ortho positions are blocked, then oxidation to the diphenoquinone occurs²¹⁶.

The mechanism²¹⁷ for the latter reaction involves electrophilic attack at the phenolic OH by the benzoyl peroxide, followed by loss of benzoic acid, to give a peroxyester as an intermediate which then undergoes para coupling with a molecule of unreacted phenol. However, such a coupling reaction is not typical of heterolytic phenol oxidations.

In both cases the initial reaction step is attack on the phenolic OH group, involving either carbonyl addition or displacement on oxygen. The formation of products may be formulated by a scheme such as:



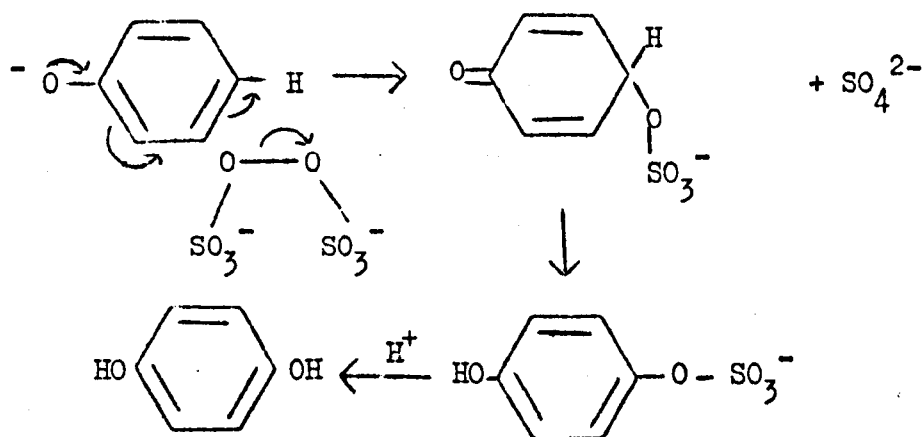
Further oxidation yields the diphenoquinone.

The earlier suggestion²¹⁶ that benzoyl radicals took part in the oxidation has been disproved.

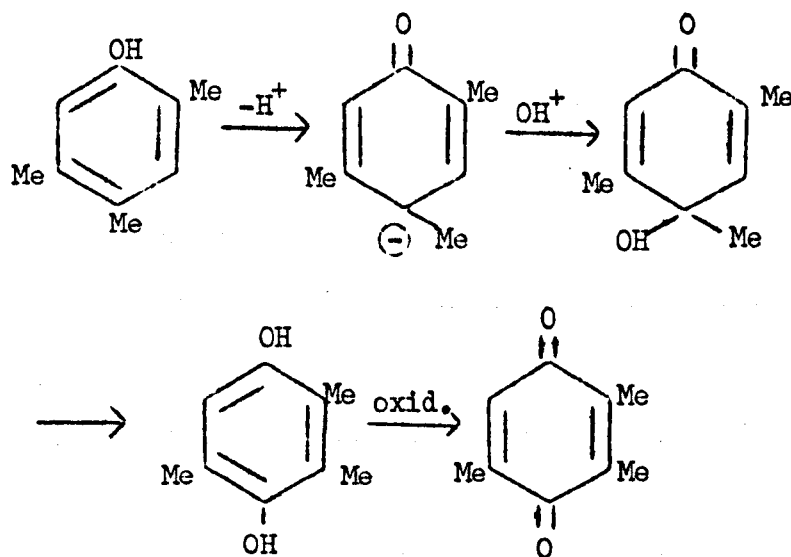
Other peroxides, e.g. *t*-butylperoxide, do effect one-electron oxidations; thus, the reaction²¹⁸ of *t*-butylperoxide with *p*-cresol yields dimeric and trimeric products, whilst a similar oxidation of di-*t*-butylphenols has been reported²¹⁹ to give a variety of products, including those resulting from radical coupling.

A kinetic study^{220,221} has shown that the oxidation of phenols such as 2,6-di-*t*-butylphenol, by the persulphate ion, $S_2O_8^{2-}$ is similarly a non-radical process. The rate determining step involves an electrophilic attack by the persulphate ion on the phenol molecule.

The product of oxidation is the para sulphate which undergoes rapid hydrolysis on acidification to yield the corresponding quinol. Only a trace of coupled product was shown to be present²²¹.

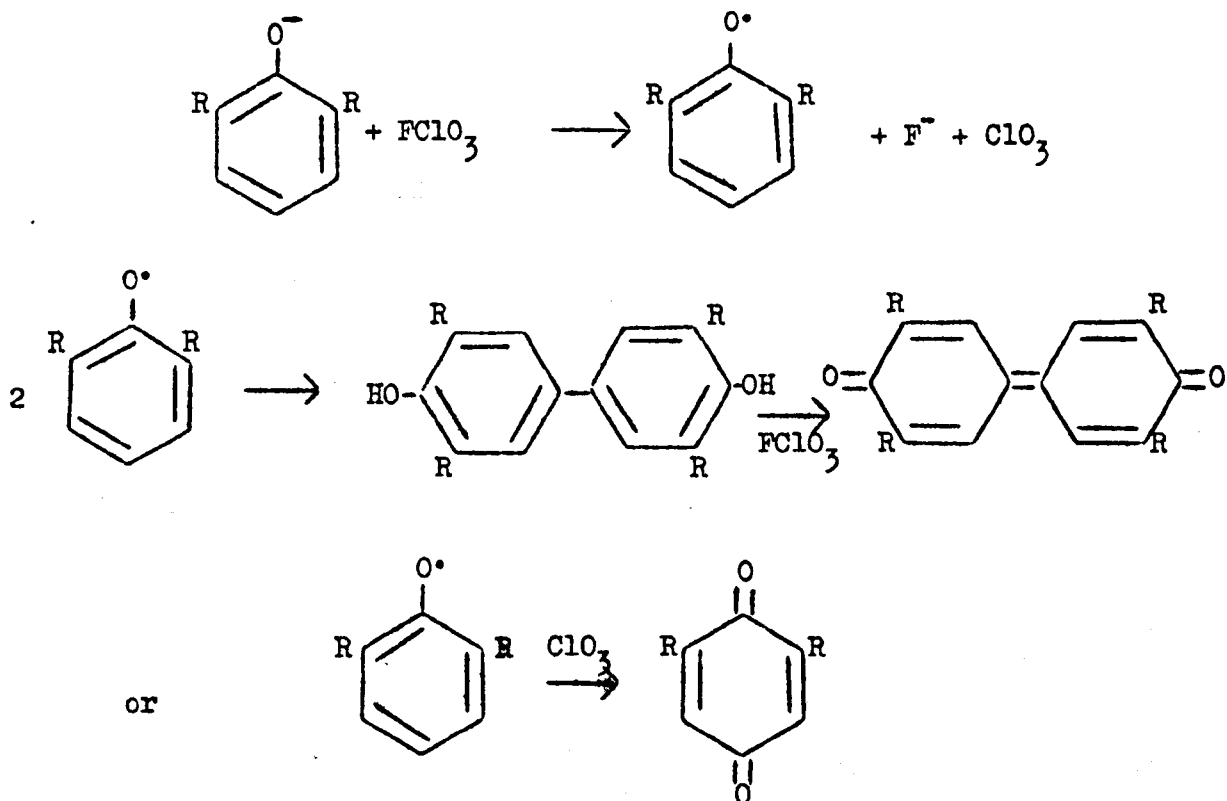


The oxidation of phenols with another peroxy compound, trifluoroperoxyacetic acid, also has a heterolytic mechanism²²². The oxidation of 2,4,5-trimethylphenol by this reagent is reported to take place by the following scheme, involving electrophilic hydroxylation:



Another oxidant which acts as an electrophile, under certain conditions, causing a two-electron oxidation of phenol, is perchloryl fluoride, ClO_3F ²²³. However, the mode of oxidation appears to be very dependent on the reaction conditions, and it is

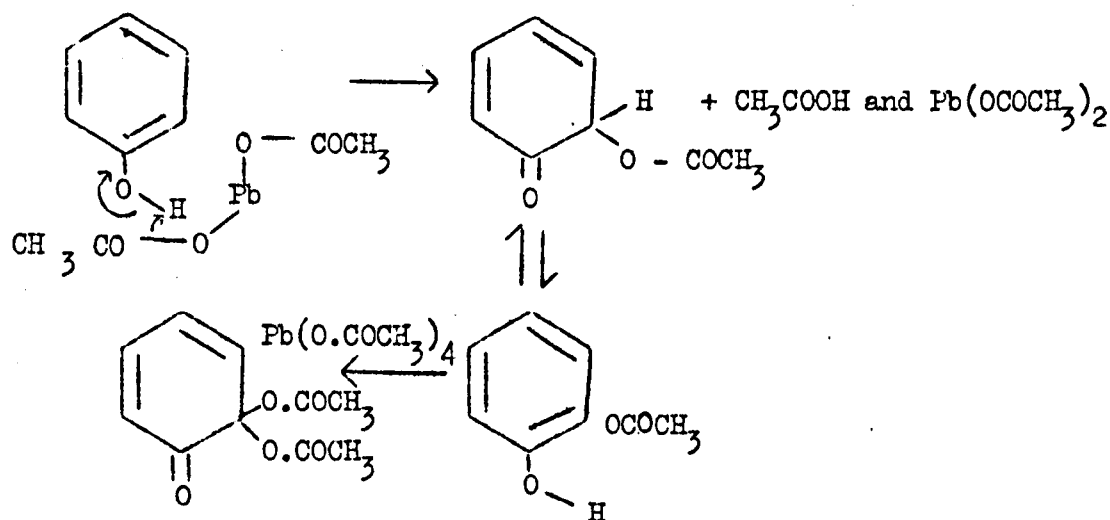
probable that both homolytic and heterolytic oxidations occur side by side. It is significant that the formation of quinonoid compounds, as opposed to other oxidation products, is believed to be formed by a one-electron transfer process e.g.²²³



The reaction of lead tetra-acetate with phenols, as well as other organic compounds, has been studied in detail, and has been the subject of reviews^{224,225}. The products of these reactions are generally dienone acetates, though quinones and coupled products have also been reported.

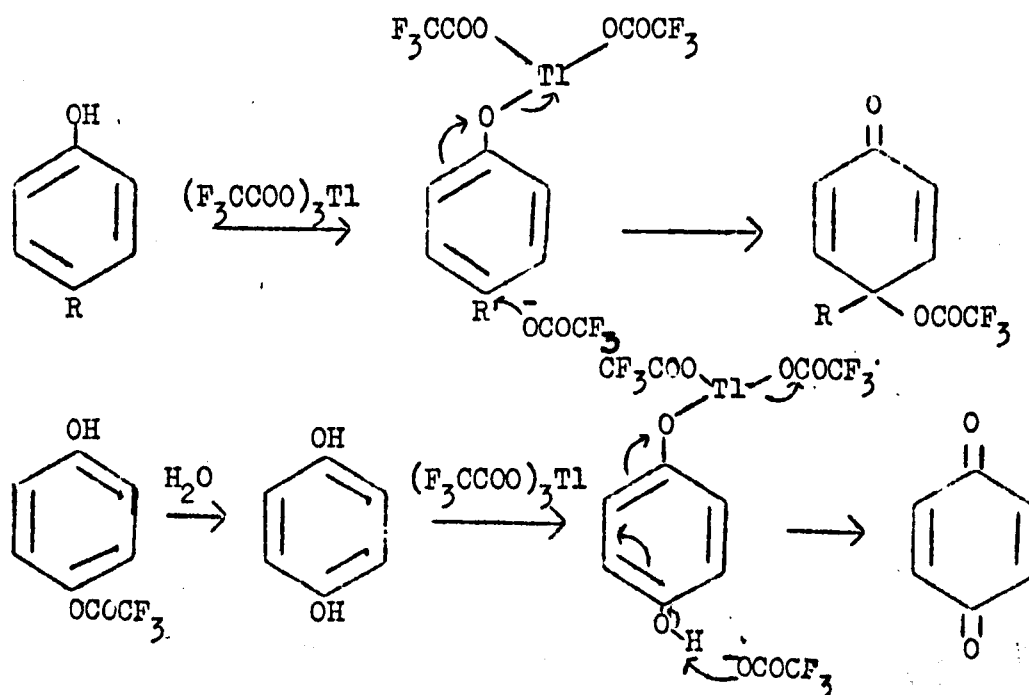
Initially it was believed that the oxidation of a phenol by lead tetra-acetate took place via a free radical mechanism; the formation of coupled products was explained on this basis²²⁶.

However, it has now been established²²⁵ that lead tetra-acetate is an oxidant of electrophilic character and that no phenoxyl or acetate radicals participate in the oxidations to any great extent.



A recent study²²⁷, has shown that the 2,4,6-tri-*t*-butyl-phenoxyl radical is oxidized much less rapidly than the corresponding phenol, by lead tetra-acetate, providing further evidence that the two-electron mechanism is favoured in such a process.

The oxidation of phenols to *p*-benzoquinones by thallium (III) trifluoroacetate has been reported²²⁸ recently, and it appears that a heterolytic, two-electron transfer is in operation in this case:



Oxidations of phenols by thallium (III) acetate show similarities to those by lead (IV) acetate²²⁹.

9.B. The Oxidation of Phenols by Chromyl Compounds

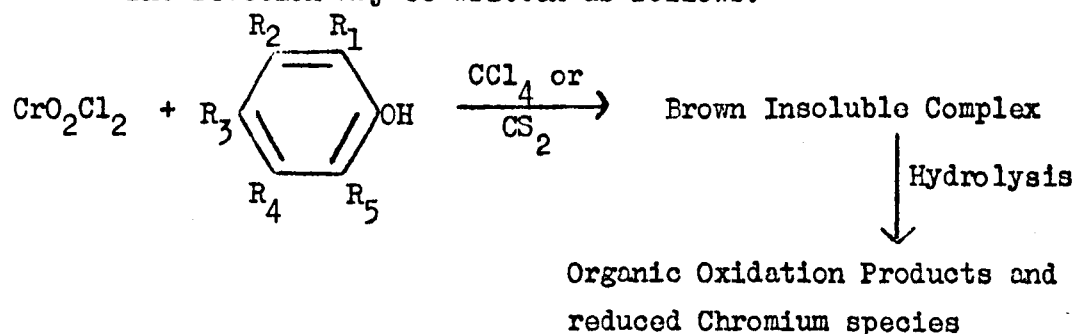
9.B.1. The Oxidation of Phenols as an Example of the Etard Reaction

From a consideration of the results presented in Chapters 5 and 6, it is apparent that the reaction of chromyl chloride with phenols is very similar, in outline, to the reaction of chromyl chloride with other organic compounds, such as hydrocarbons, i.e. the Etard reaction.

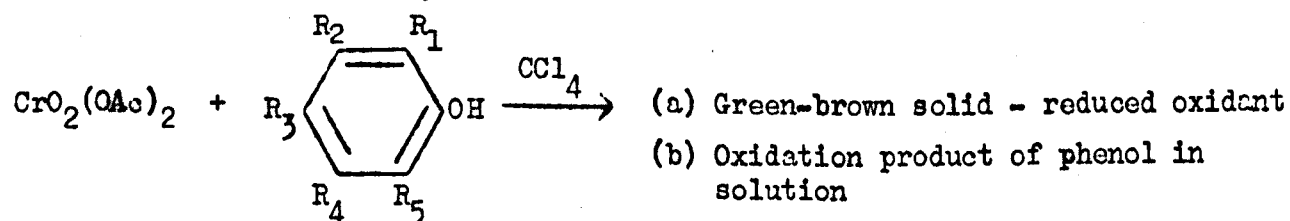
In Chapter 3, the reaction of chromyl chloride with many different classes of organic compound was reviewed and the general pattern which emerged was that the Etard reaction may be considered to be a two stage process; the first being the formation of an insoluble solid, and the second being the hydrolysis of solid yielding the oxidized form of the organic reactant.

The reaction pathway in the case of the oxidation of phenols is obviously very similar. In most cases, the phenol reacted rapidly with the oxidant to yield an insoluble brown solid, hydrolysis of which gave, usually, the corresponding p-benzoquinone. Side-chain oxidation, intermolecular coupling and ortho-quinone formation also occurred in certain instances.

The reaction may be written as follows:



The reaction pathway for oxidations by chromyl acetate is somewhat different and may be summarized:



The composition of the intermediate brown solids is discussed in section 6 of this Chapter, whilst the formation of oxidation products is discussed below.

The first question which must be discussed is at what stage of the reaction does oxidation of arphenol take place. There are two possibilities: either oxidation takes place immediately prior to (or during) the formation of the insoluble complex, or it may occur during the subsequent hydrolysis.

If the former postulate is correct, the complex will contain reduced chromium species. If the latter process occurs, chromium (VI) will be found in the solid complex, which may thus be considered a true 'adduct'.

The results given in Chapter 6 which are discussed in section 6 of this Chapter, indicate conclusively that oxidation of the phenols takes place immediately prior to the formation of the insoluble complexes.

Firstly one may consider the magnetic measurements and electron spin resonance measurements which both show that the chromium in the solids is present in an oxidation state less than (VI).

Furthermore, a study of the infrared spectra of these complexes shows the absence of bands due to unchanged phenol molecules, but it does show new bands which can be attributed to the presence of phenol oxidation products.

That the oxidation is complete before the formation of the solid complex has been confirmed by the reaction of various anhydrous coordinating solvents with the 2,5-di-t-butylphenol-chromyl chloride complex. In each case the reaction resulted in the liberation of

oxidation products, thus showing that a hydrolysis step is not part of the oxidation process. Also, this work confirms the presence of products of oxidation in the complexes hence indicating that the oxygen in these products is derived solely from the chromyl chloride.

However, it is probable that some further oxidation does occur during the hydrolysis of the complexes. The presence of residual oxidizing power has been shown in the solids derived from the chromyl acetate oxidations, and the magnetic measurements suggest that a similar situation exists with the complexes from chromyl chloride oxidations.

On hydrolysis, disproportionation of chromium (IV) or (V) will result in the formation of chromium (VI) which could then further oxidize the organic material present.

That an oxidation of this type can occur, has been shown by Slack and Waters¹¹². On hydrolysis of certain chromyl chloride-glycol complexes which they had prepared, aldehydes and ketones were released. Slack and waters showed, that unless a reducing agent was present during hydrolysis, the yield of aldehyde or ketone was much reduced, due to rapid oxidation by chromium (VI) produced by the disproportionation of the intermediate chromium species in the complex.

The addition of a ferrous compound to the water before hydrolysis provided a suitable species (Fe^{++}) to compete with the carbonyl compounds for the oxidant.

However, p-benzoquinones are not readily oxidized, and in the cases where they are the major product, further oxidation must be considered a minor reaction. Where the quinones were

formed in small yield (as was the case with, for example, monomethylphenols) the oxidation of hydrolysis products from the complexes may be more substantial.

The increase in yield of *p*-benzoquinones, especially the methyl-*p*-benzoquinones, obtained on reductive hydrolysis of the phenol-chromyl chloride complexes by zinc/water, may well have been due to the prevention of further oxidation. Side-chain oxidations have been reported for alkylated aromatic hydrocarbons by chromyl chloride and chromic acid, but very little is known of the reactivity of substituted quinones towards these oxidants.

The small proportion of chromium in oxidation state higher than (III) in the complexes does, however, confirm that whatever oxidation does occur during normal hydrolysis, it must only be of secondary importance.

9.B.2. Some General Features of the Phenol Oxidation Reactions

In Chapter 3, the various proposals for the mechanism of the Etard reaction were outlined and the differences in opinion as to whether the process was a homolytic reaction or not were discussed.

Although the mechanism for the oxidation of phenols by chromyl chloride and chromyl acetate has not been completely elucidated, the evidence is sufficient for a probable reaction path to be outlined.

The review of phenol oxidations, presented in part A of this Chapter, shows that the products, formed in the oxidations with chromyl compounds, could be produced as a consequence of

either homolytic or heterolytic processes. If a large proportion of the total product of oxidation were a coupled product e.g. a phenolic dimer or trimer, it would be possible to conclude that the reaction is homolytic. However, the experimental evidence is not so clear cut.

A review²³⁰, published in 1949, on the synthesis of *p*-benzoquinones by oxidation, considered briefly the subject of the oxidative mechanism. Although a wide variety of oxidants was considered, the general mechanism for the reactions was described in terms of a homolytic process, that is a reaction taking place via free radical intermediates.

This broad generalization was qualified by the rider that the nature of the oxidant, the experimental conditions and the character of the substituents on the aromatic ring would influence the side reactions that occur.

In the case of oxidations by chromyl chloride and chromyl acetate, the nature of these compounds is well established (see Chapters 2 and 3). The vigour of the oxidizing action and the limited choice of solvents for conducting the reactions with these compounds severely limits the variation and subsequent study of experimental conditions.

That these solvents play a part in determining the reaction pathway, and therefore the products of oxidations of phenols, can be seen from the results of the reaction of quinol with chromyl chloride in glacial acetic acid. In this case, as well as oxidation, extensive chlorination occurs. The reactions conducted in non-polar solvents do not show evidence of chlorination.

That the character of the substituents on the aromatic ring is important is shown in Tables 4 to 9. It can be seen that the

yields of p-benzoquinone increase with the number of alkyl substituents; for example, the yield of benzoquinone increases along the series phenol, monomethylphenol dimethylphenol, and similarly along the series phenol, mono-*t*-butylphenol, di-*t*-butylphenol.

Likewise the size of the ring substituent is of significance in chromyl chloride oxidations, large groups tending to lead to an increase in the yield of p-benzoquinone.

Thus the yield of the benzoquinone increases as the size of substituent increases: for example, along the series methyl, isopropyl, *t*-butyl. Phenol having no ring substituents gave only a trace of p-benzoquinone.

The position of the substituents is also a factor upon which the yield depends.

Thus, the presence of these alkyl groups in the ortho positions also increased the amount of p-benzoquinone formed on oxidation, in comparison with phenols with only one ortho substituent, or in comparison with, for example, a 3,5- or 2,5-dialkylphenol. One notable exception to this rule is to be found in the case of 2,5-di-*t*-butylphenol, which gave a higher than expected yield of p-benzoquinone on oxidation by chromyl chloride.

9.B.3. The Reaction as an Example of a Free Radical Oxidation

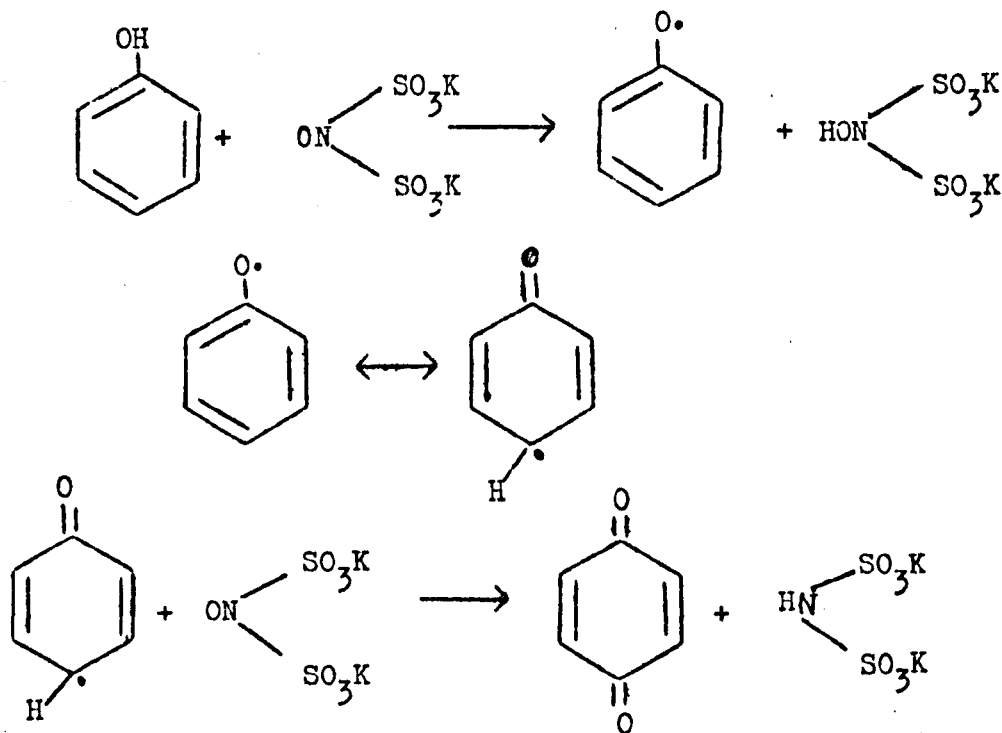
It is evident, from the results presented in Chapters 6 and 8, that there are good reasons for considering the oxidation of phenols by chromyl chloride and chromyl acetate to be a free radical reaction.

Firstly, the nature of the products of oxidation, quinones and diphenoquinones and small quantities of other coupled products,

together with intractable resinous material, is consistent with a homolytic oxidation, though coupled products are formed in certain exceptional two-electron oxidations (see part A of this Chapter).

It is significant that the variation of product yield with the nature and position of alkyl substituent closely resembles that found by Teuber and Rau²⁰⁴ for equivalent oxidations with Fremy's salt. They reported that the yield of *p*-benzoquinone increased along the sequence *m*-cresol, 3,5-dimethylphenol, *o*-cresol, 2,5-dimethylphenol, 2,6-dimethylphenol, analagous to the results illustrated in Tables 4 to 9.

The mechanism for the oxidation of phenols by Fremy's Salt has been confirmed²³¹ by isotopic methods and can be represented as follows:



Forrester and Thomson²⁰³ used similar reagents to Fremy's Salt, organic nitroxides, to oxidize phenols. These reagents are, like Fremy's Salt, quite unambiguously, free radical oxidants.

They found that the variation of ring substituents in the phenols had a similar effect on the subsequent yields of *p*-benzoquinones to that observed in the oxidations by Fremy's Salt.

Thus Forrester and Thomson²⁰³ showed that the yield of *p*-benzoquinone increased along the sequence *o*-cresol, 2,6-dimethylphenol, 2,3,6-trimethylphenol and 2,3,5,6-tetramethylphenol. This variation is comparable to the variations in yield of benzoquinone obtained in the chromyl chloride oxidations (see Tables 4 to 9).

Although, in the case of oxidations by chromyl acetate, a less representative group of phenols was used, the results shown in Table 11 tend to conform to this general pattern.

Forrester and Thomson²⁰³ considered that the poor yields of *p*-benzoquinones resulting from the oxidation of the simpler phenols was due to the relative instability of the intermediate phenoxy radicals. Being only short-lived, the radicals dimerize or polymerize, before they can be oxidized by a second mole of oxidant.

The similarity between the results obtained from oxidations with these nitroxides, and the results obtained from the oxidation with chromyl chloride, suggests that a similar mechanism could be applicable in each case.

If the analogy is correct, it is to be expected that phenols with a high degree of ring substitution, especially those substituted with bulky groups in both ortho positions, would give high yields of the corresponding *p*-benzoquinones.

The results from the chromyl chloride oxidations (Tables 4 to 9) do show this feature.

Results¹¹³ obtained from a study of the oxidation of chlorophenols by chromyl chloride, show similar effects with regard to the number of substituents; the yield of the respective chlorinated *p*-benzoquinone was shown to increase along the series 2-chlorophenol, 2,6-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol.

Like the chlorophenols, the nitrophenols were visibly slower to react with chromyl chloride than their alkyl counterparts: in the case of both the chloro and nitrophenols the rate of reaction diminished markedly with the degree of substitution.

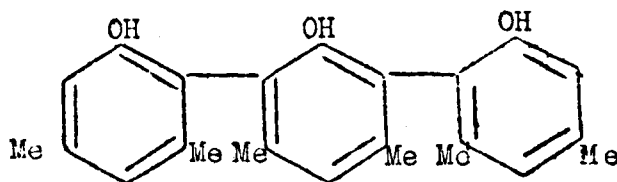
Similar results were obtained from the reactions with chromyl acetate. Again, the highest yields of *p*-benzoquinones were obtained from either sterically hindered or highly alkylated phenols.

Some further support for a homolytic mechanism is the formation of diphenoquinones from the oxidation of 2,6-dialkylphenols, albeit in smaller yields than the *p*-benzoquinones. Products such as these have been reported for both homolytic and heterolytic phenol oxidations, but are more generally associated with free radical oxidation processes (see part A of this Chapter and ref 232).

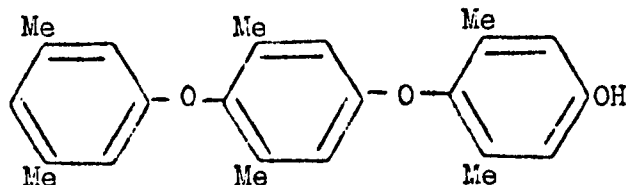
In a few specific cases, small quantities of coupled phenolic compounds were isolated.

For example, in the case of the oxidation of 3,5-dimethylphenol, a compound of molecular formula $C_{24}H_{26}O_3$ was isolated.

The most likely compounds corresponding to this formula are the trimeric phenols:



or the coupled phenol-ether:



The formation of such coupled products is typical of free radical oxidations and this must again be considered indicative of the mode of oxidation by chromyl compounds.

Other evidence for radical formation comes from the examination of the other products of oxidation. In none of the oxidations by either chromyl chloride or chromyl acetate was a quantitative yield of any product formed, though high yields of p-benzoquinone were obtained in some chromyl acetate oxidations (Table 11).

In nearly every case the non-quinonoid product of oxidation was a non-crystalline, coloured material.

These amorphous substances are soluble in alkali giving brown or brown-black solutions, which, on acidification always precipitated the resinous starting material. This behaviour is consistent with the presence of polyhydroxy compounds. The presence of phenolic OH groups was confirmed by infrared spectroscopy.

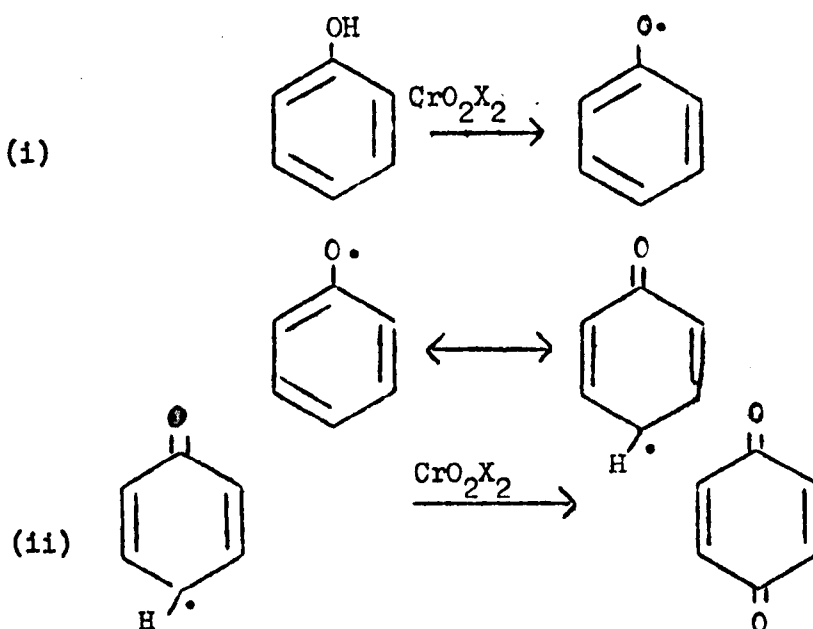
As described earlier, chemical and chromatographic methods failed to lead to the isolation of recognizable compounds from these resins and tars, except in the few cases cited.

If a free phenoxyl radical were an intermediate in these reactions, polymerization of such a radical would readily account for the formation of these products.

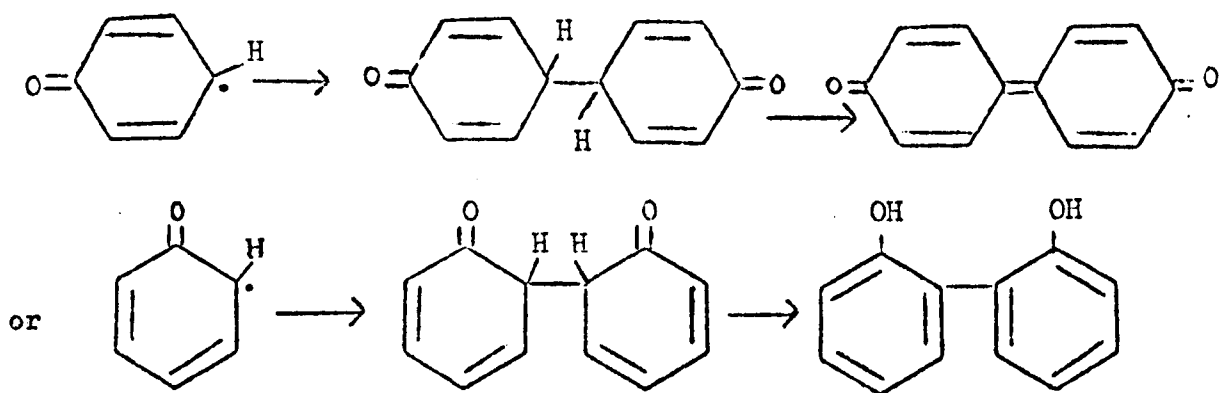
Similar resinous materials are obtained in very many oxidations^{230,233,234} of phenols by established one-electron abstractors, though it is still not clear why such polymerization takes place so readily¹⁹⁵.

It can thus be seen that there is good reason to examine further the concept of a radical process for the oxidation mechanism.

If the mechanism does involve the formation of the phenoxyl free radical, the formation of a benzoquinone can be written as follows, as a two stage reaction:



An alternative to stage (ii) is the formation of diphenoquinones or polymeric products; these would arise from the coupling of the intermediate radicals:

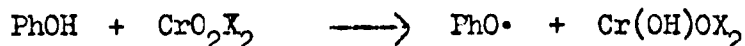


Each of the stages may comprise a number of reactions, and may indeed follow one of a number of possible pathways. These are outlined below.

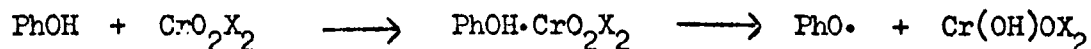
9.B.3.1. The First Stage of the Reaction

The first stage of the reaction may take place via any of the alternative pathways indicated below.

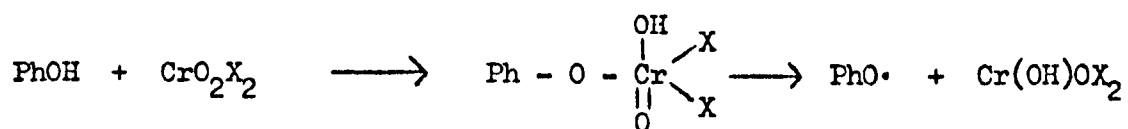
- (i) Direct formation of the phenoxyl radical by hydrogen atom abstraction:



- (ii) Formation of the radical via a molecular complex:

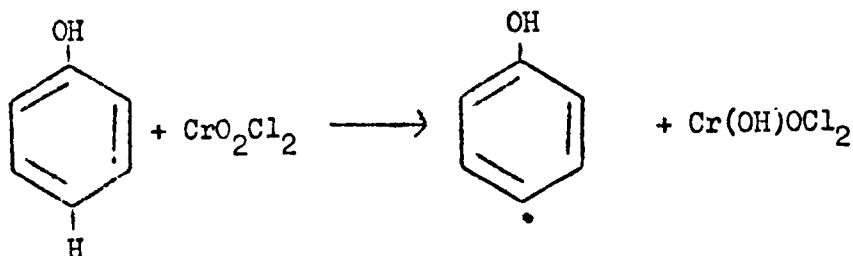


- (iii) Formation of a chromium (VI) ester, which then gives the free phenoxyl radical:



This reaction may include the first stage of scheme (ii) i.e. the formation of a molecular complex.

- (iv) Direct formation of a free radical via attack at the aromatic ring:



The formation of transient blue solutions, when chromyl chloride or chromyl acetate are added dropwise to a large excess of phenol, can be ascribed to the formation of either a molecular complex (see scheme (ii)) or a chromium (VI) ester. The electronic spectra of these solutions showed only an intense, broad band typical of charge-transfer spectra, and either type of intermediate in (ii) or (iii) could give rise to a spectrum of this type.

If such a molecular complex were formed, it could either arise from π - or σ -bonding between the phenol and oxidant. However, π -complexes are formed only rarely with metals in high oxidation states - a high electron density on the metal centre is required for successful complex formation.

The formation of a σ -complex is readily explained in terms of donation of a lone pair of electrons, on the phenolic oxygen, to chromium:



The relative reluctance of the chloro- and nitro-phenols to react with chromyl chloride can be explained by the reduction of electron density at oxygen, due to the presence of the electron

withdrawing groups in the ring. Coordination would be less likely to take place, and the complexes so formed would be less stable.

The decrease in electron density would, however, also retard reaction (i), the direct formation of the phenoxyl radical. Similar effects have been noted in the oxidation of phenols, which have electron-withdrawing substituents, by established one-electron oxidants¹⁹⁵.

By contrast, the presence of alkyl-ring substituents increases the electron density at oxygen and hence favours both reaction schemes (i) and (ii). Certainly the experimental evidence shows that the reactions of alkylated phenols with chromyl chloride and chromyl acetate are visibly much more rapid than the corresponding oxidations of the nitrophenols.

Another aspect of the reaction which must be examined is the effect of the initial reaction processes on the nature of the final product of oxidation.

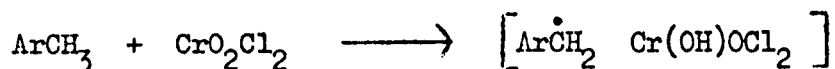
The presence of free phenoxyl radicals, as in scheme (i) might suggest high yields of coupled product. However, this does not occur in oxidations by Fremy's Salt and the parallel between this oxidant and chromyl chloride has already been drawn.

The very high yields of p-benzoquinone formed in the case of highly chlorinated phenols¹¹³ can be described in terms of any of the three processes. The deactivation of the phenolic oxygen would lead to either radical formation (i) or coordination (ii) taking place at a slow rate. Formation of the ester, scheme (iii), might also be slowed by the presence of these chloro-groups. Thus in a reaction system with a low concentration of radicals and an excess of oxidant, quinone formation, rather than radical coupling might be expected to take place.

It must be stated here, that whatever the rate of reaction, there is no evidence to suggest that the reactions which proceed at different rates, do so by different mechanisms or result in different oxidation states for the chromium in the solid complexes.

Another explanation for the formation of quinones rather than coupled products is that 'caged' radicals are formed.

The formation of these 'caged' species has been proposed by Wiberg, Marshall and Foster¹⁰⁴ (see Chapter 4, page 51) in the oxidation of n-propylbenzene by chromyl chloride. They suggested that the free-radical formed initially was always associated with a reduced chromium species, in a solvent 'cage':



It was suggested that a caged intermediate such as this would prevent a chain reaction or other coupling reactions from taking place.

The 'caged' radical rapidly recombines with the chromium (V) species to give an ester, which then reacts with more oxidant to give a diester. Hydrolysis of this gives the products of oxidation.

By analogy with this mechanistic scheme, the formation of p-benzoquinones, rather than products of radical coupling, can be explained readily.

The fourth reaction scheme, that involving the formation of an aryl radical, by hydrogen abstraction from the aromatic ring, would result in products comparable to those of the other schemes.

However, there is little evidence to support this mechanism, rather than those previously described, and certain experimental findings are difficult to explain by this process; for example the formation of the blue, non-paramagnetic species.

It is evident that the formation of a free phenoxyl radical would not be the only important factor in determining the yield and type of product.

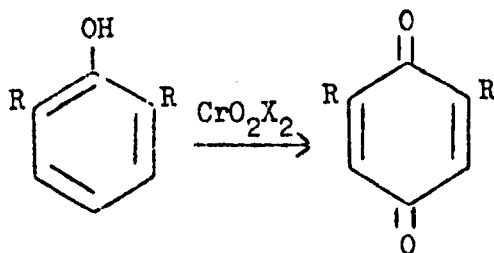
The presence of alkyl groups on the phenol ring leads to activation of the phenolic oxygen, and hence facilitates rapid reaction with chromyl oxidants.

Despite the high relative concentration of phenoxyl radicals which one would assume to be present initially in these oxidations, in comparison to those of chloro- or nitrophenols, *p*-benzoquinones are still found as well as polymeric material.

One factor which must play a part is the effect of steric hindrance, which prevents further reaction of the radical.

The ease of oxidation of sterically hindered phenols to radicals, by comparatively weak oxidants, shows that steric factors are not very important in the primary stage of the reaction.

If the ease of radical coupling is reduced by steric factors, the second oxidative stage must become important, and leads to high yields of quinones:



R = Bulky group

This hypothesis is consistent with the results in Tables 4 to 9, which show that sterically hindered or partially sterically hindered phenols tend to give higher yields of benzoquinone than those without any steric hindrance to attack at phenolic oxygen.

In certain cases, the yield of *p*-benzoquinone could be improved by increasing the mole ratio of oxidant to phenol. This again suggests that there may be competing reactions between radicals, and radicals

and excess oxidant; this evidence also shows that an important stage of the oxidation reaction is dependent on concentration.

The effect of changing the oxidant to phenol ratio is most noticeable in the methyl substituted phenols: the yield of substituted p-benzoquinone decreases for the 2,6-dimethylphenol, yet increases in the case of the 3,5-dimethylphenol, as the oxidant to phenol ratio is increased.

This can be interpreted as follows. If the radical is formed in the first step, and if it is particularly unstable, the increase in the amount of oxidant should increase the yield of p-benzoquinone. If the radical is relatively stable, then, providing there is excess oxidant, an increase in the oxidant to phenol ratio should have little effect. However, the effect of side chain oxidation is also a factor which must be considered (see below).

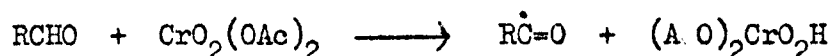
In general, the 3,5-di-substituted phenoxy free-radicals have less enhanced stability than their 2,6-counterparts. Hence the former should show increased yields of p-benzoquinones on increase of the oxidant to phenol ratio. The latter should not show this effect.

The decrease in the yield of p-benzoquinone in the case of oxidation of the 2,6-dimethylphenol, in comparison to the 3,5-dimethylphenol can be ascribed to side-chain attack leading to polymeric products; such oxidation is more likely to occur in the ortho and para positions than the meta.

It has been assumed throughout this section that chromyl acetate behaves in a similar manner to chromyl chloride, except in the formation of the insoluble complex. It seems very probable that the initial stage of the oxidation reaction is very similar for each of the two reagents.

This is indicated not only by the great similarity between the products of oxidation, but also by the magnetic measurements, which show that the chromium atoms in the two types of solid complex are in similar oxidation states.

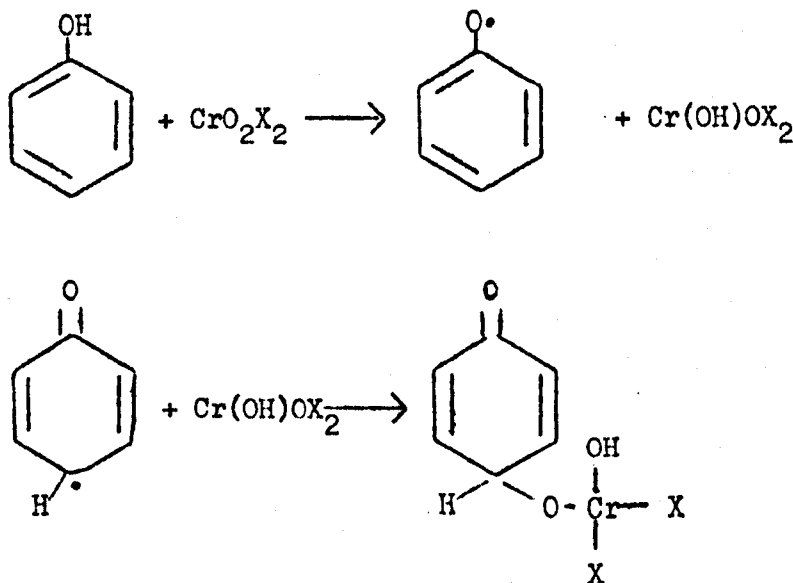
Wiberg and Lepse²⁵⁴ who studied the oxidation of aromatic aldehydes by chromyl acetate, commented on the similarity between the two oxidants. They showed that the reaction proceeded in two stages, the first giving chromium (V) and the second chromium (IV) and that their experimental findings were in accord with the initial formation of a free radical:



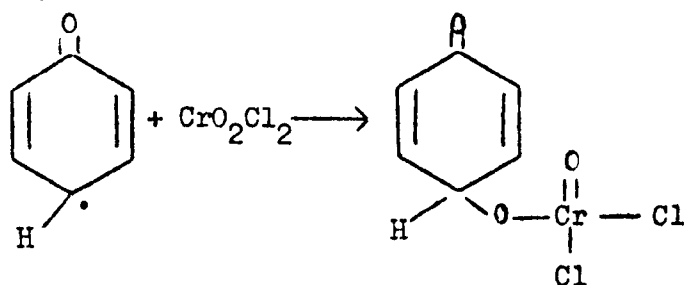
9.B.3.2. The Second Stage of the Reaction

Magnetic measurements show that the average oxidation state of the chromium in the solid complexes is between (III) and (IV). The initial reaction results in a chromium (V) species and the phenoxyl free radical; the further oxygenation, to give a quinone, must occur in the second stage of the reaction.

It is possible that the chromium (V) species formed in the first stage combines with the radical to give a chromium (IV) ester:

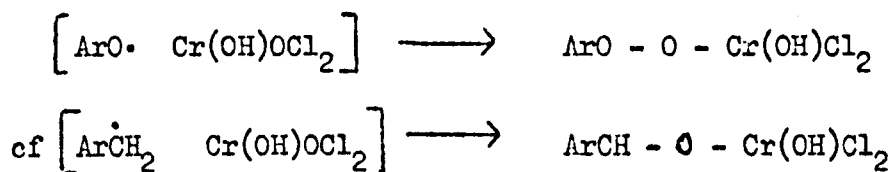


However, this is not acceptable, as it would require only one chromium per organic molecule and this is not consistent with the stoichiometry found for the solid complexes. Likewise, attack by a second molecule of chromyl chloride on the radical, resulting in a chromium (V) ester, cannot be the complete explanation of the reaction; it does not explain either the magnetic measurements or the stoichiometry of the solids, unless this stage is followed by a



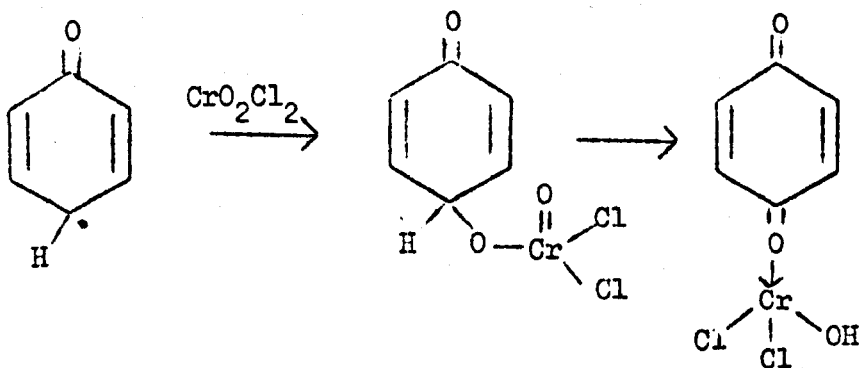
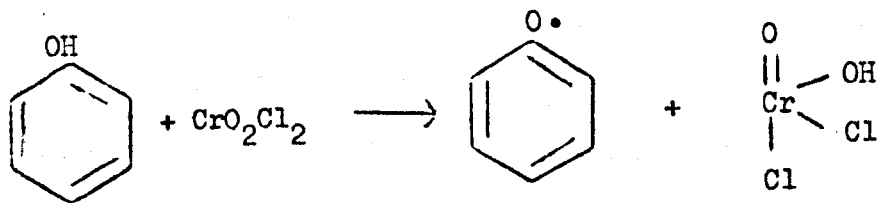
further stage during precipitation of the complex.

Similarly the recombination of a 'caged' radical as discussed previously is unlikely, as this would suggest the formation of a chromium peroxide intermediate:

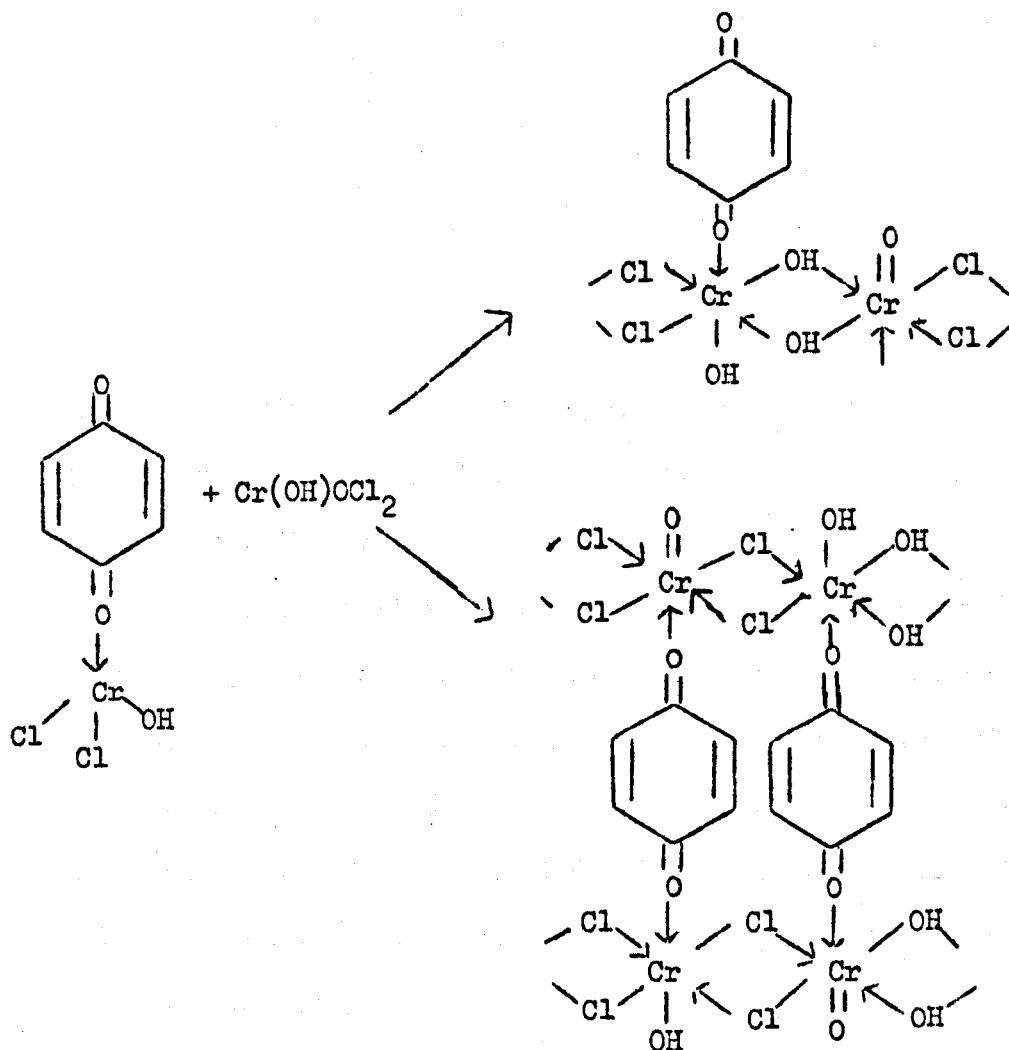


It is thus evident that, in the case of phenol-chromyl chloride complexes, no simple ester structures can be proposed, which would fit all the experimental data, and which are comparable to those proposed for the hydrocarbon-chromyl chloride 'adducts'.

A probable explanation is that after the initial oxidation, producing a phenoxyl radical, a second reaction involving hydrogen abstraction takes place, involving either a chromium (V) species or chromyl chloride molecule. This is followed by the rapid formation of hydroxyl and chlorine bridges between the chromium atoms, forming large molecular groups which then precipitate from solution:



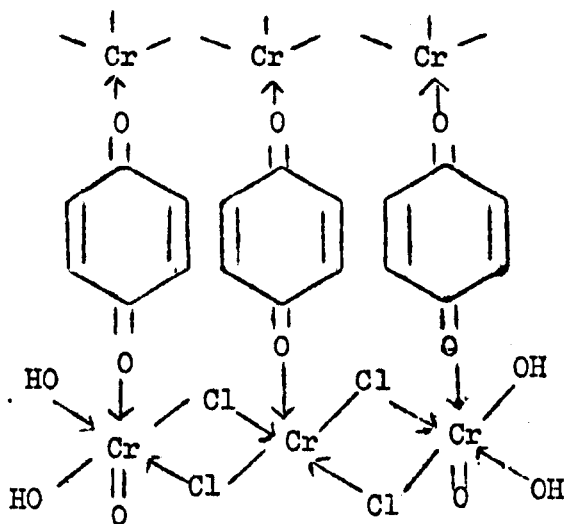
then



During the oxidation process, chromium species of oxidation state (V), (IV) and (III) could be formed. Thus various metal species could be present in the precipitated complex.

This would account for the non-stoichiometry of the complexes and the average value of the magnetic moment of the complexes suggesting an oxidation state for chromium of between (III) and (IV).

The chromium could readily acquire a coordination number of 6 by utilizing the benzoquinone molecules as ligands. Typical units in the complex may be written as follows:



The infrared data, the magnetic properties and the results of the treatment of complexes with donating solvents, are all consistent with such a structure.

Further weight is given to this proposal by the formation of a precipitate containing only reduced oxidant, and no oxidized form of the phenol, in reactions with chromyl acetate. The acetate group would be expected to be a more powerful complexing agent than a benzoquinone and hence would displace this weaker ligand, giving a bridged complex comparable to that above, but without chloro or benzoquinone groups.

9.B.3.3. Possible Confirmation of a Radical Mechanism

There are three possible experimental techniques by which the radical process suggested above might be confirmed.

The first is by electron spin resonance spectroscopy. Gragerov and Ponomarchuk¹³³ in a brief report, stated that treatment of a solution of 2,6-di-*t*-butyl-4-methylphenol with chromyl chloride, gave a signal characteristic of the corresponding phenoxyl radical. However, in their paper, they give no experimental details and whether they used a static or flow system is unclear.

In an attempt to repeat their work, solutions of chromyl chloride and various phenols in carbon tetrachloride or carbon disulphide were mixed in the cavity of an e.s.r. spectrometer, over a range of temperature.

Although no signals due to primary radicals were obtained, absorptions due to both organic and inorganic species were observed. A more detailed study using this technique and a carefully controlled mixing system for the reactants might lead to a clarification of the situation.

The use of a radical 'trap' in the reaction was considered by the author. However, the reactivity of chromyl compounds is such that the compounds commonly used as 'traps' are themselves readily attacked by the oxidants and thus the method is not applicable in these reactions.

The third diagnostic method which could be used to determine the course of the reaction is a kinetic study.

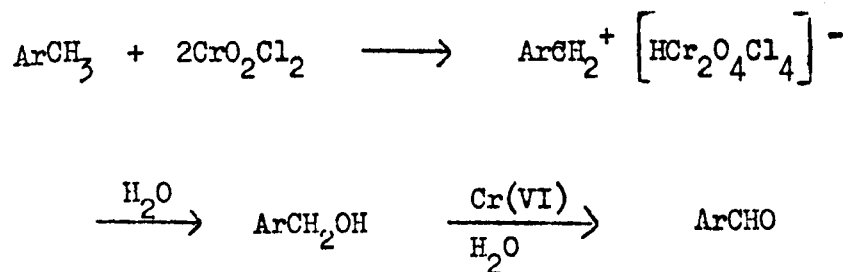
Considerable technical difficulties, however, would first have to be overcome. The reactions are, in most cases very rapid, and the formation of the solid intermediate renders normal methods for studying such reactions impractical.

In this context, it is of note that kinetic studies of the Etard reaction, with toluene and substituted toluenes, have led to results that have been difficult to interpret unambiguously (see Chapter 4, section 2.1. and refs. 96, 121, 122 and 123).

9.B.4. The Reaction as an Example of a Heterolytic Oxidation

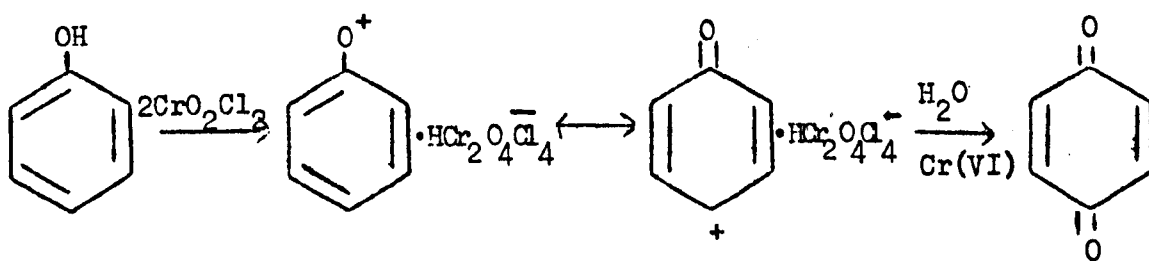
Although the experimental results appear to be consistent with a free radical mechanism, it is necessary to consider whether or not they are consistent with other types of reaction mechanism.

The ionic mechanism, suggested by Nenitzescu¹¹¹, for the oxidation of aromatic hydrocarbons, is as follows:



In the comparable oxidation scheme for phenols, it would be necessary to eliminate the hydrolysis step, because the oxidized form of the phenol can be released from the intermediate complex by other polar solvents, and in the reactions with chromyl acetate, the quinone may be obtained directly from the reaction mixture.

The analagous scheme,

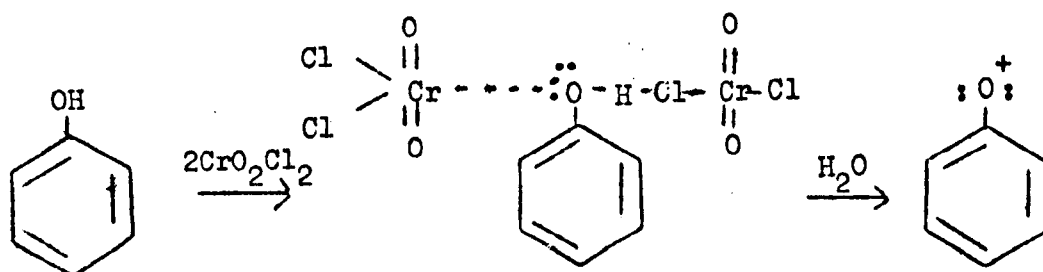


in which the oxygen is derived from water cannot apply, because quinone can be released from the intermediate complex by, for example pyridine.

Also, the average oxidation state of the chromium in the intermediate solid would be (V) rather than the experimental value, between (III) and (IV).

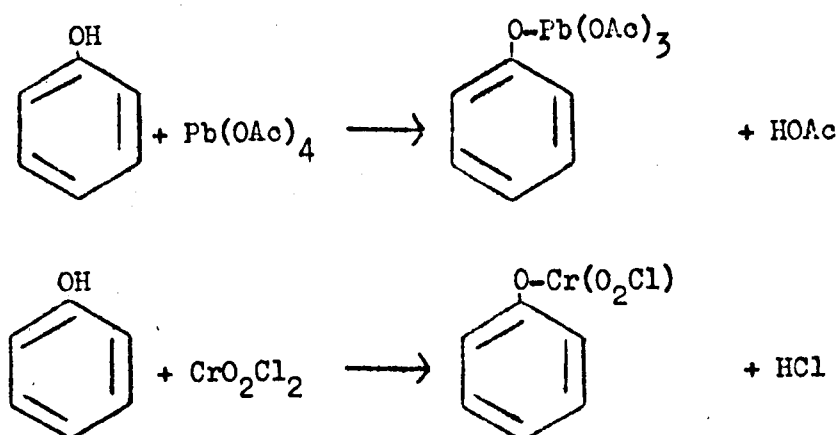
It appears therefore, that the Nenitzescu mechanism cannot be considered as a rational explanation for the Etard reaction involving phenols.

A mechanism analagous to that proposed by Mosher and Celeste⁷⁰ for the oxidation of alcohols, would involve hydride ion abstraction via a hydrogen-bonded intermediate (see Chapter 4, page 58). This would result in a free ion being formed e.g.



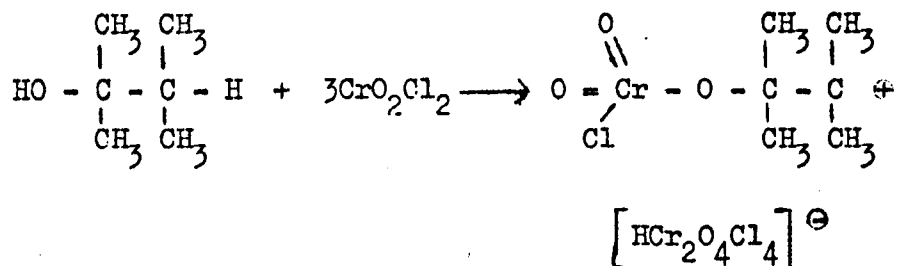
Again, this type of intermediate is unacceptable as oxidative hydrolysis is required to complete the reaction.

If the mechanism is similar to phenol oxidation by lead tetraacetate, then loss of hydrogen chloride would be observed:



A similar mechanism has been postulated¹¹¹ for the oxidation of 1,1,2,2-tetramethylethanol; no experimental details for the reaction were given, and no specific description of hydrogen chloride evolution was made. This would be required from the following

scheme, which gives a chromium (VI) ester:



This type of intermediate would require further oxidation to give the observed ketonic products.

The analysis of the phenol-chromyl chloride complexes has shown that in most cases the chromium to chlorine ratio is 1:2 (see page 122) and the analysis figures for chlorine agree well with those required for a stoichiometry $\text{ArOH} \cdot 2\text{CrO}_2\text{Cl}_2$; this confirms that there is no loss of chlorine during oxidation. Hence it may be concluded that this type of mechanism is inappropriate for the oxidation of phenols with chromyl chloride. The initial formation of a neutral chromium (VI) ester, as opposed to an ester containing a carbonium ion, has been proposed, previously as a possible reaction intermediate (see this Chapter, section B.3.1.).

Such chromium (VI) esters have been prepared by treating alcohols with chromic acid³⁶ (see Chapter 2, page 12) and they have been reported as intermediates in the oxidation of sterically hindered sterols²³⁵.

One property of the esters derived from alcohols is that they are decomposed by pyridine to give a carbonyl compound³¹. A parallel might be drawn with the liberation of p-benzoquinones on treating the phenol-chromyl chloride complexes with bases. However, not only do the infrared spectra of these complexes show the presence

of carbonyl bands, before solvolysis, but the presence of the second atom of oxygen in the solvolysis product, the benzoquinone, is not explained.

If such a chromium (VI) ester were to form with chromyl chloride or chromyl acetate further reaction with oxidant must occur, before solvolysis, to result in the solid complex containing chromium (III) or (IV). This has been discussed previously (see this Chapter, section B.3.1.).

There is further evidence which suggests that a chromium (VI) ester is not present in the solid complex. It has been shown that hydrolysis of an ester of this type would almost certainly proceed via chromium-oxygen bond cleavage; this would result in the phenol being reformed. Wiberg and Foster²³⁶ hydrolysed tetra-*t*-butoxychromium (IV) with water enriched with ¹⁸O and showed that 97% of the reaction proceeded via chromium-oxygen bond cleavage. The main product was *t*-butylalcohol. Even if the hydrolysis of the chromium (VI) ester released oxidant for further reaction, such an intermediate would be expected to give some recovery of phenol, on hydrolysis.

Slack and Waters¹¹² proposed ester formation to explain the formation of the solid complex between glycols and chromyl chloride. They believed that the Etard complex contained chromium (VI) which, on decomposition by water, gave free radicals and chromium (V) species, both of which underwent disproportionation to give the final products.

If such a mechanism were applicable to the case of phenols and chromyl chloride, a hydrolysis step would be a necessary requirement. Also the intermediate complex would be diamagnetic.

It is significant that no comparable magnetic study has been made on the complexes from the glycol reactions.

9.B.5. The Formation of Products other than p-Benzoquinones

The formation of p-benzoquinones is most conveniently explained by a radical mechanism, but the formation of the other products of oxidation can be explained in terms of either radical coupling, or a secondary competing reaction between the oxidant and the phenol, for example, side chain oxidation.

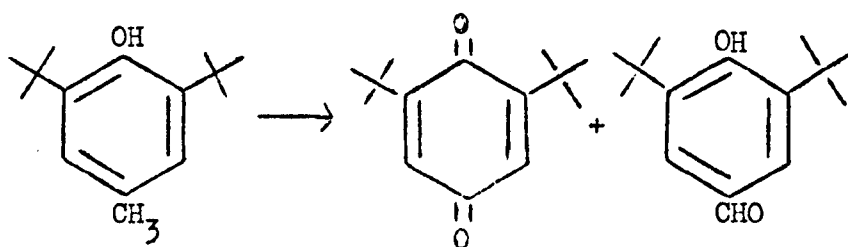
In most of the oxidations, quinone formation is accompanied by the production of a polymeric, resinous material. Whilst radical polymerization is a likely source for this type of product other routes must be considered.

It is noteworthy that, in certain cases, the use of zinc during hydrolysis increased the yields of p-benzoquinone and decreased the amount of resinous material.

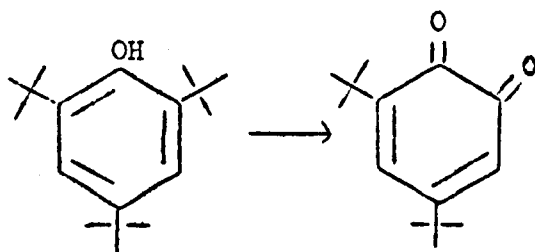
However, in the cases where the products of oxidation by chromyl chloride, followed by non reductive hydrolysis, were resins or tars, reductive hydrolysis failed to change the nature of the product. This showed that the process of tar formation was independent of secondary oxidation during hydrolysis.

In only one case was a new product obtained. This was 2-t-butylhydroquinone, formed by reduction of the p-benzoquinone, which was the initial product.

The possibility that side-chain oxidation might be more general than was initially believed has been shown by the oxidation of 2,6-di-t-butyl-4-methylphenol to the corresponding aldehyde, as well as the p-benzoquinone:



The oxidation of 2,4,6-tri-*t*-butylphenol also results in removal of a side chain, to give the orthoquinone:



The labile nature of the 2-*t*-butyl group in this phenol has been shown by other workers. Thus oxidation by nitric acid (in glacial acetic acid) also results²³⁷ in o-quinone formation. Likewise, oxidation²³⁸ of 2,6-di-*t*-butyl-4-methylphenol by Fremy's salt results in removal of a *t*-butyl group.

By analogy, o-benzoquinone formation would be expected in the oxidation of 2,4,6-trimethylphenol, 2,4-di-*t*-butylphenol and 2,4-di-*t*-butyl-6-methylphenol. In each case only resinous products were formed.

Other phenols with a vacant ortho position might be expected to give o-benzoquinones but none have been isolated. Similarly no o-benzoquinones have been obtained from oxidation of the naphthols: 1-naphthol gives the corresponding p-benzoquinone but 2-naphthol gives only polymeric, tarry material.

It is likely that o-benzoquinones are formed in these cases, and that their rapid decomposition results in polymer formation before they can be extracted from the reaction mixture.

o-Benzoquinones are, in general, a class of rather unstable compounds, but their stability increases with the degree of substitution in the ring and the size of the substituents. Thus 3,5-di-*t*-butyl-1,2-benzoquinone, the product of oxidizing 2,4,6-tri-*t*-butylphenol may be considered a relatively stable compound of its class.

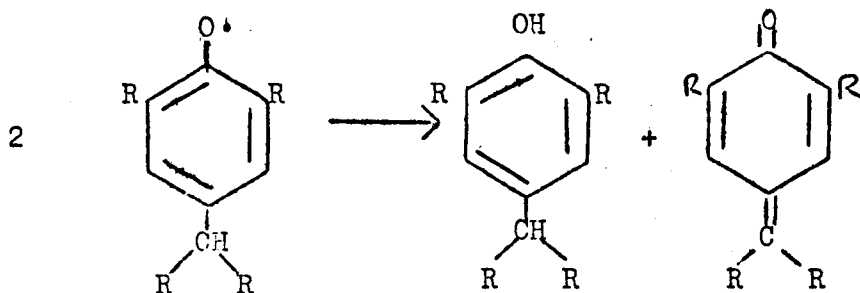
Nevertheless, under the hydrolytic conditions employed for decomposing the 2,4,6-tri-*t*-butylphenol-chromyl chloride complex, some of this quinone always polymerized, to give a red-brown tar with absorptions in the infrared at about 1650 cm^{-1} and between 1720 and 1750 cm^{-1} . Similar bands in the spectra of other polymerized o-benzoquinones have been reported²³⁹.

The formation of less stable o-benzoquinones would therefore result in more rapid polymer formation. If this is associated with radical coupling, it is understandable that resinous material is formed.

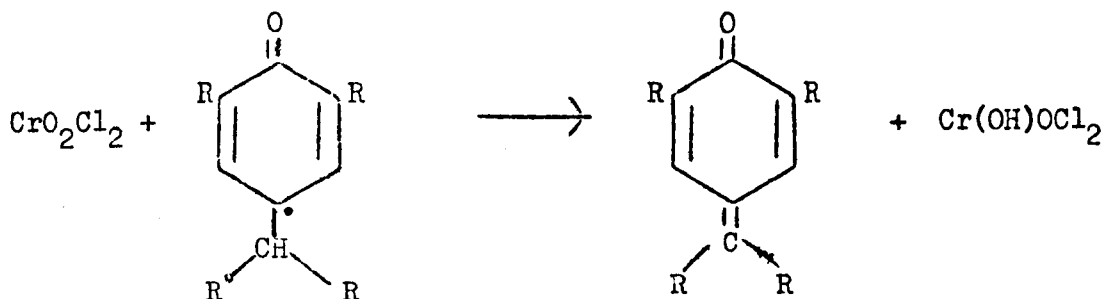
Coupling to give polymers may also occur under rather different conditions. It has been reported that dimerization, followed by further coupling occurs between phenols, phenols and quinones, and quinones themselves, under conditions of acid or base catalysis^{167,230}.

As the hydrolysis of the phenol-chromyl chloride complexes liberates hydrochloric acid as well as the organic oxidation products, such coupling may take place, especially as the hydrolysis is exothermic and high local temperatures may develop.

Where alkyl groups with α -hydrogen atoms are present on the phenol there is a third possible route for polymer formation. This route is via the formation of quinone methides, compounds which could be formed by radical disproportionation²⁰⁵, e.g.

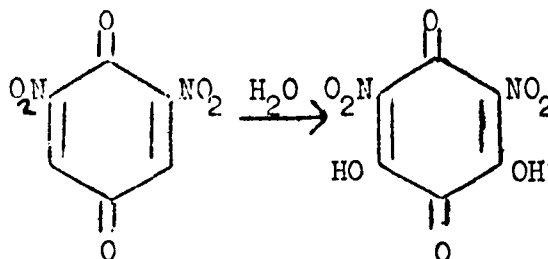


or by abstraction of hydrogen from the radical:



The polymerization of these intermediates is known to occur readily²⁴⁰.

The oxidation of the nitrophenols to resinous products probably occurs by a different reaction to those above. By comparison with the alkylphenols, oxidation would be expected to result in the formation of nitroquinones. These are known to be unstable and react readily with water especially in the presence of acids or bases, to give water soluble products, e.g. 2,6-dinitro-1,4-benzoquinone decomposes rapidly in water²⁴¹, to give nitranilic acid, as well as other products:



The formation of resinous and water soluble products on hydrolysis of the nitrophenol-chromyl chloride complexes is consistent with the formation of nitroquinones as unstable intermediates in the oxidations.

The situation with 2,6-dinitrophenol was rather different. Firstly a 1:1 complex was formed on reaction with chromyl chloride, and secondly, hydrolysis of the complex gave a good yield (ca. 70%) of the original phenol. The measurement of the magnetic susceptibility of the complex showed that the value of the effective magnetic moment was of the order obtained for the other complexes, indicating reduction of the chromium.

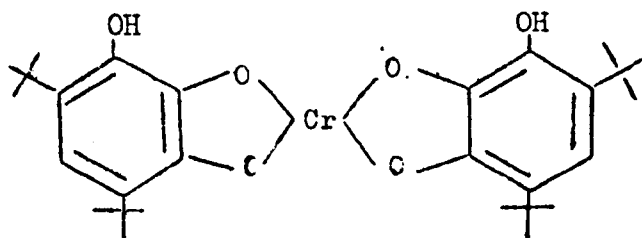
This is a parallel situation to that reported for nitrotoluenes. Despite a reduction of the chromium the apparent oxidation of the nitrotoluene only takes place to a small extent. No conclusive explanation has been offered to explain this.

Very few reports of the oxidation of nitrophenols have been made. The oxidation of 2,6-dinitrophenol by permanganate ion has been studied²⁴², and the reaction was said to be appreciably slower than that of phenol itself. This was ascribed to the presence of the two nitro groups. The mechanism of this oxidation has not been finally elucidated, though a radical intermediate has been suggested. No oxidation products have been isolated: due to extensive ring oxidation a complex mixture resulted²⁴².

The product obtained from the oxidation of 3,5-di-t-butylcatechol defied attempts to elucidate its structure. All attempts at crystallization failed and elemental analyses of the resinous products were not consistent with the formation of a single compound.

Mass spectral evidence showed that the resinous products contained components of high molecular weight. From a consideration of this and of the infrared spectrum of the compound it is suggested that it is a mixture of dimeric and trimeric forms of a catechol ester, contaminated with high molecular weight substances. A

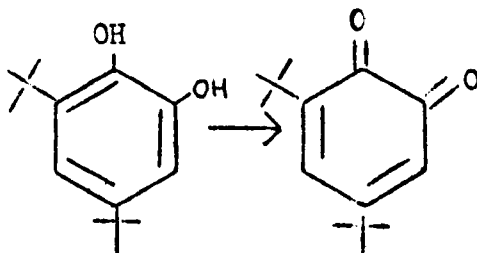
possible form of the dimeric component could be as follows:



The striking features of these products were their complete solubility in non polar solvents and their intense e.s.r. absorptions (see Fig 22).

Similar paramagnetic, red tars were obtained when 3,5-di-*t*-butyl-1,2-benzoquinone was shaken in a dry organic solvent with anhydrous chromic chloride. Traces of a similar material were also isolated on oxidation of 2,4,6-tri-*t*-butylphenol and 2,4-di-*t*-butylphenol by chromyl chloride. This suggests that the formation of this type of compound occurs after the initial formation of an o-benzoquinone, by a condensation reaction with the reduced chromium in solution.

It would thus seem probable that one of the primary products of oxidation of the disubstituted catechol is the o-benzoquinone:



9.B.6. The Nature of the Solid Products Derived from Chromyl Chloride and Chromyl Acetate Oxidations

9.B.6.1. Complexes derived from Reactions with Chromyl Chloride

The attempts to elucidate the nature of the Etard 'adducts', that is the complexes obtained by treating toluene or other hydrocarbons with chromyl chloride have been outlined in Chapter 4. Because of the nature of the problem it would appear that it is not one which will be rapidly solved.

The following facts have now been established:

- (1) The complexes tend to have an empirical composition approximating to $\text{ArH} \cdot 2\text{CrO}_2\text{Cl}_2$ but discrepancies from this general ratio have been frequently reported.
- (2) Despite their title, the complexes are not simple 'adducts'.
- (3) Magnetic measurements suggest that the valency of the chromium in the complexes is between (III) and (IV) and not (VI).
- (4) No organic solvent has yet been found which will dissolve the Etard adducts reversibly.
- (5) Hydrolysis of the 'adducts' releases products of hydrocarbon oxidation.

The properties of the complexes obtained by treating phenols with chromyl chloride show properties very similar to these hydrocarbon 'adducts'.

That the complexes are not simple addition compounds has been shown by a number of means.

Elemental analysis has shown that, in most cases, the complexes do not have a simple stoichiometry although in a few cases there is a tendency for the stoichiometry to approximate to 1:2 (phenol: chromyl chloride). It is significant that in many reactions,

this mole ratio of phenol to oxidant gave better yields of the quinone than other ratios.

There is no evidence in any of the elemental analyses for loss of chlorine, for example as hydrogen chloride; the ratio of chromium to chlorine in the complexes is always approximately 1:2 (see page 122).

Hartford and Darrin⁵ proposed a hydrogen bonded structure for the Etard 'adduct' formed from toluene. This is now not accepted as a possible structure for these complexes (see page 61).

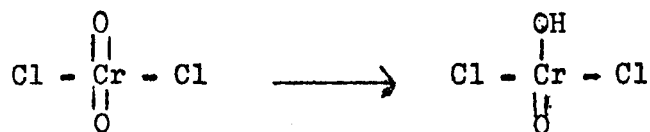
If such a structure did exist, or if the 'adducts' contained chromyl chloride coordinated in some way to a phenol, treatment with non-aqueous solvents might be expected to liberate the original phenol. No phenol is liberated in such reactions; the compound which is released is a *p*-benzoquinone.

This confirms the proposal that the phenol-chromyl chloride complexes contain reduced chromium species and products of phenol oxidation.

The exact nature of the complexes is still a matter for speculation. That different organic oxidation products result on hydrolysis suggests that the complexes are in fact mixtures. Gragerov and Ponomarchuk¹³¹ have suggested that Etard 'adducts' of toluene derivatives are not individual compounds.

The infrared spectra of the complexes are not always well defined. One feature common to all, is the presence of a broad band, which can be assigned to the O-H stretching frequency. Similar bands are observed in the spectra of hydrocarbon-chromyl chloride 'adducts'⁸⁸. The presence of such a band is consistent with the transfer of the hydrogen from a phenolic

oxygen of the chromyl chloride during the initial oxidation:



Most of the complexes show absorptions which can be assigned to oxidized forms of the organic reagent. The variations between the spectrum of the pure compound and the complex can be attributed to the effects of coordination. For example, absorptions assigned to carbonyl stretching occur at lower frequencies in the complexes. This may be correlated with the coordination of the oxygen to the chromium.

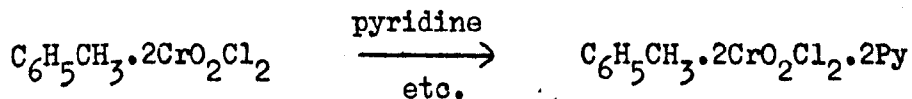
This leads to the conclusion that, as in the reaction of toluene with chromyl chloride, the formation of the complex occurs either after oxidation, or as an integral part of the oxidation process, by coordination of the oxygenated organic compound to reduced chromium species.

The complete insolubility of the complexes in non-polar solvents suggests that they are polymeric or ionic. Polymerization might occur by the formation of hydroxyl or chlorine bridges between the chromium atoms. The formation of such a complex has been described previously in this Chapter (see page 199 et seq.).

Examination of the solid complexes by mass spectrometry failed to show the existence of any simple species with molecular weight less than 800. Under conditions identical to those used to obtain the spectra of the organovanadates, no well-defined mass spectra could be obtained for any of the complexes. No parent peaks were evident.

The nature of the reaction of the complex derived from 2,5-di-*t*-butylphenol with the various donor solvents under anhydrous conditions tends to support the coordination theory. The displacement of the weakly coordinated *p*-benzoquinones by electron donating ligands such as pyridine or dioxan, which would be expected to occur, has been observed.

The new complexes which result from such reactions do not show a simple composition but this is not unexpected because the phenol complexes themselves do not have a simple stoichiometry. The presence of traces of *p*-benzoquinone found on hydrolysis of certain of these solvent-containing complexes shows that displacement by the donors is not complete. This could be explained by the formation of ternary complexes as reported by Stairs and Makhija¹¹⁷ with the toluene 'adduct':



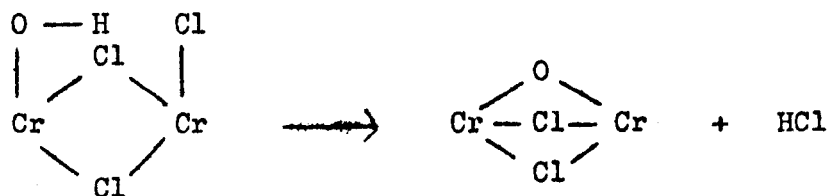
A similar situation with phenol complexes might occur, followed by displacement of the coordinated *p*-benzoquinone by the donor ligand. If the coordination theory is correct, the Etard toluene complex contains benzaldehyde coordinated to reduced chromium. Benzaldehyde would be expected to form more stable complexes, than a quinone, with a metal acceptor, and thus a displacement by the donor would be less easy.

Further evidence for coordination in the chromyl chloride-phenol complexes was obtained from the behaviour of the complex derived from 2,5-di-*t*-butylphenol, on being heated.

During mild pyrolysis both 2,5-di-*t*-butyl-1,4-benzoquinone and hydrogen chloride were liberated. The empirical formula of the residue, obtained after the release of the benzoquinone was approximately $C_9H_{16}Cl_3Cr_2O_6$.

A coordinated ligand such as a quinone might be expected to break away from the central metal atom under the influence of heat. It is apparent that the chromium-oxygen bond has been broken under these conditions.

The elimination could take place as follows:



A survey of the literature has shown that complexes of *p*-benzoquinones with metal acceptors, similar to those proposed above, have been reported. Thus, antimony pentachloride forms adducts with anthraquinone²⁵⁸ and 1,4-benzoquinone²⁵⁹. The latter complex is a red solid, unstable at room temperature.

An attempt thus was made to prepare similar complexes between substituted benzoquinones and anhydrous chromic chloride, in order to see if there was a similarity between these and the phenol-chromyl chloride complexes.

However, the lack of non-donor solvents in which both the metal chloride and quinone were soluble prevented this. Polar solvents e.g. acetone or ethanol tended to dissolve both the potential ligand and acceptor, but interaction between the solvent and chromic chloride always occurred rapidly.

A similar attempt was made with antimony pentachloride and substituted p-benzoquinones, using carbon tetrachloride as solvent. Complexes were prepared but they were very sensitive to moisture and rather unstable in dry air, although the compounds, formed from highly substituted benzoquinones, were more stable than the complex reported earlier²⁵⁹. Infrared spectra of these complexes were obtained; they showed shifts to lower frequency for the carbonyl C=O stretch, which were similar to those observed in the phenol-chromyl chloride complexes.

It is relevant to mention here that π -complexes containing alkyl-p-benzoquinones are well known; they possess much more stability than their σ -bonded equivalents. Bisduroquinone nickel (0) was one of the first to be prepared²⁴³. It is completely unaffected by air and even dilute non-oxidizing acids. Solubility in non-polar organic solvents is slight, but recrystallization may be effected from chloroform.

Considering these properties, it is most unlikely that the phenol-chromyl chloride complexes are π -complexes of benzoquinones and chromium (IV) or chromium (III).

9.B.6.2. Complexes derived from Reaction with Chromyl Acetate

Whilst the mechanism of the initial oxidation reaction is apparently identical for both chromyl chloride and chromyl acetate, the formation and nature of the solid complexes is different for each oxidant.

Analysis showed that, in each reaction with chromyl acetate, the solid complex obtained had an empirical formula $C_4H_8CrO_6$. The infrared spectrum and the magnetic properties of this compound suggest that a likely formulation is $(CH_3COO)_2Cr(OH)_2$. However, the

insolubility of the compound in organic solvents suggests that the complex is polymeric. As with the chromyl chloride complexes hydroxy, or acetate bridges could link the chromium atoms.

The formation and precipitation of this complex during the oxidation by chromyl acetate is readily explained in terms of a coordination complex.

In the oxidations by chromyl chloride, precipitation of a complex between chromium and the oxidized form of the phenol occurs. In an oxidation by chromyl acetate a similar situation occurs, but the weakly bonded ligand, the benzoquinone, is rapidly displaced by the more strongly coordinating acetate groups.

Similar forms of reduced oxidant have been reported in many oxidations by chromium (VI). Thus the oxidation of diphenylmethane by chromium (VI) oxide in glacial acetic acid yielded a greenish-brown solid whose analysis agreed fairly closely to that for a chromium (III) acetochromate $\text{Cr}(\text{HCrO}_4)(\text{OAc})_2$ ¹³⁵. The presence of chromium (VI) in this compound was shown by iodometric titration after hydrolysis. Thus, a mean figure for the oxidation state of chromium was obtained and it is conceivable that a chromium (IV) or (V) species may have been present.

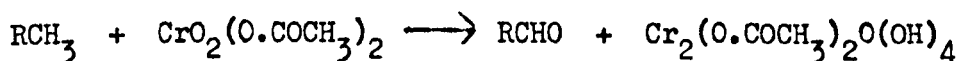
The oxidation of olefins by bistriphenylsilyl chromate, $[(\text{C}_6\text{H}_5)_3\text{SiO}]_2\text{CrO}_2$, results²⁴⁴ in the formation of carbonyl compounds, with precipitation of a green, inorganic solid. This has been shown²⁴⁴ to be a compound consisting of reduced silylchromate. The same reduced chromium compound is formed regardless of which olefin is oxidized.

Bartecki¹¹⁹ oxidized various hydrocarbons with chromyl acetate in carbon tetrachloride and found that each oxidation resulted in the precipitation of a green-brown solid. The infrared spectra of

these solids were independent of the hydrocarbon which had been oxidized.

A marked similarity between the spectra of reduced chromyl acetate as obtained by Bartecki and that obtained in the oxidation of phenols can be seen. However, Bartecki has proposed a formula $\text{Cr}_2(\text{CH}_3\text{COO})_2\text{O}(\text{OH})_4$ for his compound, the odd oxygen being a bridge between two chromium atoms. The actual elemental analysis of this compound showed quite large discrepancies from that required for the compound as formulated; in one case the chromium analysis differed by over five per cent.

It is interesting to note that, in the last two cases described above, more oxygen was found in the reduced oxidant than would be expected from a consideration of the reactants, e.g.



In the case of the reduced bisphenylsilylchromate, either air oxidation or oxidation by excess oxidant is assumed to have taken place²⁴⁴. Bartecki has offered no explanation of the anomaly apparent in his results.

Although no oxygen uptake was noted during the oxidation of phenols by chromyl acetate this may well have occurred. If this is the case, a free-radical mechanism for the process would again seem probable; this type of reaction has been proposed²⁴⁵ to explain the uptake of oxygen which takes place during the oxidation of alcohols by chromium (VI) oxide in glacial acetic acid.

It is now apparent, from these results, that future studies on this topic must consider fully the possibility of oxygen absorption.

9.B.7. The Reaction of Vanadium (V) Oxytrichloride and
Chromium (V) Oxytrichloride with Phenols

9.B.7.1 Vanadium (V) Oxytrichloride

Oxidations of organic compounds by vanadium (V) species in aqueous solution are well documented². Alcohols, glycols, hydroxyacids and hydroxyketones are amongst the compounds containing the OH group which have been studied in this respect. The oxidation of hydrocarbons has also been the subject of considerable research.

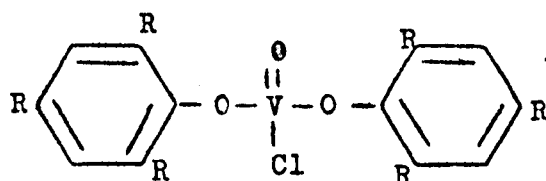
Phenols also are readily oxidized by aqueous vanadium (V) but the reactions are very rapid, and little is known about the kinetics or products of these oxidations, though one report has suggested that the oxidation of phenol in the presence of vanadium (V) catalysts may be a free radical process²⁴⁶. Similarly, a free radical mechanism has been proposed for the oxidation of phenols by vanadium (V) in the presence of light²⁴⁷.

Oxidations by vanadium compounds in organic solvents are limited by the small number of vanadium compounds of high oxidation state which are soluble in organic media.

Apart from vanadium (V) oxytrichloride, the only compounds which meet this requirement and have been the subject of recent study are vanadium (V) acetate², vanadium (IV) tetrachloride¹⁶¹ and t-butyl~~ortho~~vanadate (V)². Vanadium (V) acetate has been used in glacial acetic acid, whilst the other compounds may be used in non-polar solvents such as carbon tetrachloride. All these vanadium (V) compounds have been reported to be much less powerful oxidants than aqueous vanadium (V) species².

The reaction of vanadium (V) oxytrichloride, VOCl_3 , with organic compounds has not been thoroughly studied, though the oxidation of carboxylic acids²⁴⁸ and amines²⁴⁹ has been reported. These reactions were carried out in non-aqueous media: the oxychloride being very prone to hydrolysis.

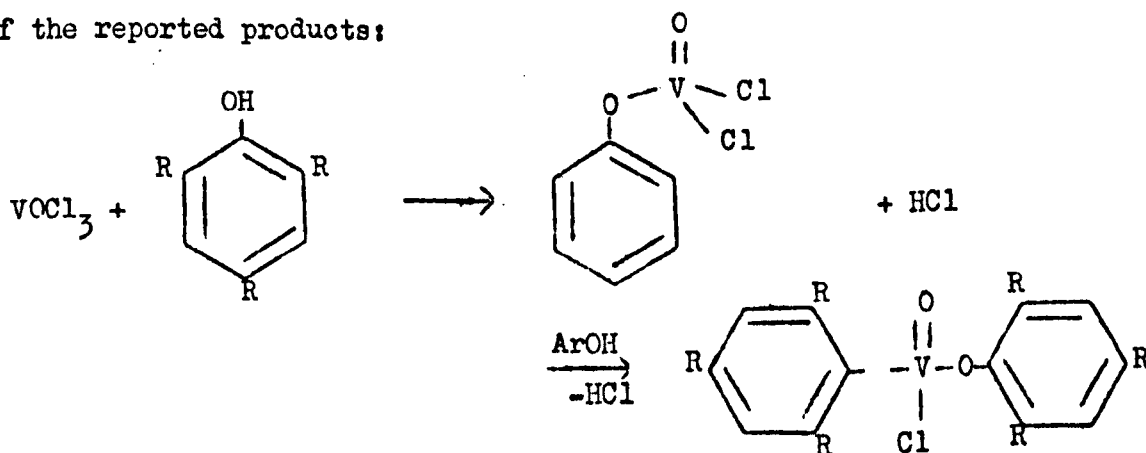
The results cited in Chapter 7 confirm that vanadium (V) oxytrichloride is not a powerful oxidant. The reaction of phenols having bulky alkyl groups results in the formation of diphenyl chlorovanadates (V), compounds of general structure:



As described previously (Chapter 7) these compounds are identical in nature to those prepared by Funk¹⁵³ et al but they differ considerably from those reported by Prasad and Upadhyaya¹⁵⁴ which were described as brown solids, relatively stable to hydrolysis and insoluble in organic solvents.

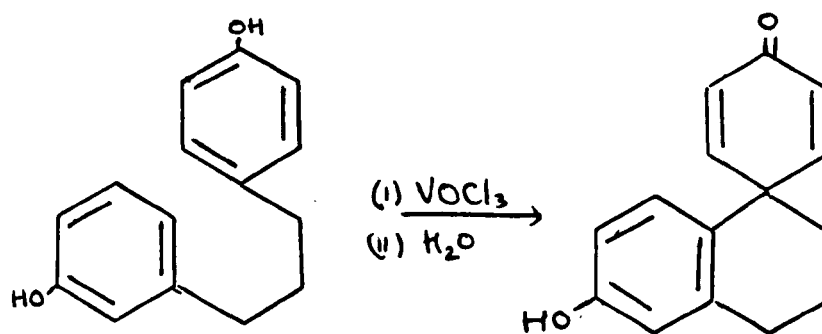
The compounds prepared by Funk and his co-workers and those prepared by the author are all deeply coloured compounds, readily soluble in organic solvents, and very susceptible to hydrolysis.

A simple two-stage process probably leads to the formation of the reported products:



A comparison may also be made to the work of Carrick, Karapinka and Kwiatowski¹⁶¹ who reported both substitution as above and intermolecular oxidative coupling to take place. They found that phenol itself reacted readily with vanadium oxytrichloride, but could be recovered completely on hydrolysis of the reaction mixture. Refluxing the reaction mixtures for extended periods of time only resulted in traces of diphenols being formed. However the reaction of vanadium oxytrichloride with the naphthols and the cresols resulted in larger amounts of coupled product being released on hydrolysis. This is parallel to the aforementioned work of Funk, Weiss and Zeising¹⁵³ who reported the rapid oxidation of cresols under these conditions, but the formation of stable vanadates with other phenols.

Similarly, it was reported that the oxidation of 1,3-bis(hydroxyphenyl)propane¹⁶² was a slow process below room temperature and only gave an appreciable yield of product after boiling the reaction mixture under reflux for a considerable time:



It is thus apparent that the oxidation potential of the phenols is an important factor, which has a great influence in determining the reaction pathway.

However sterically hindered and partially sterically hindered phenols often do not exhibit the properties suggested by their electrode potentials²⁵⁰ and an anomalous situation with

2,5-di-*t*-butylphenol, 2,4,6-tri-*t*-butylphenol and 2,6-di-*t*-butylphenol might thus be expected. This has been confirmed recently by a report²⁵¹ of the preparation of other stable arylchlorovanadates without oxidation taking place.

It is relevant to mention at this point that vanadium tetrachloride, VCl_4 , does oxidize phenol to *p,p'*-diphenol in 30 - 50% yield¹⁶¹. This coupled product may then react further with vanadium tetrachloride to give a black solid, presumably a chlorovanadium (IV) phenoxide. Hydrolysis of this solid liberates the diphenol quantitatively¹⁶¹.

The naphthols and all three cresols react readily with this reagent to give varying yields of coupled product together with resinous products. 2,4,6-trimethylphenol did not react with vanadium tetrachloride despite its low oxidation potential²⁵⁰, confirming the proposals above.

Oxidations similar to those above have been reported to occur with molybdenum (VI) oxychloride, MoOCl_4 ²⁵². This compound is a green solid which dissolves in carbon tetrachloride or chloroform to form red-brown solutions.

Direct oxidation of phenol by molybdenum (VI) oxychloride at high temperature resulted in the formation of a polyphenol resin and the para-coupled diphenol (19.6%). Similar reactions with o- and p-cresol gave only polymeric material²⁵².

Under more moderate conditions, in carbon tetrachloride solution, the oxidation of phenol¹⁶¹ gave a high yield of *p,p'*-diphenol as well as smaller amounts of chlorophenols and products of ortho-coupling. Polymeric substances were again a substantial part of the product (35%).

9.B.7.2. Chromium (V) Oxytrichloride

It was hoped that information as to the possible role of chromium (V) species, in chromyl chloride oxidations, would be obtained from the study of the interaction of chromium (V) oxytrichloride and phenols. As has been shown in Chapter 7, the position is still unclear: the instability of this oxychloride makes such a study an impractical one.

It is unfortunate that, whilst there are a variety of chromium (VI) compounds which may be used as oxidants, the number of chromium (V) compounds of comparable utility is very small indeed.

The so-called 'Weinland Salts', compounds of the type M_2CrOCl_5 (M = an alkali metal) could possibly be used in this context. Another chromium (V) compound which might be used as an oxidant is trichlorochromium (V) dibenzoate $Cl_3Cr(OCOC_6H_5)_2$ ¹⁷¹. Like chromium (V) oxytrichloride, the properties of this compound have not been well investigated - similar problems due to disproportionation may occur.

CHAPTER 10

EXPERIMENTAL SECTION

10.1. The Choice of Solvent for Reactions with Chromyl Compounds

The use and choice of solvents used in reactions involving chromyl chloride has been discussed in Chapter 3, section 2. The problems associated with the use of these solvents in the Etard reaction are similar to those apparent in this study of the oxidation of phenols.

Carbon tetrachloride and carbon disulphide appear to be the most suitable solvents for these oxidations but they suffer from the disadvantages outlined below.

10.1.1. Carbon Tetrachloride

When carbon tetrachloride is used as a solvent it is often impossible to remove all of the solvent from the phenol-chromyl chloride complexes; even prolonged treatment under high vacuum leaves appreciable amounts of solvent (up to 5% by weight) in the solid product. Thus the infrared spectra of many of these complexes show an absorption at about 800 cm^{-1} due to the C-Cl stretching frequency of carbon tetrachloride. In many cases, the solvent was found in the hydrolysis products of the complexes.

Similar difficulties to these have been reported for the 'adducts' formed from hydrocarbons and chromyl chloride; the solvent was believed to be occluded in the solid¹⁰⁰.

A consequence of this trapping of solvent is that the weight of the phenol-chromyl chloride complex does not afford a true measure of the percentage yield of complex. In most cases, analysis of the filtrate obtained on removal of the solid complex showed the absence of phenol or oxidized forms thereof, indicating that the complex contained all of the phenol in one form or another.

If this solvent trapping were not considered, the yield of certain complexes would appear to be greater than 100%. No consistent correction for this occluded solvent could be made, as elemental analyses of the various complexes failed to show a simple relationship between weight and composition of the complex and the weight of occluded solvent.

10.1.2. Carbon Disulphide

The disadvantage in the use of carbon disulphide is that it is not entirely inert; it reacts slowly with chromyl chloride under the conditions employed for the reactions of phenols.

Thus it was observed that when solutions of chromyl chloride in carbon disulphide were stored even for a comparatively short time, a small amount of precipitate formed. The absence of light did not prevent the formation of this precipitate.

To compare the reactivities of carbon disulphide and carbon tetrachloride towards chromyl chloride, reaction mixtures of comparable concentrations were heated under reflux: the carbon disulphide mixture showed an appreciable amount of solid formation after two hours, but no solid was precipitated in the solution of chromyl chloride in carbon tetrachloride after heating for ten hours.

Also no change in the infrared spectrum of this solution was observed over the ten hour period.

The reactivity of carbon disulphide towards chromyl chloride has been confirmed by other workers⁶.

Similar experiments, carried out with dichloromethane and chloroform showed that these solvents were not inert towards chromyl chloride.

The choice of solvent for the reaction of phenols with chromyl chloride was decided by the nature of the investigation. Where quantitative information relating to yields of products of hydrolysis of the complexes, carbon tetrachloride was used as the solvent.

Where solvent-free complexes were required, e.g. for magnetic susceptibility measurements, the reactions were carried out rapidly in carbon disulphide.

10.2 The Preparation and Purity of the Reagents

Wherever possible, commercially available reagents were used; in all cases compounds were further purified before use. Reagents not commercially available were prepared and purified by methods cited in the literature.

10.2.1. The Purification of Carbon Tetrachloride

Carbon tetrachloride ('Technical Grade') was fractionally distilled, twice, from phosphorus pentoxide.

The initial 10% of the distillate was rejected and the fraction, b.p. $76 - 77^{\circ}$ at atmospheric pressure, was collected as pure reagent²⁵⁶. The purity of the reagent was confirmed by examination of its absorption spectrum in both the infrared and ultraviolet regions.

10.2.2. The Purification of Carbon Disulphide

Carbon disulphide ('Technical Grade') was dried by standing it over calcium chloride. The solvent was then fractionally distilled from phosphorus pentoxide, in diffuse light²⁵⁶.

The initial 10% of the distillate was rejected and the fraction b.p. $46 - 46.5^{\circ}$, at atmospheric pressure, was collected as pure reagent.

The purity of the solvent was again confirmed by spectroscopic means.

10.2.3. The Purification of Acetone

'Analar' grade acetone was dried over anhydrous calcium sulphate and then stored over type 4A Linde molecular sieve.

10.2.4. The Purification of Acetonitrile

Acetonitrile was stirred with calcium hydride until no further hydrogen was evolved on addition of fresh desiccant. This treatment removed both water and acetic acid.

The reagent was then distilled from phosphorus pentoxide (0.5 - 1% w/v). The fraction b.p. $81 - 82^{\circ}$ at atmospheric pressure was collected.

10.2.5. The Purification of 1,4-Dioxan

'Analar' grade dioxan was dried by standing the reagent over sodium wire. It was further purified by distillation. The fraction b.p. $101 - 101.5^{\circ}$ at atmospheric pressure was used as pure reagent.

10.2.6. Purification of Diethyl Ether

'Analar' grade diethyl ether was dried over sodium wire, and then distilled. The fraction b.p. $34 - 35^{\circ}$ at atmospheric pressure was collected as pure reagent.

10.2.7. The Purification of Piperidine

Piperidine was stirred with calcium hydride until no further evolution of hydrogen was observed, and was then distilled. The fraction b.p. $115 - 116^{\circ}$ at atmospheric pressure was collected as pure reagent.

10.2.8. The Purification of Tetrahydrofuran

The tetrahydrofuran was stirred with calcium hydride until no further evolution of hydrogen was observed on addition of fresh desiccant.

The solvent was then distilled from sodium and the fraction b.p. $65 - 66^{\circ}$ at atmospheric pressure was collected as pure reagent.

10.3 Preparation and Purification of Metal Oxychlorides

10.3.1. Chromyl Chloride

Chromyl chloride was obtained from Hopkins and Williams Ltd.

The reagent was first purified by distillation at atmospheric pressure, the fraction b.p. $115 - 116^{\circ}$ being collected. Care was taken to ensure that all the apparatus was quite dry and further that all moisture was excluded during the distillation.

The reagent prepared in this way was further purified, immediately prior to use, by distillation under reduced pressure.

10.3.2. Chromium (V) Oxytrichloride

This compound was prepared by the method of Johannesen and Krauss¹⁷².

Boron trichloride (20 ml) and chromyl chloride (2 ml; approximate mole ratio 10:1) were mixed in a dry round-bottomed 250 ml flask at 0° . Care was taken to exclude moisture; the handling of the reagents was carried out in a dry glove-box.

The contents of the flask were then allowed to warm to the boiling point of boron trichloride ($+ 13^{\circ}$) and the mixture was allowed to boil under reflux for four hours, using a cold finger (-30°) to condense the reactants. Whilst this was being carried out, a slow stream of dry nitrogen was passed through the flask to remove chlorine.

The reaction mixture was then allowed to stand for twelve hours at 0° and was then distilled at 15° under high vacuum.

The chromium (V) oxytrichloride sublimed under these conditions and was collected on the cold finger as a black crystalline solid (1.7 g, 40% based on chromyl chloride).

Found: Cr, 31.0; calculated for CrOCl_3 : Cr, 29.9%.

10.3.3. Chromyl Acetate

Chromyl acetate was prepared by the method of Krauss²⁷.

'Analar' chromium trioxide (5.0 g, 0.05 mole) was mixed with acetic anhydride (2.0 g, 0.02 mole) in carbon tetrachloride (20 ml). Care was taken to exclude moisture by handling the reagents in a dry glove-box.

The mixture was then shaken mechanically for five hours, at room temperature in a sealed flask. The reaction vessel was wrapped in metal foil to exclude light.

The mixture was then filtered under dry nitrogen using a covered filter as illustrated in Fig. 23.

The solution of chromyl acetate thus prepared was used directly for the oxidation of phenols.

The electronic absorption spectra of this solution was identical to that recorded by Krauss (maxima at 283 nm and 400 nm)²⁷.

10.3.4. Vanadium (V) Oxytrichloride

Vanadium (V) oxytrichloride (99%) was obtained from Koch-Light Laboratories Ltd. The reagent was purified by distillation at room temperature under reduced pressure.

(Found: Cl, 61.0%. Calculated for VOCl_3 : Cl, 61.6%).

10.4 Preparation and Purification of Phenols

The majority of the phenols were commercially available and were used after purification.

Phenols not commercially available were prepared by methods cited in the literature.

Purification of all these reagents was by recrystallization to constant melting point (for solid phenols) or by fractional distillation (for liquid phenols).

The experimental details of these processes are summarized in Table 65.

10.4.1. The Preparation of 3,5-Di-t-butylcatechol

This compound was prepared by the method of Schulze and Flaig²⁵⁷.

Concentrated sulphuric acid (10 ml) was added to a solution of catechol (22 g, 0.2 mole) in t-butanol (25 ml, approx. 0.5 mole) with constant stirring. Care was taken to ensure that the temperature of the reaction mixture did not rise above 20° during this addition.

When the addition of the acid was complete, the mixture was allowed to stand for twenty-four hours, during which time the mixture solidified.

This solid product was then added to a large excess of ice/water. The crude 3,5-di-t-butylcatechol was collected by filtration, washed with cold water and dried under reduced pressure. The yield of crude product was 92%.

After recrystallization from benzene-petroleum ether (b.p. 60 - 80°) the pure catechol was collected as white feathery needles, m.p. 99° (Lit. 99°)²⁵⁷. Found: C, 75.6; H, 10.0%. Calculated for C₁₄H₂₂O₂: C, 74.7; H, 9.9%.

10.4.2. Preparation of 4,6-Di-t-butylpyrogallol

4,6-Di-t-butylpyrogallol was prepared by the method of Schulze and Flaig²⁵⁷.

TABLE 65

The Purification of Phenols

| Phenol | Recrystallization Solvent | M.P. (°C) | Lit. M.P. (°C) | Ref. |
|------------------------------------|-----------------------------|--------------|----------------------|------|
| Phenol | Petroleum ether (below 40°) | 41- 42 | 43 | a |
| 2,5-Dimethylphenol | Ethanol-ether | 75 | 75 | a |
| 2,6-Dimethylphenol | Ethanol-ether | 49 | 49 | a |
| 2,6-Dimethoxyphenol | Aq. ethanol | 56 | 55- 56 | a |
| 3,5-Dimethylphenol | n-Hexane | 68 | 68 | |
| 3-t-Butylphenol | n-Hexane | 40 | 41 | a |
| 4-t-Butylphenol | Petroleum ether (60-80°) | 98 | 99 | b |
| 2,4-Di-t-butylphenol | Petroleum ether (60-80°) | 56- 57 | 57 | b |
| 2,5-Di-t-butylphenol | Petroleum ether (60-80°) | 121 | 120- 121 | c |
| 2,6-Di-t-butylphenol | n-Hexane | 37- 38 | 39 | b |
| 2,6-Di-t-butyl-4-methyl- phenol | Aq. Ethanol | 70 | 70 | b |
| 2,4,6-Tri-t-butylphenol | Aq. Ethanol | 131 | 131 | b |
| 3,5-Di-t-butylcatechol | See Chapter 10.4.1. | | | |
| 3,5-Di-t-butylpyrogallol | See Chapter 10.4.2. | | | |
| 1-Naphthol | Aq. methanol (charcoal) | 94 | 94 | a |
| 2-Naphthol | Aq. methanol (charcoal) | 122 | 123 | a |
| 2-Nitrophenol | Aq. ethanol | 43- 44 | 44.9 | a |
| 3-Nitrophenol | Chloroform | 96 | 97 | a |
| 4-Nitrophenol | Chloroform | 113- 114 | 114 | a |
| 2,6-Dinitrophenol | Benzene-petrol (60-80°) | 63- 64 | 63- 64 | a |
| 2,3,5-Trimethylphenol | Aq. ethanol | 94- 95 | 95- 96 | a |

(a) Dictionary of Organic Compounds, Eyre and Spottiswoode, (1965).

(b) R. Stroh, R. Seydel and W. Hahn, Angew. Chem., **69**, 699 (1957).

(c) H. Hart and W.G. Vosburgh, J. Amer. Chem. Soc., **73**, 4983 (1951).

TABLE 65 continued

| Phenol | Recrystallization Solvent | M.P. (°C) | Lit. M.P. | Ref. |
|---------------------------|---------------------------|-----------|-----------|------|
| 2,3,6-Trimethylphenol | Aq. ethanol | 62 | 62 | d |
| 2,4,6-Trimethylphenol | Aq. ethanol | 69 | 69 | a |
| 2,3,5,6-Tetramethylphenol | Aq. ethanol | 117 | 118-119 | a |

| Phenol | Boiling Point (°C) | Lit. B.P. (°C) | Ref. |
|------------------------|--------------------|-----------------|------|
| 2,6-Di-isopropylphenol | 138 - 142 (50 mm) | 149 (50 mm) | b |
| 2,5-Di-isopropylphenol | 110 - 118 (5 mm) | 110-115 (5 mm) | e |
| 2,6-Di-sec-butylphenol | 166 - 168 (52 mm) | 169 (50 mm) | b |
| 2-Methylphenol | 107 - 109 (50 mm) | 110 (50 mm) | a |
| 2-t-Butylphenol | 125 - 128 (50 mm) | 136-137 (50 mm) | b |

(a) 'Dictionary of Organic Compounds', Eyre and Spottiswoode, (1965).

(b) R. Stroh, R. Seydel and W. Hahn, Angew. Chem., **69**, 699 (1957).

(d) G.T. Morgan and A.E.J. Pettel, J. Chem. Soc., 418 (1934).

(e) C.L. Mogle and E.M. Van Duzee, U.S. Patent, 2,207,753 (1934).

TABLE 66

Identification of Quinones and other Oxidation Products

| | Compound | M.P. (°C) | Other Details | Lit. M.P. (°C) | Reference |
|-----|--------------------------------------|--------------|--------------------------------|----------------------|--|
| (a) | 1,4-Benzoquinone | 112 | Recrystallized from chloroform | 111-113 | <u>Org. Synth.</u> , XVI, 73 (1936) |
| (b) | 2-Methyl-1,4-benzoquinone | 68 | Purified by vacuum sublimation | 69 | Z. Schniter, <u>Ber.</u> , <u>20</u> , 2283 (1887) |
| (c) | 2,5-Dimethyl-1,4-benzoquinone | 125 | " " " " | 125 | Ref.. 204 |
| (d) | 2,6-Dimethyl-1,4-benzoquinone | 75 | " " " " | 73-75 | L.I. Smith, J.W. Opie, S. Wawzonek, and W.W. Pritchard, <u>J.Org.Chem.</u> , <u>4</u> , 318 (1939) |
| (e) | 2,3,5-Trimethyl-1,4-benzoquinone | 27 | " " " " | 29 | L.I. Smith, <u>E.Amer.Chem.Soc.</u> , <u>56</u> , 472 (1934) |
| (f) | 2,3,5,6-Tetramethyl-1,4-benzoquinone | 108-109 | " " " " | 110-111 | See ref. (d) |
| (g) | 2-t-Butyl-1,4-benzoquinone | 68 | " " " " | 68 | W.K.T. Gleim and A. Graydasch, U.S. Patent, 257-3136 (1953) |

TABLE 66 continued

| | Compound | M.P. (°C) | Other Details | Lit. M.P. (°C) | Reference |
|-----|--|--------------|--|----------------------|---|
| (h) | 2,5-Di-t-butyl-1,4-benzoquinone | 153-154 | Purified by vacuum sublimation or recrystallized from ethanol (aq) | 153 | W.A. Waters and F.J. Lopez Aparicio <u>J.Chem.Soc.</u> , 4666 (1952) |
| (i) | 2,6-Di-t-butyl-1,4-benzoquinone | 68 | " " " | 68 | A.F. Bickel and E.C. Kocyman <u>J.Chem.Soc.</u> , 3211 (1953) |
| (j) | 2,6-Dimethoxy-1,4-benzoquinone | 255 | Recrystallized from chloroform | 252-256 | H. Richtzenhain, <u>Ber.</u> , 77, 409 (1944) |
| (k) | 2,6-Di-isopropyl-1,4-benzoquinone | - | B.P. 130-130° (4-6 mm) Lit. 92° (2 mm) | - | British Patent, 783,042 (1957) |
| (l) | 1,4-Naphthoquinone | 124 | Recrystallized from 60-80 petrol | 125 | <u>Org.Synth.</u> XVII, 68 (1937) |
| (m) | 3,5-di-t-butyl-1,2-benzoquinone | 109-111 | Recrystallized from carbon tetrachloride | 112 | E. Muller, K. Ley, <u>Chem.Ber.</u> , 89, 1402 (1956) |
| (n) | 3,5-Di-t-butyl-1,4-hydroxy-benzaldehyde | 189 | Recrystallized from ethanol | 189 | T.W. Campbell & G.M. Coppinger <u>J.Amer.Chem.Soc.</u> , 74, 1469, (1952) |
| (o) | 3,3',5,5'-Tetramethyldiphen-quinone | 210 | Recrystallized from ethanol | 210-215 | R.F. Moore and W.A. Waters <u>J. Chem. Soc.</u> , 243 (1954) |
| (p) | 3,3',5,5'-Tetraisopropyldiphen-quinone | 197-198 | Recrystallized from chloroform | 196-198 | Ref. 232(a) |
| (q) | 3,3',5,5'-Tetra-t-butyldiphen-quinone | 245-246 | Recrystallized from MeOH/CHCl ₃ | 245 | Ref. 232(a) |
| (r) | 3,3',5,5'-Tetra-sec-butyldi-phen-quinone | 199-200 | " " " | 201.5 | R. Stroh, R. Seydel and W. Hahn, <u>Angew. Chem.</u> , 69, 669 (1957) |

Satisfactory n.m.r. and mass spectral data were obtained for all the compounds.

Their infrared spectra are listed in Tables 39 - 58.

TABLE 66 continued

| Compound | Found | | | | |
|-----------------------------------|-------|-----|---------------------------------------|------|-----|
| | C% | H% | | C% | H% |
| 2,5-Di-isopropyl-1,4-benzoquinone | 74.6 | 8.7 | Calculated for $C_{12}H_{16}O_2$: | 75.0 | 8.6 |
| 2,6-Di-sec-butyl-1,4-benzoquinone | 76.2 | 9.2 | Calculated for $C_{14}H_{20}O_2$: | 76.3 | 9.1 |

Pyrogallol (75.6 g, 0.6 mole), t-butanol (150 ml) and glacial acetic acid (150 ml) were mixed together and then cooled to 0°. Concentrated sulphuric acid (30 ml) was added dropwise with constant stirring. Care was taken to ensure that the temperature did not rise above 25° during this addition.

After thirty hours, when the mixture had solidified, an ice-water mixture (200 ml) was added to it; after stirring, the crude product was collected by filtration, washed with cold water and dried under reduced pressure. The yield of crude product was 89%.

Recrystallization from petroleum ether (b.p. range 40 - 60°) gave pure 4,6-di-t-butylpyrogallol, m.p. 121°. (Lit¹²²)²⁵⁷ Found: C, 70.5; H, 9.4%. Calculated for $C_{14}H_{22}O_3$: C, 70.6; H, 9.2%.

10.5 The Preparation and Handling of the Phenol-Chromyl Chloride Complexes

10.5.1. Special Precautions

The phenol-chromyl chloride complexes were all found to be extremely reactive towards water. All apparatus used in the preparation and subsequent handling of the phenol-chromyl chloride complexes was carefully dried before use and all product transference was carried out in a glove-box maintained in a dry condition by trays of phosphorus pentoxide.

10.5.2. The Apparatus

The reactions between phenols and chromyl chloride were carried out in round bottomed, three-necked flasks fitted with an external stirrer. Both the flask, and funnels, used for introducing reagents into it, were protected from moisture by drying tubes containing phosphorus pentoxide or calcium chloride.

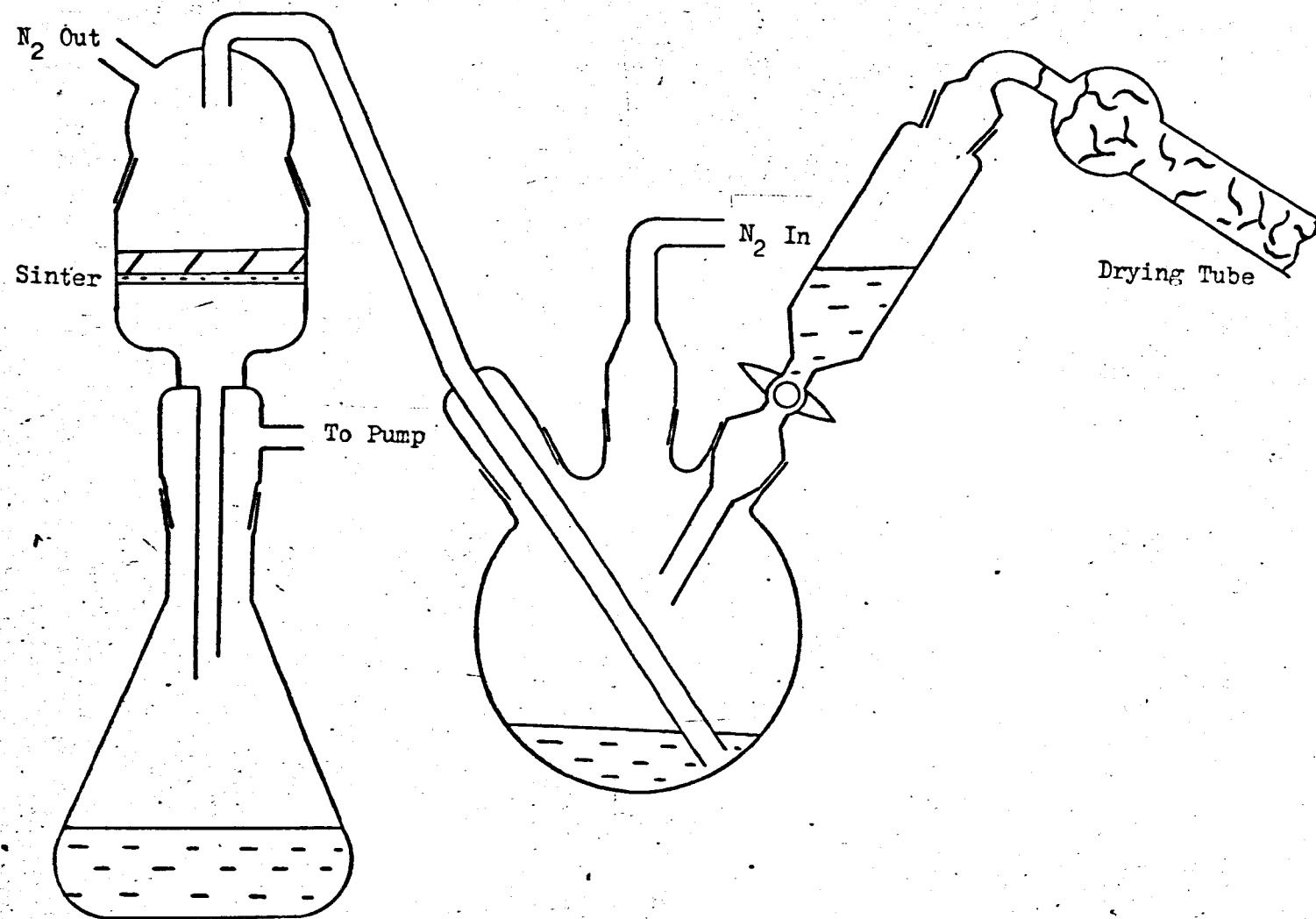


Fig.23. The Apparatus used to filter the Complexes.

The reaction mixture was filtered in each case under dry air or nitrogen by means of the covered sintered funnel illustrated in Fig 23. The mixture was transferred directly from the reaction vessel to the funnel through a polythene tube.

After filtration and subsequent washing of the complex, excess solvent was removed without removing the complex from the funnel.

Typical procedures are described below for the reaction of phenols with chromyl chloride. With the exception of the nitrophenols, all the reactions were conducted in a similar manner and on a similar scale.

If the order of addition was reversed, i.e. if the oxidant was added to the solution of phenol, and providing the mole ratio of reactants was kept constant, complexes with similar elemental analyses resulted. In all reactions where the oxidant was added to the phenol, a transient blue colour was observed.

10.5.3. The Reaction of Chromyl Chloride with Phenol

A solution of phenol (4.94 g, 0.053 mole) in dry carbon tetrachloride (175 ml) was added dropwise, with stirring, to a solution of chromyl chloride (24.6 g, 0.159 mole) in the same solvent (100 ml) contained in a three necked flask fitted with a mechanical stirrer and a calcium chloride drying tube.

The addition of reagent was carried out over two hours; the slow addition of the reagent, and the application of external cooling ensured that the reaction temperature did not rise higher than 30°.

The mixing of the reagents resulted in the rapid formation of a brown precipitate.

After addition was complete, the mixture was stirred for a further three hours. The brown complex was then collected by filtration under dry air, washed with dry solvent (4 x 50 ml portions) and the excess solvent was then removed under reduced pressure (0.1 mm of mercury).

The yield of the complex, a chocolate-brown amorphous solid, was 16.0 g.

Analysis of the filtrate showed the presence of unreacted chromyl chloride and the absence of organic material.

10.5.4. The Reaction of Chromyl Chloride with 2-Methylphenol

A solution of 2-methylphenol (2.16 g, 0.02 mole) was added, dropwise and with stirring, to a solution of chromyl chloride (6.2 g, 0.04 mole) also in carbon tetrachloride (100 ml) over a period of two hours.

The solution rapidly assumed a deep brown colour as the reagents were mixed and precipitation of a brown solid was observed. The mixture was stirred for four hours after the final addition of reagent and was then filtered under dry air, yielding a brown solid. The complex was washed with carbon tetrachloride (3 x 50 ml) and then excess solvent was removed under reduced pressure (0.1 mm of mercury). The yield of the dark brown complex was 8.25 g.

10.5.5. The Reaction of Chromyl Chloride with 2,5-Di-*t*-butylphenol

A solution of chromyl chloride (8.66 g, 0.056 mole) in carbon tetrachloride (100 ml) was added dropwise and with stirring to a solution of 2,5-di-*t*-butylphenol (5.65 g, 0.028 mole) in the same solvent (120 ml) over a period of one hour. External cooling was applied to prevent the temperature of the reaction mixture rising above 30°.

Immediately the first portion of oxidant was added to the phenol solution, a deep blue colour was observed. Continued addition of chromyl chloride led to the dissipation of the colouration and the formation of a light-brown precipitate. After the final addition of reagent, the mixture was stirred for a further two hours.

The precipitate was isolated by filtration under dry air, washed with dry carbon tetrachloride (4 x 50 ml) and the excess solvent removed under reduced pressure (0.1 mm of mercury).

The yield of the complex was 15.55 g which is in excess of the combined weights of the reactants, indicating the presence of carbon tetrachloride in the complex.

Analysis of the filtrate showed the presence of both a trace of chromyl chloride and trace of 2,5-di-t-butyl-1,4-benzoquinone.

10.5.6. The Reaction of Chromyl Chloride with 3,5-di-t-butylphenol

3,5-Di-t-butylphenol (2.53 g, 0.0123 mole) in dry carbon disulphide (75 ml) (see this Chapter, section 1.2.) was added rapidly with vigorous stirring to a solution of chromyl chloride (3.80 g, 0.0246 mole) also in carbon disulphide (120 ml). The reaction vessel was cooled with an ice-water mixture to moderate the ensuing exothermic reaction.

After complete mixing of the reactants, during which a brown solid was precipitated, the mixture was stirred for a further ten minutes and then filtered under dry air. The collected solid was washed thoroughly with carbon disulphide and then dried under reduced pressure (0.1 mm of mercury) for ten hours. The yield of the dry complex was 5.82 g.

10.5.7. The Reaction of Chromyl Chloride with 2,6-Di-t-butylphenol

2,6-Di-t-butylphenol (2.79 g, 0.0135 mole) in carbon disulphide (75 ml) (see this Chapter, section 1.2.) was added rapidly and with vigorous stirring to a solution of chromyl chloride (4.20 g, 0.027 mole) in carbon disulphide (100 ml). The reaction mixture was stirred vigorously for fifteen minutes after the addition had been completed. External cooling was applied to moderate the exothermic reaction. The mixture was then filtered under dry air, to yield a light brown solid. This solid was washed thoroughly with dry solvent and then excess solvent was removed under reduced pressure (0.1 mm of mercury) for six hours.

The yield of the complex was 6.40 g.

10.5.8. The Reaction of Chromyl Chloride with 2,6-Dinitrophenol

(a) A solution of chromyl chloride (1.70 g, 0.011 mole) in carbon tetrachloride (25 ml) was added directly to a solution of 2,6-dinitrophenol (1.00 g, 0.0055 mole) in the same solvent (30 ml). No reaction was observed to take place.

The mixture was allowed to stand for twenty-four hours in the dark, at room temperature, but no precipitate formation occurred. The infrared spectrum of the mixture showed only bands due to the phenol and chromyl chloride.

(b) A solution of chromyl chloride (8.0 g, 0.052 mole) and 2,6-dinitrophenol (1.75 g, 0.0095 mole) in carbon tetrachloride (150 ml) was boiled under reflux for thirty-six hours.

On filtration of the mixture, a brown solid was collected. The bright red colour of the filtrate indicated the presence of unreacted oxidant.

After washing with carbon tetrachloride (50 ml) the solid was dried under reduced pressure (0.1 mm of mercury) to yield a chocolate-brown, finely powdered complex, 2.82 g.

10.6 The Oxidations with Chromyl Acetate

Oxidations were conducted in a similar manner to those by chromyl chloride (see this Chapter, section 5.2.).

The solution of chromyl acetate (Chapter 10, section 3.3.) was filtered directly into the reaction vessel and the phenol was then added to the oxidation.

A typical reaction is outlined below.

10.6.1. The Oxidation of 2,3,5,6-tetramethylphenol by Chromyl Acetate

A solution of 2,3,5,6-tetramethylphenol (1.5 g, 0.01 mole) in carbon tetrachloride (40 ml) was added dropwise and with constant stirring to a solution of chromyl acetate in carbon tetrachloride. The solution contained 0.02 mole of oxidant and was prepared as described in section 3.3. of this Chapter.

The exothermic reaction resulted in the rapid formation of a green-brown precipitate.

When the addition was complete, the mixture was stirred for four hours and then filtered to remove the precipitated solid. This solid was then washed with solvent (3 x 30 ml) and the excess solvent was removed under reduced pressure, to give a green-brown, powdery solid (4.12 g).

The filtrate was found to contain, after evaporation of the solvent, mainly 2,3,5,6-tetramethyl-1,4-benzoquinone (1.30 g, 82% yield based on the original phenol). The quinone was recrystallized (60 - 80 petrol) and collected as yellow needles m.p. 110° (Lit. m.p. 111°)²⁵⁵.

10.7. The Reactions of Vanadium (V) Oxytrichloride with Phenols

These reactions were conducted in a manner very similar to that used for oxidations by chromyl chloride. A typical reaction is described below.

10.7.1. The Reaction of Vanadium (V) Oxytrichloride with 2,5-Di-t-butylphenol

2,5-Di-t-butylphenol (3.7 g, 0.018 mole) in carbon tetrachloride (20 ml) was added dropwise and with stirring to a solution of vanadium oxytrichloride (6.2 g, 0.036 mole) in the same solvent (100 ml).

The immediate formation of a deep violet solution was followed by rapid evolution of hydrogen chloride.

After the final addition of phenol, the solution was stirred for two hours by which time no more hydrogen chloride was being evolved.

The solution was filtered under dry air but no precipitate was apparent.

Concentration of the solution yielded a black-purple solid, bis (2,5-di-t-butylphenyl)chlorovanadate (V). Found: Cl, 7.5; V, 9.3%; calculated for $C_{28}H_{42}ClO_3V$: Cl, 6.93; V, 9.95% (see Chapter 7, section 1).

Hydrolysis of either the solid, or the reaction solution with water or dilute acid, followed by extraction with ether yielded only the original phenol.

10.8. The Reaction of the Chromyl Chloride-Phenol Complexes with Water

The method adopted for the hydrolysis of the complexes was to add a known weight of the complex slowly, with vigorous stirring, to a large excess of an ice-water mixture.

The organic products were then extracted from the hydrolysis mixture with various solvents, e.g. ether, chloroform or petroleum ether, followed by the removal of the solvent under reduced pressure, or fractional crystallization.

Some products, for example the di-*t*-butylbenzoquinones and the diphenoquinones precipitated out from the hydrolysis mixture and were separated by filtration.

The oxidation products collected by these methods were often quite impure and purification was effected by recrystallization or vacuum sublimation. The latter method was especially successful in the purification of the lower molecular weight 1,4-benzoquinones.

Where mixtures of discrete compounds resulted, e.g. 1,4-benzoquinones and the corresponding diphenoquinones, separation was achieved by column chromatography on silica or neutral alumina, using petroleum ether or dichloromethane/petroleum ether (5% v/v solution) as eluant.

In all cases the identification of the oxidation products was effected by the comparison of their melting points and infrared spectra with those cited in the literature or with those of authentic samples. Where the latter were available, mixed-melting point determinations were carried out. In addition molecular weights of the products were confirmed by mass spectrometry and additional data for identification purposes was obtained from nuclear magnetic resonance spectroscopy.

Further characterization was achieved by reducing the *p*-benzoquinones to the quinols which were identified by the methods outlined above. The details of the methods used to identify and characterize the oxidation products are shown in Table 66.

Typical examples of extraction procedures used to isolate the oxidation products are described below.

10.8.1. The Reaction of the 2-Methylphenol-Chromyl Chloride Complex with Water

The complex (5 g) derived from the reaction of chromyl chloride with 2-methylphenol was dissolved in a vigorously stirred ice-water mixture (50 ml). The complex dissolved rapidly and the temperature of the hydrolysis mixture was observed to rise.

When all the complex had dissolved, the brown solution was stirred for one hour, and then filtered. However no solid material was separated by this means, and the solution was extracted with petroleum ether (2 x 50 ml, 40 - 60° petrol).

Evaporation of the petrol (after drying the solution over anhydrous sodium sulphate overnight) yielded only a trace of 2-methyl-1,4-benzoquinone (identified by infrared spectroscopy).

Further extraction of the aqueous solution with diethyl ether (3 x 50 ml) yielded, on evaporation, (after predrying with anhydrous sodium sulphate) a red-brown tarry solid (1.2 g) which failed to crystallize.

Column chromatography carried out with a proportion of this resinous material (using silica and 1:1 dichloromethane/petroleum ether) again yielded only a trace of the quinone; the majority of the material adhered firmly to the top of the column and defied elution with more polar solvents.

The remainder of the resinous material was heated (at 100°) under reduced pressure (1 mm of mercury) in a vacuum sublimation apparatus and pure 2-methyl-1,4-benzoquinone was obtained (0.05 g, approximately 1% yield based on the original phenol).

10.8.2. The Reaction of the 2,5-Di-t-butylphenol-Chromyl Chloride Complex with Water

The complex (14.1 g; see this Chapter, section 5.5.) was added in batches (about 3 g) to a vigorously stirred ice-water mixture (100 ml). When all the complex had been added, the mixture was stirred for one hour and then allowed to stand for a further hour. A yellow-brown precipitate was observed, the supernatant liquid being a deep green.

Filtration of the mixture yielded the yellow brown solid, crude 2,5-di-t-butyl-1,4-benzoquinone (83%, based on the original phenol) identified by infrared spectroscopy. Recrystallization from ethanol (aqueous) gave a reduced yield of the pure quinone.

Extraction of the filtrate with diethyl ether yielded only a trace of 2,5-di-t-butyl-1,4-benzoquinone as well as carbon tetrachloride.

10.8.3. Reaction of 1-Naphthol-Chromyl Chloride Complex with Water

The complex (7.3 g) was added in batches (about 2 g) to a vigorously stirred ice-water mixture (75 ml). Stirring was continued for two hours after the complete addition of the complex. Filtration of the mixture gave a brown solid, the infrared spectrum of which showed the presence of 1,4-naphthoquinone.

Continuous extraction of this solid (with n-pentane) in a Soxhlet apparatus gave pure 1,4-naphthoquinone (0.7 g, 25.3% yield based on the original naphthol).

Analysis of the residual tarry material suggested that it was polymeric in nature.

Extraction of the filtrate with diethylether gave a small quantity (0.12 g) of resinous solid, from which no discrete compounds could be isolated.

10.9. The Reductive Hydrolysis of the Phenol-Chromyl Chloride Complexes

The reductive hydrolyses of the complexes were all carried out in a similar manner. The method used is illustrated by the example outlined below.

10.9.1. The Reductive Hydrolysis of the 2,3,5,6-Tetramethylphenol-Chromyl Chloride Complex

2,3,5,6-Tetramethylphenol (1.92 g, 0.0128 mole) in carbon tetrachloride (200 ml) was added rapidly, with vigorous stirring to chromyl chloride (4 g, 0.0256 mole) in the same solvent (100 ml). The reaction vessel was cooled externally with an ice-water mixture. When the addition of reagent was complete (after five minutes) the resulting deep brown mixture was stirred vigorously for a further ten minutes.

Powdered zinc (15 g, 'Analar' grade) was then added in small portions over a period of five minutes. Water (20 ml) was then added (4 x 5 ml) over a period of a further five minutes. The vigorous stirring was continued for a further fifteen minutes; care was taken to ensure the mixture did not overheat as the hydrolysis was strongly exothermic.

The resulting yellow-green solution was then rapidly filtered at the pump to remove excess zinc and the carbon tetrachloride layer (a deep yellow colour) was separated and dried over anhydrous sodium sulphate. Further extraction with carbon tetrachloride (4 x 25 ml) yielded less-yellow solutions, the final extract being almost colourless.

The combined dried extracts were evaporated under reduced pressure to yield yellow plates (1.10 g) of 2,3,5,6-tetramethyl-1,4-benzoquinone.

Ether extraction of the aqueous phase gave a further small amount of the quinone (0.30 g). The total yield of quinone based on the original phenol was 68%.

10.10. Instrumentation and Analytical Techniques

10.10.1. Infrared Spectroscopy

Infrared spectra were run on either a Unicam S.P.200 or a Perkin-Elmer 457 grating infrared spectrometer.

Spectra were obtained using Nujol mulls (between sodium chloride, potassium bromide or polythene plates) or using solutions in carbon tetrachloride or carbon disulphide (with sodium chloride or potassium bromide cells).

10.10.2. Nuclear Magnetic Resonance Spectroscopy

N.m.r. spectra were obtained using a Perkin Elmer R.10 spectrometer which operated at 60 MHz. Solutions for analysis by this method were made up in carbon tetrachloride or deuteriochloroform solution. Tetramethylsilane was used as an internal standard in most cases, but as an external standard in the study of the phenylvanadates.

10.10.3. Mass Spectrometry

Mass spectra were obtained using an A.E.I. MS.2 instrument, operating at 70 eV with a probe temperature of about 120°.

10.10.4. Electron Spin Resonance Spectroscopy

E.s.r. spectra were obtained using a Varian E.3 spectrometer fitted with a variable temperature probe.

10.10.5. Electronic Absorption Spectroscopy

Ultraviolet and visible spectra were obtained using a Unicam S.P.800 spectrometer.

Solutions for compounds absorbing in the ultraviolet region were made up in n-hexane.

10.10.6. Elemental Analyses

Whilst some analyses for carbon and hydrogen were carried out using a Baird and Tatlock semimicro combustion apparatus, many of these elemental analyses were performed by a commercial analyst, Mikroanalytisches Laboratorium Beller, Germany.

Likewise, some analyses for total chlorine were carried out by a combustion process, but the majority were determined by the above analytical laboratories.

Analysis for chromium in the complexes was achieved by one of the two methods described below.

10.10.6.1. Gravimetric Determination of Chromium

A small sample of the complex (0.2 - 0.3 g) was weighed into a silica crucible fitted with a lid, both of which had been previously ignited to constant weight. Special precautions were taken to prevent hydrolysis of the complex during weighing.

A small quantity of absolute ethanol (0.5 ml) was then added to reduce any chromium (IV) to chromium (III).

The liquid was then gently evaporated and the crucible and contents were ignited strongly for 2 - 3 hours, allowed to cool in a desiccator and then weighed, to constant weight. The chromium was weighed as Cr_2O_3 .

10.10.6.2. Titrimetric Determination of Chromium

A small quantity of the complex (0.2 g) was weighed and then transferred into a 650 ml beaker. Precautions were taken to ensure that no hydrolysis of the complex took place during weighing.

Sodium hydroxide solution (25 ml, 0.1N) and hydrogen peroxide (25 ml, 3% v/v) were then added, in order to oxidize the chromium to chromium (VI). The solution was then heated to

ensure complete oxidation and was then boiled, to destroy excess peroxide.

After being allowed to cool, the solution was acidified with sulphuric acid (25 ml, 0.4N). 'Analar' grade potassium iodide (3 - 4 g) was added, and the liberated iodine was titrated with standard sodium thiosulphate solution using soluble starch as indicator. A blank titration was carried out concurrently, using the same reagents.

10.10.7. Magnetic Susceptibility Measurements

These measurements were made using a variable temperature Gouy balance system, manufactured by Newport Instruments Ltd.

The instrument was calibrated for a range of magnet currents using mercury (II) tetrathiocyanato-cobalt (II), $\text{HgCo}(\text{CNS})_4^{253}$. The measurements were carried out using magnet currents of 10A and 15A (corresponding to magnetic fields of 5.65 Kgauss and 6.59 Kgauss respectively) over a temperature range 93 to 303°K.

APPENDIX

TABLES

TABLE 22

The N.M.R. Data for Bis(2,5-di-t-butylphenyl)chlorovanadate (V)

2,5-Di-t-butylphenol

| Chemical Shift τ | Multiplicity | Integrated Area | Assignment |
|--------------------------|--------------|-----------------|------------------|
| 8.75 | Singlet | 9 | t-Butyl Protons |
| 8.65 | Singlet | 9 | " " |
| 5.59 | Singlet | 1 | Phenolic O-H |
| Centre ~3.05 | Complex | 3 | Aromatic Protons |

Bis(2,5-di-t-butylphenyl) chlorovanadate (V)

| Chemical Shift τ | Multiplicity | Integrated Area | Assignment |
|--------------------------|--------------|-----------------|------------------|
| 8.54 | Singlet | 9 | t-Butyl Protons |
| 8.55 | Singlet | 9 | " " |
| 2.70 | Singlet* | 2 | Aromatic Protons |
| 1.91 | Singlet* | 1 | |

* Some splitting observed under high resolution.

TABLE 23

The Electronic Spectra of Bis(2,5-di-t-butylphenyl)chloro-
vanadate (V)

| 2,5-Di-t-butylphenol | | Bis(2,5-di-t-butylphenyl) chlorovanadate (V) | |
|----------------------|-------------------------|---|-------------------------|
| max (nm) | Assignment | max (nm) | Assignment |
| 275 | $\pi \rightarrow \pi^*$ | 277 | $\pi \rightarrow \pi^*$ |
| 280 | $\pi \rightarrow \pi^*$ | 281 | $\pi \rightarrow \pi^*$ |
| | | 510 | Charge Transfer |

TABLE 24

Magnetic Susceptibility Measurements for 2,5-Dimethylphenol-

Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|---|---|
| A | 113 | 52.99 | 11535 | 3.23 |
| | 143 | 42.55 | 9279 | 3.26 |
| | 163 | 38.34 | 8371 | 3.30 |
| | 183 | 34.00 | 7433 | 3.30 |
| | 203 | 30.88 | 6759 | 3.31 |
| | 233 | 26.90 | 5900 | 3.32 |
| | 253 | 24.98 | 5485 | 3.33 |
| | 293 | 22.31 | 4909 | 3.39 |
| B | 113 | 53.00 | 11538 | 3.23 |
| | 143 | 42.66 | 9308 | 3.26 |
| | 163 | 37.83 | 8260 | 3.28 |
| | 183 | 33.99 | 7431 | 3.30 |
| | 203 | 30.98 | 6780 | 3.32 |
| | 233 | 27.04 | 5930 | 3.32 |
| | 253 | 25.07 | 5504 | 3.34 |
| | 293 | 22.34 | 4915 | 3.39 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 25

Magnetic Susceptibility Measurements for 2,3,5-Trimethylphenol-

Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 93 | 61.96 | 13911 | 3.22 |
| | 123 | 48.15 | 10831 | 3.26 |
| | 153 | 38.72 | 8730 | 3.27 |
| | 193 | 31.09 | 7029 | 3.29 |
| | 223 | 27.23 | 6168 | 3.32 |
| | 253 | 23.95 | 5435 | 3.32 |
| | 293 | 21.28 | 4841 | 3.37 |
| B | 93 | 61.69 | 13852 | 3.21 |
| | 123 | 47.79 | 10745 | 3.25 |
| | 153 | 38.74 | 8735 | 3.27 |
| | 193 | 30.99 | 7005 | 3.29 |
| | 223 | 27.25 | 6172 | 3.32 |
| | 253 | 23.94 | 5433 | 3.32 |
| | 293 | 21.20 | 4822 | 3.36 |

A: Magnet Current 10A (Field Strength 5.65 Kgauss)

B: Magnet Current 15A (Field Strength 6.59 Kgauss)

TABLE 26

Magnetic Susceptibility Measurements for 2,3,6-Trimethyl-
phenol-Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|---|---|
| A | 113 | 51.55 | 11590 | 3.24 |
| | 143 | 41.94 | 9447 | 3.29 |
| | 173 | 35.27 | 7960 | 3.32 |
| | 203 | 30.61 | 6921 | 3.35 |
| | 223 | 26.03 | 5901 | 3.24 |
| | 263 | 23.49 | 5332 | 3.35 |
| | 303 | 20.89 | 4755 | 3.39 |
| B | 113 | 51.88 | 11665 | 3.25 |
| | 143 | 42.05 | 9471 | 3.29 |
| | 173 | 35.39 | 7988 | 3.32 |
| | 203 | 30.44 | 6883 | 3.34 |
| | 223 | 26.58 | 6023 | 3.28 |
| | 263 | 23.78 | 5399 | 3.37 |
| | 303 | 20.88 | 4751 | 3.39 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 27

Magnetic Susceptibility Measurements for 2,3,5,6-Tetramethyl-
phenol-Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 103 | 59.00 | 12703 | 3.23 |
| | 133 | 46.93 | 10104 | 3.28 |
| | 163 | 38.61 | 8307 | 3.29 |
| | 193 | 33.34 | 7222 | 3.34 |
| | 223 | 29.02 | 6299 | 3.35 |
| | 253 | 25.68 | 5587 | 3.36 |
| | 293 | 23.02 | 5018 | 3.43 |
| B | 103 | 58.59 | 12616 | 3.22 |
| | 133 | 46.94 | 10128 | 3.28 |
| | 163 | 38.89 | 8407 | 3.31 |
| | 193 | 33.35 | 7223 | 3.34 |
| | 223 | 20.09 | 6314 | 3.36 |
| | 253 | 25.73 | 5598 | 3.37 |
| | 293 | 22.73 | 4957 | 3.41 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 28

Magnetic Susceptibility Measurements for 2,6-Di-isopropylphenol-
Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 113 | 51.29 | 12628 | 3.38 |
| | 143 | 40.59 | 10016 | 3.38 |
| | 163 | 36.03 | 8903 | 3.41 |
| | 193 | 30.49 | 7553 | 3.41 |
| | 223 | 26.58 | 6599 | 3.43 |
| | 253 | 23.31 | 5799 | 3.43 |
| | 293 | 20.66 | 5154 | 3.47 |
| B | 113 | 51.13 | 12590 | 3.37 |
| | 143 | 40.81 | 10070 | 3.39 |
| | 163 | 35.94 | 8882 | 3.40 |
| | 193 | 30.51 | 7558 | 3.42 |
| | 223 | 26.45 | 6566 | 3.42 |
| | 253 | 23.44 | 5832 | 3.44 |
| | 293 | 20.84 | 5199 | 3.49 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 29

Magnetic Susceptibility Measurements for 2,5-di-t-butylphenol-
Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 113 | 46.36 | 12085 | 3.30 |
| | 133 | 39.60 | 10341 | 3.32 |
| | 163 | 32.26 | 8448 | 3.32 |
| | 203 | 26.05 | 6847 | 3.33 |
| | 243 | 21.76 | 5740 | 3.34 |
| | 273 | 19.35 | 5118 | 3.34 |
| | 303 | 17.48 | 4634 | 3.35 |
| B | 113 | 46.65 | 12161 | 3.31 |
| | 133 | 40.02 | 10450 | 3.33 |
| | 163 | 32.42 | 8489 | 3.33 |
| | 203 | 25.96 | 6824 | 3.33 |
| | 243 | 21.94 | 5785 | 3.35 |
| | 273 | 19.17 | 5072 | 3.33 |
| | 303 | 17.72 | 4697 | 3.37 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 30

Magnetic Susceptibility Measurements for 2,6-Di-t-butylphenol-
Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M' \times 10^{-6}$) | Effective Magnetic Moments (μ_{eff} B.M.) |
|---|---------------------|--|--|--|
| A | 113 | 50.55 | 12764 | 3.40 |
| | 133 | 43.46 | 10991 | 3.42 |
| | 163 | 35.70 | 9051 | 3.43 |
| | 193 | 30.39 | 7723 | 3.45 |
| | 233 | 24.97 | 6367 | 3.44 |
| | 263 | 22.13 | 5657 | 3.45 |
| | 303 | 19.46 | 4989 | 3.48 |
| B | 113 | 50.45 | 12735 | 3.39 |
| | 133 | 43.37 | 10966 | 3.42 |
| | 163 | 35.78 | 9069 | 3.44 |
| | 193 | 30.50 | 7750 | 3.46 |
| | 233 | 25.09 | 6395 | 3.45 |
| | 263 | 22.01 | 5629 | 3.44 |
| | 303 | 19.65 | 5039 | 3.49 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 31

Magnetic Susceptibility Measurements for 3,5-Di-t-butylphenol-
Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|---|---|
| A | 113 | 47.99 | 12411 | 3.35 |
| | 133 | 41.13 | 10654 | 3.37 |
| | 163 | 32.90 | 8546 | 3.34 |
| | 193 | 28.03 | 7299 | 3.36 |
| | 233 | 23.90 | 6243 | 3.34 |
| | 263 | 21.56 | 5644 | 3.38 |
| | 303 | 18.39 | 4833 | 3.42 |
| B | 113 | 48.22 | 12470 | 3.36 |
| | 133 | 40.98 | 10716 | 3.38 |
| | 163 | 33.00 | 8573 | 3.34 |
| | 193 | 28.19 | 7342 | 3.37 |
| | 233 | 24.03 | 6276 | 3.35 |
| | 263 | 21.57 | 5646 | 3.38 |
| | 303 | 18.65 | 4899 | 3.45 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 32

Magnetic Susceptibility Measurements for 2,4,6-Tri-t-butylphenol-
Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M' \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 93 | 55.54 | 13638 | 3.18 |
| | 123 | 43.75 | 10767 | 3.25 |
| | 163 | 33.79 | 8350 | 3.30 |
| | 193 | 29.21 | 7237 | 3.34 |
| | 223 | 25.29 | 6286 | 3.35 |
| | 253 | 22.57 | 5626 | 3.37 |
| | 303 | 21.01 | 5246 | 3.56 |
| B | 93 | 54.75 | 13436 | 3.16 |
| | 123 | 43.81 | 10780 | 3.26 |
| | 163 | 33.87 | 8367 | 3.30 |
| | 193 | 29.00 | 7185 | 3.33 |
| | 223 | 25.19 | 6261 | 3.34 |
| | 253 | 22.41 | 5587 | 3.36 |
| | 303 | 19.52 | 4885 | 3.44 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 33

Magnetic Susceptibility Measurements for 2,6-Di-t-butyl-4-methyl-phenol-Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 103 | 56.51 | 13409 | 3.32 |
| | 123 | 48.29 | 11478 | 3.36 |
| | 153 | 40.18 | 9573 | 3.42 |
| | 183 | 33.94 | 8106 | 3.44 |
| | 213 | 29.74 | 7119 | 3.48 |
| | 253 | 26.41 | 6336 | 3.58 |
| | 293 | 22.57 | 5433 | 3.57 |
| B | 103 | 56.70 | 13454 | 3.33 |
| | 123 | 48.49 | 11525 | 3.37 |
| | 153 | 40.11 | 9557 | 3.42 |
| | 183 | 34.06 | 8135 | 3.45 |
| | 213 | 29.79 | 7130 | 3.49 |
| | 253 | 26.42 | 6339 | 3.58 |
| | 293 | 22.60 | 5440 | 3.57 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 34

Magnetic Susceptibility Measurements for 3,5-Di-t-butylcatechol

Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M' \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 113 | 41.54 | 11175 | 3.18 |
| | 133 | 36.14 | 9740 | 3.22 |
| | 163 | 29.56 | 7989 | 3.23 |
| | 193 | 25.04 | 6788 | 3.24 |
| | 223 | 21.77 | 5918 | 3.25 |
| | 253 | 19.12 | 5214 | 3.25 |
| | 303 | 15.91 | 4360 | 3.25 |
| B | 113 | 42.11 | 11328 | 3.20 |
| | 133 | 36.28 | 9778 | 3.23 |
| | 163 | 29.92 | 8086 | 3.25 |
| | 193 | 25.38 | 6879 | 3.26 |
| | 223 | 21.91 | 5954 | 3.26 |
| | 253 | 19.15 | 5222 | 3.25 |
| | 303 | 16.34 | 4475 | 3.29 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 35

Magnetic Susceptibility Measurements for 2,6-Dinitrophenol-

Chromyl Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 113 | 33.26 | 11334 | 3.20 |
| | 143 | 27.10 | 9246 | 3.25 |
| | 163 | 23.95 | 8179 | 3.27 |
| | 193 | 20.45 | 6992 | 3.29 |
| | 223 | 17.79 | 6091 | 3.30 |
| | 253 | 15.58 | 5342 | 3.29 |
| | 293 | 13.33 | 4580 | 3.29 |
| B | 113 | 33.58 | 11445 | 3.22 |
| | 143 | 27.00 | 9215 | 3.25 |
| | 163 | 24.04 | 8211 | 3.27 |
| | 193 | 20.37 | 6965 | 3.28 |
| | 223 | 17.85 | 6110 | 3.30 |
| | 253 | 15.74 | 5395 | 3.30 |
| | 293 | 13.54 | 4647 | 3.30 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 35

Magnetic Susceptibility Measurements for 1-Naphthol-Chromyl
Chloride Complex

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M' \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 103 | 52.32 | 11972 | 3.14 |
| | 123 | 44.58 | 10215 | 3.17 |
| | 153 | 36.46 | 8373 | 3.20 |
| | 183 | 30.81 | 7090 | 3.22 |
| | 213 | 26.49 | 6109 | 3.23 |
| | 243 | 23.26 | 5377 | 3.23 |
| | 283 | 19.89 | 4612 | 3.23 |
| B | 103 | 52.39 | 11988 | 3.14 |
| | 123 | 44.64 | 10229 | 3.17 |
| | 153 | 36.56 | 8395 | 3.21 |
| | 183 | 30.72 | 7070 | 3.22 |
| | 213 | 26.53 | 6119 | 3.23 |
| | 243 | 23.23 | 5370 | 3.23 |
| | 283 | 20.07 | 4652 | 3.24 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15 A (Field Strength = 6.59 Kgauss)

TABLE 37

Magnetic Susceptibility of Solid derived from the Chromyl Acetate

Oxidation of 2,5-Di-isopropylphenol

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|---|---|
| A | 103 | 45.92 | 9451 | 2.79 |
| | 133 | 38.64 | 7966 | 2.91 |
| | 163 | 33.47 | 6912 | 3.00 |
| | 193 | 29.77 | 6157 | 3.08 |
| | 223 | 26.34 | 5457 | 3.12 |
| | 253 | 23.62 | 4902 | 3.15 |
| | 293 | 21.32 | 4437 | 3.22 |
| B | 103 | 45.88 | 9443 | 2.79 |
| | 133 | 38.88 | 8015 | 2.92 |
| | 163 | 33.46 | 6910 | 3.00 |
| | 193 | 29.60 | 6122 | 3.07 |
| | 223 | 26.32 | 5454 | 3.12 |
| | 253 | 23.74 | 4926 | 3.16 |
| | 293 | 21.33 | 4436 | 3.22 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 38

Magnetic Susceptibility of Solid derived from the Chromyl

Acetate Oxidation of 2,5-Di-t-butylphenol

| | Temperature (°K) | Gram Susceptibility ($\chi_g \times 10^{-6}$) | Molar Susceptibility ($\chi'_M \times 10^{-6}$) | Effective Magnetic Moment (μ_{eff} B.M.) |
|---|---------------------|--|--|---|
| A | 103 | 47.55 | 9784 | 2.84 |
| | 123 | 42.12 | 8676 | 2.92 |
| | 153 | 35.67 | 7361 | 3.00 |
| | 163 | 32.41 | 6696 | 2.95 |
| | 203 | 28.58 | 5915 | 3.10 |
| | 233 | 25.43 | 5273 | 3.13 |
| | 263 | 23.86 | 4952 | 3.23 |
| | 293 | 21.34 | 4437 | 3.22 |
| B | 103 | 47.76 | 9828 | 3.84 |
| | 123 | 42.15 | 8663 | 2.92 |
| | 153 | 35.70 | 7366 | 3.00 |
| | 163 | 32.71 | 6757 | 2.98 |
| | 203 | 28.51 | 5900 | 3.09 |
| | 233 | 25.40 | 5265 | 3.13 |
| | 263 | 22.95 | 4766 | 3.17 |
| | 293 | 21.26 | 4422 | 3.22 |

A: Magnet Current 10A (Field Strength = 5.65 Kgauss)

B: Magnet Current 15A (Field Strength = 6.59 Kgauss)

TABLE 39

The Infrared Spectrum of the Phenol-Chromyl Chloride Complex

| Phenol cm ⁻¹ | Complex cm ⁻¹ | 1,4-Benzoquinone cm ⁻¹ |
|----------------------------|-----------------------------|--------------------------------------|
| 3100 broad | 3300 broad | |
| 1928 w | | |
| 1832 w | | 1755 w |
| 1700 w | | 1707 w |
| | | 1670 s |
| | 1640 sh | 1655 sh |
| | 1612 m | |
| 1590 s | 1600 m | 1595 m |
| 1505 sh | 1544 w | |
| 1317 w | 1311 w | 1308 s |
| 1250 broad | 1220 w | |
| 1165 w | 1180 w | |
| 1152 w | 1160 w | 1110 w |
| 1072 m | 1078 w | 1065 s |
| 1025 m | 1025 w | |
| 1008 w | | |
| 985 w | 984 m | 950 m |
| 968 w | 930 w | |
| 896 m | 900 w | 889 s |
| 821 m | 871 w | |
| | 775 sh | 750 sh |
| 758 s | 728 m | 730 m |
| 691 m | | |

TABLE 40

The Infrared Spectrum of the 2-t-Butylphenol-Chromyl Chloride

Complex

| 2-t-Butylphenol cm ⁻¹ | Complex cm ⁻¹ | 2-t-Butyl-1,4- benzoquinone cm ⁻¹ |
|-------------------------------------|-----------------------------|--|
| 3505 sh | | |
| 3450 s | 3300 broad | 3320 w |
| | 1645 sh | 1659 s |
| 1609 m | 1640 m | |
| 1580 m | 1589 m | 1592 m |
| 1510 s | 1530 w | 1512 sh |
| 1485 sh | | |
| 1362 s | | 1362 sh |
| 1330 m | | 1333 m |
| | 1302 m | |
| 1293 m | | 1283 s |
| 1263 sh | 1250 w | 1258 sh |
| 1243 m | | |
| 1182 s | 1195 w | |
| | 1163 w | |
| 1155 m | 1150 m | |
| 1125 s | 1109 w | 1103 w |
| 1085 s | | |
| 1051 m | 1038 w | 1039 w |
| | 1009 m | 1011 s |
| | 975 m | |
| 935 m | 930 w | 931 w |
| | 908 m | 912 s |
| 860 s | 880 w | |
| 817 s | 835 m | 837 s |
| 751 s | 783 m | |
| 722 sh | 717 m | |
| 682 sh | | |

TABLE 41.

The Infrared Spectra of the Complexes derived from 4-t-Butylphenol and 3-t-Butylphenol, and Chromyl Chloride

| 4-t-Butylphenol Complex cm ⁻¹ | 3-t-Butylphenol Complex cm ⁻¹ |
|---|---|
| 3325 broad | 3300 broad |
| 1640 m | 1639 m |
| 1598 broad | 1597 m |
| 1560 sh | 1560 sh |
| 1540 sh | 1540 sh |
| 1316 w | 1317 w |
| 1270 w | 1250 w |
| 1220 w | |
| 1175 w | 1190 w |
| 1158 w | 1158 w |
| 1080 w | 1148 w |
| 1023 w | 1016 m |
| 981 w | 975 w |
| 952 w | 930 w |
| 928 w | 910 w |
| 891 m | 891 w |
| 850 w | 870 w |
| 725 m | 832 w |
| | 720 m |

TABLE 42

The Infrared Spectrum of the 2,5-Dimethylphenol-Chromyl

Chloride Complex

| 2,5-Dimethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,5-Dimethyl-1,4- benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3520 w | | 3325 w |
| 3250 broad | 3250 broad | |
| 1708 w | | 1684 sh |
| | | 1664 s |
| | 1644 sh | 1639 m |
| 1621 m | 1610 broad | 1618 m |
| 1585 m | | |
| 1530 m | | |
| | 1310 w | 1342 s |
| 1295 m | | |
| 1275 m | 1270 w | |
| 1243 m | | 1245 s |
| 1230 sh | | |
| | 1209 w | |
| 1170 w | 1170 sh | |
| 1153 m | 1160 m | 1150 s |
| 1121 s | | |
| 1110 sh | | |
| | 1080 w | |
| 1042 m | 1040 w | 1037 w |
| 1004 m | 1011 w | 1000 s |
| | 980 m | |
| 942 m | 920 w | 911 s |
| 872 s | | |
| 810 s | | |
| 763 m | 775 sh | |
| 730 m | 727 s | |
| 717 w | | 661 m |

TABLE 43

The Infrared Spectrum of the 2,6-Dimethylphenol-Chromyl Chloride Complex

| 2,6-Dimethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,6-Dimethyl-1,4- benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3520 s | 3350 broad | 3315 w |
| 3400 broad | | |
| | 1658 sh | 1665 s |
| 1650 w | 1651 s | |
| 1618 s | 1618 m | |
| 1593 s | 1598 s | |
| | 1559 sh | |
| | 1542 sh | |
| 1324 m | 1317 w | 1310 m |
| 1280 sh | 1285 w | 1284 m |
| 1263 s | | |
| 1220 m | 1221 m | |
| 1195 s | 1196 w | 1196 w |
| 1158 m | 1178 m | 1176 m |
| 1090 m | 1050 m | 1040 w |
| 1025 m | 1023 sh | 1019 m |
| 993 w | 980 w | |
| | 942 m | 935 m |
| 919 m | 920 s | 918 s |
| 835 m | 860 | 898 w |
| 768 s | | |
| 737 m | 723 s | |
| 675 w | | 651 m |

TABLE 44

The Infrared Spectrum of the 3,5-Dimethylphenol-Chromyl Chloride

Complex

| 3,5-Dimethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,6-Dimethyl-1,4- benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3175 broad | 3325 broad | 3300 w |
| | 1645 s | 1660 s |
| 1618 s | 1610 broad | 1620 m |
| 1500 s | | |
| 1310 sh | 1300 w | 1311 m |
| 1298 sh | | 1281 m |
| 1230 m | 1260 w | |
| | | 1193 w |
| | 1179 m | 1175 m |
| 1150 s | 1145 w | |
| 1038 sh | | 1040 w |
| 1023 m | 1020 m | 1019 m |
| | 990 w | |
| | 985 w | |
| 950 m | 950 w | 938 m |
| | 907 m | 918 s |
| 839 s | 880 w | |
| | 785 m | |
| | 758 w | |
| 720 w | 717 w | |
| 680 w | | |

TABLE 45

The Infrared Spectrum of the 2,3,5-Trimethylphenol-Chromyl

Chloride Complex

| 2,3,5-Trimethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,3,5-Trimethyl-1,4- benzoquinone cm ⁻¹ |
|---|-----------------------------|--|
| 3550 m | | |
| 3380 broad | 3250 broad | 3250 w |
| | | 1780 w |
| | | 1707 w |
| | 1641 m | 1652 s |
| 1620 m | 1609 sh | 1620 m |
| 1582 s | 1582 w | |
| | 1348 sh | 1361 w |
| 1309 m | 1306 w | 1320 m |
| 1262 s | 1275 sh | 1263 m |
| | 1196 m | 1226 w |
| 1180 w | 1172 w | 1190 m |
| 1157 m | 1155 w | |
| 1137 m | | |
| | 1119 w | 1117 m |
| 1080 s | 1002 w | |
| | 1019 w | 1018 m |
| 978 m | 982 m | 991 sh |
| 918 w | 925 w | 922 w |
| | 901 w | 895 m |
| 840 m | 862 w | |
| 830 s | | |
| 710 m | 725 s | 702 w |
| | | 682 m |
| | | 675 w |

TABLE 46

The Infrared Spectrum of 2,3,6-Trimethylphenol-Chromyl

Chloride Complex

| 2,3,6-Trimethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,3,5-Trimethyl-1, 4-benzoquinone cm ⁻¹ |
|---|-----------------------------|--|
| 3550 w | | |
| 3350 broad | 3250 broad | 3250 w |
| | | 1780 w |
| 1718 w | | 1707 w |
| | 1641 m | 1652 s |
| 1620 m | 1610 m | 1620 m |
| 1580 m | 1582 m | |
| 1495 s | | |
| | 1350 sh | 1361 w |
| 1310 m | | 1320 m |
| 1270 m | 1275 m | 1263 w |
| 1224 m | | 1226 w |
| 1196 w | 1198 m | 1190 m |
| 1141 w | 1157 w | |
| | 1119 w | 1117 m |
| 1082 s | 1072 w | |
| 1030 m | 1019 w | 1018 m |
| 1006 m | | |
| 990 m | 983 w | 991 sh |
| 946 m | 963 w | |
| | 928 w | 922 w |
| | 892 m | 895 m |
| 806 s | | |
| 731 m | 725 m | |
| | 706 w | 702 w |
| | | 692 m |
| | | 675 w |

TABLE 47

The Infrared Spectra of 2,4,6-Trimethylphenol and Complex
with Chromyl Chloride

| 2,4,6-Trimethylphenol cm ⁻¹ | Complex cm ⁻¹ |
|---|-----------------------------|
| 3550 m | |
| 3480 broad | 3270 broad |
| | 1630 sh |
| 1600 sh | 1590 broad |
| 1575 sh | No |
| 1485 s | distinct |
| 1372 m | bands in |
| 1316 m | this region |
| 1300 s | 1308 w |
| 1258 m | 1255 m |
| 1226 s | |
| 1218 w | 1200 w |
| 1185 | 1178 w |
| 1143 | 1150 m |
| 1059 | 1080 w |
| | 1038 sh |
| 1003 s | 1019 m |
| | 978 w |
| 952 m | 958 w |
| 921 m | 915 w |
| | 890 w |
| | 782 m |
| | 760 w |
| 718 s | 717 m |

TABLE 48

The Infrared Spectrum of the 2,3,5,6-Tetramethylphenol-

Chromyl Chloride Complex

| 2,3,5,6-Tetramethylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,3,5,6-Tetramethyl- 1,4-benzoquinone cm ⁻¹ |
|---|-----------------------------|--|
| 3580 w | 3300 broad | 3220 w |
| 3400 broad | | 2900 m |
| 1620 w | 1638 sh | 1685 m |
| | 1600 broad | 1644 s |
| 1503 w | | 1503 sh |
| 1470 m | | |
| | | 1453 m |
| 1419 m | | |
| 1385 w | 1350 m | 1383 s |
| 1315 m | 1318 w | |
| 1299 m | | 1308 s |
| 1244 m | 1260 w | 1265 s |
| 1208 s | | |
| | 1165 w | |
| | 1156 w | |
| 1094 s | 1122 w | |
| 1030 m | 1025 w | |
| | 1000 w | |
| | 983 w | |
| 920 w | 925 w | |
| 856 m | | 879 w |
| | 795 w | |
| | 762 w | |
| | 724 w | 707 w |

TABLE 49

The Infrared Spectrum of the 2,5-Di-isopropylphenol-

Chromyl Chloride Complex

| 2,5-Di-isopropylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,5-Di-isopropyl-1, 4-benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3505 w | | |
| 3400 broad | 3305 broad | 3265 w |
| 1620 m | 1637 s | 1654 s |
| 1581 s | 1603 s | 1607 s |
| 1523 w | | |
| 1509 m | | |
| 1389 m | | |
| 1369 m | | |
| 1344 m | 1330 w | 1310 m |
| 1297 m | | 1291 sh |
| | 1250 m | 1238 s |
| 1218 m | | 1217 s |
| 1177 m | 1170 w | 1180 w |
| 1151 s | | |
| 1111 w | | 1100 m |
| 1095 w | | 1086 w |
| 1080 w | 1065 m | 1063 s |
| 1072 m | 1050 sh | 1047 w |
| 1008 w | 1010 w | |
| 980 w | 980 w | |
| 949 m | 918 m | 920 s |
| 896 w | 890 w | |
| 864 m | | |
| | 790 w | |
| | 720 w | |
| 708 w | | |

TABLE 50

The Infrared Spectrum of the 2,6-Di-isopropylphenol-

Chromyl Chloride Complex

| 2,6-Di-isopropylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,6-Di-isopropyl-1,4- benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3500 m | | |
| 3400 broad | 3250 broad | 3313 w |
| 1657 m | 1642 m | 1655 s |
| | 1606 sh | 1610 s |
| 1592 m | 1581 m | |
| | 1525 m | |
| 1349 m | 1350 w | |
| 1317 s | 1310 w | 1310 s |
| | | 1290 s |
| 1259 s | | 1275 m |
| 1200 s | 1209 w | 1195 s |
| 1170 s | 1175 w | |
| 1147 s | 1159 w | |
| 1109 m | | 1105 w |
| 1061 m | 1071 w | 1067 s |
| 1046 m | | 1050 w |
| | 1022 w | |
| | 975 w | |
| 961 w | 941 w | |
| 934 s | 930 w | 931 sh |
| 892 m | 900 sh | |
| 830 s | | 826 s |
| | 797 s | |
| | 775 sh | |
| | 730 m | 700 w |
| 670 w | | 603 w |

TABLE 51

The Infrared Spectrum of the 2,5-Di-t-butylphenol-Chromyl
Chloride Complex

| 2,5-Di-t-butylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,5-Di-t-butyl-1, 4-benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3548 m | 3300 broad | 3250 w |
| | 1650 sh | 1650 s |
| 1616 m | 1625 s | 1636 sh |
| | 1600 sh | 1596 s |
| 1564 m | 1585 s | |
| | 1550 sh | |
| 1417 s | 1418 w | |
| | | 1342 s |
| 1318 sh | 1315 v | |
| 1301 m | | |
| | 1258 s | 1243 s |
| 1224 m | | |
| 1202 s | | 1198 w |
| 1185 s | 1185 m | 1179 s |
| 1146 s | | |
| 1070 s | 1079 s | 1079 s |
| 1020 w | 1023 s | 1020 s |
| | 984 | |
| 940 s | 968 w | |
| | 911 m | 919 s |
| | 890 sh | |
| 859 m | 855 sh | 841 s |
| | 795 s | |

TABLE 52

The Infrared Spectrum of the 2,6-Di-t-butylphenol-Chromyl

Chloride Complex

| 2,6-Di-t-butylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,6-Di-t-butyl-1,4- benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3500 s | 3280 broad | 3300 w |
| 3040 sh | | |
| | 1661 sh | 1654 s |
| | 1630 s | 1648 sh |
| 1580 w | 1578 s | 1599 m |
| | 1539 w | |
| 1485 s | | 1493 m |
| 1430 s | 1420 w | |
| 1396 m | | |
| 1363 s | | |
| 1318 s | 1320 w | 1310 s |
| 1276 w | | |
| 1249 s | 1250 m | 1243 s |
| 1230 s | | |
| 1196 w | | 1193 w |
| 1176 s | 1160 m | 1155 s |
| 1121 s | | |
| 1112 m | | |
| 1115 m | | |
| 1095 m | 1094 m | |
| | 1030 m | 1078 m |
| 1024 w | 1020 w | 1028 w |
| | 982 w | |
| | 964 w | |
| 938 m | 940 w | 931 m |
| | 920 m | 920 s |
| 885 s | 886 m | 880 s |
| 850 s | 794 m | |
| | 723 w | 682 w |

TABLE 53

The Infrared Spectrum of the 3,5-Di-t-butylphenol-

Chromyl Chloride Complex

| 3,5-Di-t-butylphenol cm ⁻¹ | Complex cm ⁻¹ | 2,6-Di-t-butyl-1, 4-benzoquinone cm ⁻¹ |
|--|-----------------------------|---|
| 3500 w | 3300 broad | 3300 w |
| 3300 broad | | |
| | 1660 sh | 1660 s |
| 1608 sh | 1633 s | 1600 s |
| 1600 s | 1585 s | |
| | 1550 sh | |
| 1482 m | 1480 w | 1493 m |
| 1430 s | | 1400 m |
| 1397 m | 1395 m | |
| 1302 s | | 1243 s |
| 1249 s | 1245 m | |
| | 1220 w | |
| 1200 s | 1200 w | |
| 1180 sh | 1160 m | 1155 s |
| 1120 m | 1122 w | |
| | 1078 m | 1078 m |
| | 1037 sh | |
| 1025 m | 1030 m | 1028 w |
| 1000 w | 1000 sh | |
| | 982 w | |
| 960 s | 960 w | |
| | 938 sh | 938 m |
| 903 m | 920 m | 924 s |
| | 892 m | 885 s |
| 869 s | 840 w | |
| | 795 m | |
| 707 s | 710 w | 682 w |

TABLE 54

The Infrared Spectrum of the 2,6-Di-t-butyl-4-methylphenol-

Chromyl Chloride Complex

| 2,6-Di-t-butyl-4-methyl- phenol cm ⁻¹ | Complex cm ⁻¹ | 3,5-Di-t-butyl-4- hydroxybenzaldehyde cm ⁻¹ |
|--|-----------------------------|--|
| 3550 s | 3350 broad | 3358 broad |
| 1735 w | | |
| | 1660 sh | 1665 s |
| | 1640 sh | |
| 1605 w | 1619 broad | |
| | 1580 s | 1592 m |
| | | 1575 m |
| 1317 m | 1313 m | 1300 m |
| 1264 w | 1262 m | 1262 m |
| 1248 m | 1250 sh | |
| 1216 m | 1211 m | 1200 m |
| | | 1190 sh |
| | 1153 m | |
| 1121 m | | 1103 m |
| | 1075 w | |
| 1030 m | 1030 w | 1034 sh |
| | 980 w | |
| 940 w | 941 w | 942 w |
| | | 922 w |
| 892 m | 897 w | 901 m |
| 866 s | | 828 m |
| 818 w | | 818 w |
| 780 s | 790 m | 790 w |
| 775 s | | 760 sh |
| 728 w | 721 m | 730 m |
| | | 688 m |

TABLE 55

The Infrared Spectrum of the 2,4,6-Tri-t-butylphenol-Chronyl
Chloride Complex

| 2,4,6-Tri-t-butylphenol cm ⁻¹ | Complex cm ⁻¹ | 3,5-Di-t-butyl-1, 2-benzoquinone cm ⁻¹ |
|---|-----------------------------|---|
| 3575 s | | |
| 3350 broad | 3250 broad | 3270 w |
| 1755 w | | 1758 w |
| 1751 w | | 1680 w |
| | 1662 sh | 1663 s |
| | 1641 m | 1621 w |
| | 1582 m | 1570 m |
| | 1524 m | |
| | 1310 w | 1319 w |
| 1270 w | | 1270 s |
| 1235 s | 1249 m | 1242 s |
| 1200 m | 1205 w | 1207 sh |
| | 1170 w | |
| 1157 s | 1157 w | 1152 w |
| 1118 m | | |
| | | 1070 w |
| | 1030 m | 1021 m |
| 1010 w | | 1010 m |
| | 993 w | |
| 984 w | 980 w | 980 w |
| 937 w | 941 w | 960 w |
| | 923 w | 931 w |
| 892 sh | | 894 m |
| 884 m | | 874 m |
| 775mm | 810 w | |
| 725 m | 723 s | |

TABLE 56

The Infrared Spectra of the Complexes derived from 3,5-Di-t-butylcatechol and 4,6-Di-t-butylpyrogallol, and Chromyl Chloride

| 3,5-Di-t-butylcatechol Complex cm ⁻¹ | 4,6-Di-t-butylpyrogallol Complex cm ⁻¹ |
|---|---|
| 3300 broad | 3300 broad |
| 1755 sh | 1755 m |
| 1618 sh | 1690 sh |
| 1588 s | 1660 sh |
| 1558 sh | 1610 broad |
| 1540 sh | 1310 w |
| 1318 m | 1270 w |
| 1265 w | 1205 w |
| 1250 m | 1173 m |
| 1208 w | 1158 m |
| 1175 w | 1080 w |
| 1158 w | 1030 w |
| 1095 w | 980 m |
| 1075 w | 940 w |
| 1037 m | 928 w |
| 998 w | 900 w |
| 945 w | 880 sh |
| 902 w | 795 s |
| 880 w | 772 m |
| 840 w | 728 s |
| 798 s | |
| 770 w | |
| 729 s | |

TABLE 57

The Infrared Spectra of the Complexes derived from Nitrophenols
and Chromyl Chloride

| 3-Nitrophenol Complex cm ⁻¹ | 4-Nitrophenol Complex cm ⁻¹ | 2,6-Di-nitrophenol Complex cm ⁻¹ |
|--|--|---|
| 3350 broad | 3250 broad | 3380 broad |
| 1678 m | 1645 sh | 1670 sh |
| 1618 broad | 1615 broad | 1619 s |
| 1555 sh | 1570 sh | 1560 sh |
| 1535 s | 1518sh | 1539 m |
| 1361 m | 1348 s | 1517 sh |
| 1306 w | 1248 w | 1316 w |
| 1278 w | 1170 m | 1220 m |
| 1220 m | 1150 sh | 1200 sh |
| 1110 w | 1119 m | 1155 m |
| 1087 w | 1080 m | 1100 w |
| 1061 w | 1031 m | 1030 w |
| 1030 m | 987 m | 983 w |
| 1007 w | 930 w | 968 w |
| 982 sh | 900 w | 940 w |
| 955 m | 881 w | 921 w |
| 900 w | 800 sh | 885 m |
| 885 w | 727 s | 849 w |
| 830 m | | 824 w |
| 302 m | | 800 w |
| 750 m | | 760 sh |
| 728 w | | 743 sh |
| | | 730 sh |

TABLE 58

The Infrared Spectrum of the 1-Naphthol-Chromyl Chloride

Complex

| 1-Naphthol cm ⁻¹ | Complex cm ⁻¹ | 1,4-Napthoquinone cm ⁻¹ |
|--------------------------------|-----------------------------|---------------------------------------|
| 3500 w | 3420 broad | |
| 3200 broad | | 1775 w |
| | | 1762 w |
| | 1660 sh | 1660 s |
| 1626 m | 1630 s | 1603 m |
| 1595 s | | 1590 m |
| | 1578 s | |
| 1518 s | | |
| 1403 s | | |
| 1390 s | | 1385 s |
| 1358 m | 1320 m | 1334 s |
| 1275 s | | 1304 s |
| 1240 s | 1268 w | |
| 1230 s | | 1224 w |
| 1208 w | | |
| 1195 m | | |
| 1172 m | 1165 m | |
| 1150 m | | 1158 m |
| 1139 m | 1122 w | 1143 m |
| | | 1112 m |
| 1078 s | 1075 w | 1089 w |
| 1037 s | 1030 w | 1057 m |
| 1017 s | | 1019 m |
| | 985 w | 998 w |
| | 968 w | 985 w |
| 880 m | 867 w | 868 w |
| 792 s | 797 s | 773 s |
| 775 m | 770 s | 719 sh |
| 707 m | 725 m | 684 m |

TABLE 59

Infrared Spectra of the Solids resulting from the Treatment
of the 2,5-Di-t-butylphenol-Chromyl Chloride Complex with
Donor Solvents

| Solid obtained from 1,4-Dioxan cm ⁻¹ | 1,4-Dioxan cm ⁻¹ | Solid obtained from Tetrahydro- furan cm ⁻¹ | Tetrahydro- furan cm ⁻¹ |
|---|--------------------------------|---|--|
| 3250 broad | 3030 s | 3250 broad | 2994 s |
| | 2747 w | | 2747 w |
| | 1988 m | | 1980 w |
| 1719 broad | 1730 w | 1651 w | |
| 1640 broad | | 1600 broad | |
| 1577 w | | | 1460 s |
| | 1451 s | 1310 m | 1366 m |
| | 1366 s | 1250 m | 1290 w |
| | 1319 w | 1179 m | 1182 s |
| | 1292 s | 1077 w | 1076 s |
| 1257 s | 1255 s | 1050 m | |
| 1119 s | 1124 s | 1020 s | |
| 1081 m | 1085 s | 980 m | 978 m |
| 1050 m | 1049 s | 963 m | |
| 1020 w | | 925 m | 909 s |
| 981 m | | 865 s | |
| 961 m | | 724 s | |
| 901 m | | | |
| 879 s | 879 s | | |
| 830 m | | | |
| 725 m | | | |

Spectra of solids: Nujol mulls; Spectra of liquids: thin film.

TABLE 60

Infrared Spectra of the Solids resulting from the Treatment
of the 2,5-Di-t-butylphenol-Chromyl Chloride Complex with

Donor Solvents (cont)

| Solid obtained from Acetone cm ⁻¹ | Acetone cm ⁻¹ | Solid obtained from Ether cm ⁻¹ | Ether cm ⁻¹ |
|--|-----------------------------|--|---------------------------|
| 3200 broad | 2960 s | 3200 broad | 2910 s |
| | 1725 s | | 2790 s |
| 1688 sh | | 1650 w | |
| 1651 s | 1618 w | 1610 w | |
| 1599 w | | | 1495 w |
| 1578 w | | | 1442 m |
| 1552 w | | | 1384 s |
| | 1431 s | 1310 m | 1350 m |
| 1312 w | 1364 s | | 1297 w |
| 1262 w | | 1157 m | 1150 sh |
| 1202 m | 1220 s | 1126 s | 1120 s, broad |
| 1176 m | | 1080 w | 1078 m |
| 1138 m | | 1025 m | 1042 w |
| 1079 w | | 942 w | |
| 1023 w | | 930 w | 940 w |
| 980 m | 1092 s | 900 m | |
| 940 w | | 850 m | 855 m |
| 922 m | 909 s | 780 m | |
| 881 w | | 724 s | |
| 827 m | | | 675 w |
| 775 w | | | |
| 722 s | 675 w | | |

TABLE 61

Infrared Spectra of the Solids resulting from the Treatment
of the 2,6-Di-t-butylphenol-Chromyl Chloride Complex with
Donor Solvents (cont.)

| Solid obtained from Acetonitrile cm ⁻¹ | Acetonitrile cm ⁻¹ |
|---|----------------------------------|
| 3300 broad | 2900 w |
| 2320 s | 2294 m |
| 2290 s | 2256 s |
| 2250 sh | |
| 1650 m | |
| 1610 w | |
| 1575 w | |
| | 1443 broad |
| 1310 w | 1376 s |
| 1220 w | |
| 1158 w | |
| 1119 w | |
| 1077 w | |
| 1041 m | 1047 s |
| | 1018 m |
| 960 m | 917 s |
| 795 s | |
| 770 m | 749 m |
| 725 m | |
| 700 w | |

TABLE 62

Infrared Spectra of the Solids resulting from the Treatment
of the 2,5-Di-~~t~~-butylphenol-Chromyl Chloride Complex with
Donor Solvents

| Solid obtaining from Pyridine cm ⁻¹ | Pyridine cm ⁻¹ | Solid obtained from Piperidine cm ⁻¹ | Piperidine cm ⁻¹ |
|--|------------------------------|---|--------------------------------|
| 3380 broad | 3350 s | 3380 broad | 3290 broad |
| | 3004 s | 3230 broad | 2670-2850 s |
| | 1987 w | 2500 s | |
| 1650 w | 1599 s | 2420 m | |
| 1607 s | 1583 s | 2150 w | |
| 1577 w | | 1595 s | |
| 1542 w | | | |
| | 1482 s | | 1475 m |
| | 1441 s | | 1443 s |
| 1244 w | | | 1387 w |
| 1218 s | 1217 s | | 1330 m |
| 1157 m | 1148 s | 1322 w | 1319 s |
| 1075 s | 1068 s | 1280 w | 1255 m |
| 1049 m | 1030 s | | 1190 m |
| 1020 m | | 1165 m | 1162 s |
| | 991 s | | 1146 m |
| 980 w | | | 1116 s |
| 900 w | | 1081 m | 1055 m |
| 860 w | | 1038 s | 1038 m |
| 788 w | | | 1011 m |
| 768 s | | 958 s | |
| 725 w | 703 s | 950 s | 947 w |
| 695 s | 675 w | | 909 m |
| | | 887 m | 863 s |
| | | 872 m | |
| | | 725 s | |

TABLE 63

The Infrared Spectra of Chromyl Acetate and its Reduction

Product:

| Chromyl Acetate ^(a) cm ⁻¹ | Reduction Product of ^(b) Chromyl Acetate cm ⁻¹ |
|--|--|
| 3100 - 3000 broad | 3500 - 3000 broad |
| 2620 w | |
| 1713 s | 1701 sh |
| | 1652 sh |
| 1500 w | 1620 - 1530 broad s |
| 1415 sh | 1308 w |
| 1382 m | 1161 sh |
| 1335 m | 1148 w |
| 1290 s | 1042 sh |
| 1051 w | 1030 m |
| 960 s | 972 m |
| 937 m | 956 sh |
| | 845 w broad |
| 709 m | 720 w |
| | 675 m |
| 628 m | 630 w broad |
| 480 m | 490 w |
| | 430 w |

(a) In carbon tetrachloride solution

(b) As a Nujol mull

Table 64

Mass Spectral Data for Bis(2,5-di-t-butylphenyl) chlorovanadate(V)

| M/E | RELATIVE INTENSITY | M/E | RELATIVE INTENSITY | M/E | RELATIVE INTENSITY |
|-------|-----------------------|--------|-----------------------|--------|-----------------------|
| 12.00 | 2.14 | 101.00 | 1.68 | 174.00 | 4.86 |
| 15.00 | 1.36 | 102.00 | 10.62 | 175.00 | 24.68 |
| 27.00 | 4.02 | 103.00 | 8.23 | 176.00 | 4.99 |
| 29.00 | 13.54 | 104.00 | 4.21 | 177.00 | 1.75 |
| 35.00 | 16.52 | 105.00 | 14.31 | 179.00 | 0.97 |
| 36.00 | 58.61 | 106.00 | 2.66 | 182.00 | 1.17 |
| 37.00 | 5.31 | 107.00 | 9.52 | 183.00 | 0.97 |
| 38.00 | 19.17 | 108.00 | 1.23 | 186.00 | 1.81 |
| 39.00 | 8.61 | 109.00 | 0.97 | 189.00 | 6.35 |
| 41.00 | 35.75 | 115.00 | 12.89 | 190.00 | 14.96 |
| 42.00 | 1.55 | 116.00 | 5.18 | 191.00 | 37.69 |
| 43.00 | 6.02 | 117.00 | 14.44 | 192.00 | 5.89 |
| 47.00 | 10.10 | 118.00 | 1.55 | 193.00 | 2.72 |
| 49.00 | 3.49 | 119.00 | 13.47 | 195.00 | 1.10 |
| 51.00 | 4.59 | 120.00 | 2.78 | 196.00 | 1.10 |
| 52.00 | 1.42 | 121.00 | 6.54 | 197.00 | 1.42 |
| 53.00 | 4.73 | 123.00 | 1.42 | 198.00 | 1.17 |
| 55.00 | 8.49 | 127.00 | 2.91 | 199.00 | 1.42 |
| 57.00 | 100.00 | 128.00 | 6.09 | 200.00 | 2.20 |
| 58.00 | 4.47 | 129.00 | 5.12 | 201.00 | 1.88 |
| 59.00 | 1.49 | 130.00 | 3.24 | 204.00 | 1.36 |
| 63.00 | 2.59 | 131.00 | 6.28 | 205.00 | 2.98 |
| 64.00 | 1.75 | 132.00 | 2.78 | 206.00 | 6.54 |
| 65.00 | 4.02 | 133.00 | 7.12 | 207.00 | 4.59 |
| 66.00 | 1.75 | 134.00 | 1.49 | 208.00 | 1.29 |
| 67.00 | 4.02 | 135.00 | 3.69 | 209.00 | 1.23 |
| 68.00 | 0.97 | 137.00 | 4.92 | 212.00 | 1.55 |
| 69.00 | 1.17 | 138.00 | 2.39 | 213.00 | 1.88 |
| 72.00 | 1.49 | 139.00 | 4.02 | 214.00 | 2.46 |
| 73.00 | 7.84 | 140.00 | 1.04 | 220.00 | 4.27 |
| 74.00 | 2.85 | 141.00 | 3.11 | 221.00 | 2.53 |
| 75.00 | 2.07 | 142.00 | 2.27 | 222.00 | 1.49 |
| 77.00 | 9.78 | 143.00 | 2.46 | 223.00 | 2.33 |
| 78.00 | 2.78 | 144.00 | 1.29 | 224.00 | 1.74 |
| 79.00 | 5.64 | 145.00 | 3.95 | 225.00 | 6.02 |
| 80.00 | 15.28 | 146.00 | 2.07 | 226.00 | 1.55 |
| 81.00 | 14.05 | 147.00 | 9.59 | 227.00 | 2.53 |
| 82.00 | 49.29 | 148.00 | 2.66 | 228.00 | 1.55 |
| 83.00 | 17.36 | 153.00 | 1.04 | 233.00 | 1.17 |
| 84.00 | 23.51 | 155.00 | 1.49 | 235.00 | 1.55 |
| 85.00 | 2.27 | 156.00 | 1.04 | 236.00 | 2.33 |
| 86.00 | 25.84 | 157.00 | 2.01 | 237.00 | 1.55 |
| 87.00 | 3.43 | 158.00 | 1.81 | 238.00 | 1.88 |
| 88.00 | 11.59 | 159.00 | 2.98 | 239.00 | 1.88 |
| 89.00 | 9.65 | 160.00 | 1.88 | 240.00 | 3.89 |
| 90.00 | 4.40 | 161.00 | 3.63 | 241.00 | 1.36 |
| 91.00 | 53.04 | 162.00 | 1.29 | 245.00 | 1.36 |
| 92.00 | 1.68 | 163.00 | 4.79 | 250.00 | 3.89 |
| 93.00 | 1.29 | 169.00 | 1.68 | 251.00 | 3.37 |
| 94.00 | 1.68 | 170.00 | 1.29 | 252.00 | 1.88 |
| 95.00 | 5.69 | 171.00 | 1.17 | 253.00 | 1.36 |
| 96.00 | 1.49 | 172.00 | 3.89 | 255.00 | 4.86 |
| 98.00 | 1.62 | 173.00 | 6.74 | 256.00 | 5.44 |

Table 64 (cont.)

| M/E | RELATIVE INTENSITY | M/E | RELATIVE INTENSITY |
|--------|-----------------------|--------|-----------------------|
| 257.00 | 1.62 | 363.00 | 1.42 |
| 258.00 | 1.88 | 368.00 | 1.29 |
| 259.00 | 2.46 | 369.00 | 5.77 |
| 260.00 | 2.91 | 370.00 | 2.59 |
| 261.00 | 1.55 | 371.00 | 3.24 |
| 265.00 | 0.97 | 372.00 | 1.10 |
| 267.00 | 1.17 | 384.00 | 1.42 |
| 269.00 | 2.46 | 386.00 | 0.84 |
| 271.00 | 2.14 | 399.00 | 7.77 |
| 273.00 | 0.97 | 400.00 | 2.65 |
| 274.00 | 2.85 | 401.00 | 4.08 |
| 275.00 | 2.39 | 402.00 | 1.23 |
| 276.00 | 2.78 | 403.00 | 0.85 |
| 277.00 | 0.91 | 427.00 | 0.45 |
| 280.00 | 2.46 | 428.00 | 0.39 |
| 281.00 | 4.08 | 429.00 | 0.32 |
| 282.00 | 2.14 | 430.00 | 0.19 |
| 283.00 | 4.08 | 439.00 | 0.26 |
| 284.00 | 1.04 | 440.00 | 0.26 |
| 286.00 | 1.42 | 441.00 | 1.23 |
| 288.00 | 1.04 | 442.00 | 0.53 |
| 290.00 | 0.91 | 443.00 | 0.71 |
| 291.00 | 21.37 | 444.00 | 0.32 |
| 292.00 | 4.27 | 445.00 | 0.19 |
| 293.00 | 7.06 | 456.00 | 0.32 |
| 294.00 | 2.07 | 458.00 | 0.13 |
| 295.00 | 7.19 | 459.00 | 1.36 |
| 296.00 | 2.07 | 460.00 | 0.45 |
| 297.00 | 3.37 | 471.00 | 2.27 |
| 298.00 | 0.91 | 472.00 | 0.78 |
| 306.00 | 1.55 | 473.00 | 1.23 |
| 307.00 | 2.20 | 474.00 | 0.45 |
| 309.00 | 1.17 | 475.00 | 0.26 |
| 310.00 | 10.68 | 494.00 | 0.26 |
| 311.00 | 2.91 | 496.00 | 1.75 |
| 312.00 | 5.25 | 497.00 | 0.52 |
| 313.00 | 1.94 | 498.00 | 0.52 |
| 314.00 | 1.17 | 512.00 | 3.43 |
| 318.00 | 2.01 | 513.00 | 1.17 |
| 323.00 | 14.77 | 514.00 | 1.29 |
| 326.00 | 4.27 | | |
| 327.00 | 81.61 | | |
| 328.00 | 13.60 | | |
| 329.00 | 48.58 | | |
| 330.00 | 7.77 | | |
| 331.00 | 8.74 | | |
| 332.00 | 1.75 | | |
| 333.00 | 1.36 | | |
| 341.00 | 12.24 | | |
| 342.00 | 2.33 | | |
| 343.00 | 8.16 | | |
| 344.00 | 1.26 | | |
| 345.00 | 1.75 | | |
| 354.00 | 1.94 | | |
| 355.00 | 1.42 | | |
| 356.00 | 1.29 | | |
| 361.00 | 1.49 | | |

Short courses attended during the period 1967 - 1970 in
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- 'Applications of Mass Spectrometry.' (6 lectures)
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- 'Spectroscopic methods in Organometallic Chemistry.'
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