STUDIES OF THE MECHANISM OF OXIDATION AT BENZYLIC CARBON BY CHROMYL CHLORIDE

by

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ABSTRACT

The reactions of chromyl chloride with aromatic hydrocarbons have been reviewed.

The adducts formed from toluene and benzyl chloride have been shown by chemical and physical methods to consist of benzaldehyde co-ordinated to the reduced chromium. A range of other adducts have been similarly investigated, and the results are discussed.

The kinetics of oxidation of a series of substituted toluenes and benzyl chlorides has been investigated. The results obtained have been correlated with the Hammett relationship. It has been possible to show that the oxidations proceed through a cyclic transition stage. The kinetic results have been investigated using Exner's criterion.

A series of new compounds, involving substituted benzaldehydes co-ordinated to chromic chloride have been prepared.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

1. INTRODUCTION

Certain compounds of the first series of transition elements are commonly used as oxidizing agents in organic chemistry (95,120). The best known examples are chromic acid and permanganate. Many other transition metal compounds have also been used as oxidants, for instance compounds of cobalt III, vanadium IV, manganese III, and various compounds of chromium VI. This expanding field is currently causing considerable interest, especially as regards mechanism (120). However it is evident that some compounds although potentially interesting are not receiving the attention they deserve. One such coqound is chromyl chloride.

Chromyl chloride (CrO_2Cl_2) is unusual in being a deep red, transparent, volatile liquid, mp. -96•5, bp. 115•7. It is extremely hygroscopic, reacts with many compounds explosively and causes skin ulceration if used with impropriety. Chromyl chloride, however has received attention as an oxidising agent, because a carbonyl compound is often the product (42) in contrast to the more usual carboxylic acid.

A thorough study of the literature dealing with this compound showed, somewhat surprisingly, that although many oxidation products have been identified, little is known about its role as an oxidant. Unlike the majority of oxidations by transition metal compounds which are carried out in aqueous or acetic acid solution, (120) the reactions of chromyl chloride are carried out in non-polar solvents (42). This allows for the isolation of solid intermediates; no comparable intermediates are obtained during the more usual oxidations, involving transition metal ions. It has therefore been suggested (107) that chromyl chloride oxidations offer a unique opportunity to obtain mechanistic information which might well be relevant to other transition metal oxidations.

It was therefore decided to investigate the oxidation of aromatic hydrocarbons with chromyl chloride, with special reference to the mechanism involved.

The following historical survey has been arranged in three parts because this allows the clearest presentation of the available information. The first section deals with the oxidation products of various reactions, the second reviews the structures postulated for the intermediate adduct and the final section deals with the proposed mechanisms.

CHAPTER II

HISTORICAL SURVEY

II. HISTORICAL SURVEY

a) Oxidation products

The work prior to that of Etard, has been summarized first because the reaction conditions were not those now normally used. This can cause marked differences in the products formed.

Thomson (102), 1827 was the first to study the reaction of chromyl chloride with organic compounds. He studied the reaction of chromyl chloride with various compounds including turpentine, olive oil, camphor and absolute alcohol the oxidations being carried out without a solvent. He reported that many of the reactions were violent.

The next researcher was Walter (106) who also attempted a reaction with absolute alcohol. The mixture exploded and inflamed, badly burning him: he abandoned further work.

Nothing further was attempted until the work of Carstanjen (13) thirty years later. He was responsible for more work than subsequent authors have credited him with. The first reaction he studied was between chromyl chloride and benzene: the reaction was violent, and therefore he added acetic acid as a solvent in all subsequent reactions. Carstanjen studied many compounds. Naphthalene and anthracene, for instance gave quinones and chloroquinones which he considered showed that chromyl chloride was acting simultaeously as an oxidizing and chlorinating agent.

With phenol, tri- and tetra-chloroquinones formed, and with nitrobenzene, instead of the expected chloronitroquinones, Carstanjen reported an acid, thought to be trichloronitrobenzoic acid (now thought to have come from nitrotoluene, an impurity) and an unidentified lachrymatory substance. Aniline gave yellow crystals on hydrolysis of the reaction mixture: these were not identified, although Rohde (14) considered that they might well be a quinone.

Carstanjen was surprised by the products he obtained from toluene and its homologues. He had postulated that either the ring only, or the ring and side chain would be attacked. Instead only the side chain was attacked, yielding in the case of toluene, benzoic acid. Similarly xylene and mesitylene gave toluic and mesitylenic acids respectively. Quantities of anhydrides were also isolated from the reaction mixtures which led Carstanjen to postulate that anhydrides were the initial products, which were then converted to the acids on hydrolysis.

Diphenyl gave benzoic acid by rupture of a benzene ring. Although doing no further experimental work Carstanjen suggested numerous topics for further study.

After Carstanjen came the most prolific worker—the French chemist Etard—after whom the oxidations, embodying chromyl chloride have subsequently been named. Although his work is excellent (20-32) some of his conclusions are erroneous, due to the incomplete knowledge of structural chemistry at his time. He initially repeated Carstanjen's work with toluene but used non-polar solvents, in place of acetic acid. Etard did not use acetic acid as a solvent as did Carstanjen, because he found that there was a reaction between chromyl chloride and acetic acid forming a compound (92) reported as: $Cr_2O_7 \cdot 2(Cr_2(C_2H_3O_2)_5) \cdot 8H_2O$. In attempting to find a suitable solvent Etard treated carbon disulphide and chloroform with chromyl chloride and found that although both reacted at elevated temperatures in sealed tubes, little reaction occured at normal temperatures. Etard chose to use carbon disulphide because the temperature of the reaction, could then not exceed 46°, the boiling point of carbon disulphide. Other solvents, (42) especially carbon tetrachloride, have been used by later workers. It should be emphasized that it was only the use of such non-polar solvents that enabled Étard and subsequent workers to isolate the brown amorphous adducts so characteristic of these reactions.

For convenience the remainder of this section is arranged in a number of parts, each dealing with the oxidation of related compounds.

i) Oxidation of benzenes and substituted benzenes.

Étard (21) reported that benzene formed an adduct analysing as $C_6H_4.2(CrO_2Cl)$, hydrogen chloride being expelled during the reaction. However no solvent was used and, indeed the reaction solution was boiled. The adduct gave on hydrolysis, a quinone. Gragerov and Ponomarchuk (37) reacted a mixture of benzene and monodeuterobenzene with chromyl chloride at room temperature, to show that the oxidation did not proceed with an isotope effect. No evolution of hydrogen chloride occurred during the oxidation and the adduct was found to analyse as $C_6H_6.2(CrO_2Cl_2)$.

Etard (21) reported that bromoquinone, p-dibromoquinone, chloroquinone and dibromo-p-quinone were formed on hydrolysis of the adducts obtained by heating chromyl chloride and the corresponding halogeno benzenes. As the product from nitrobenzene Etard reported nitroquinone: this was subsequently shown by Henderson and Campbell (45) to be nitrobenzoic acid, presumably due to contamination by nitrotoluene. Hartford and Darrin (42) found that if chromyl chloride and nitrobenzene were heated at 100°, in chloroform solution hydrogen chloride was evolved and a dark brown precipitate obtained. This was found to analyse approximately as $C_6H_5NO_2.2(CrO_2Cl_2)$ and to regenerate nitrobenzene on hydrolysis.

Etard (21) reported a vigorous reaction between phenol and chromyl chloride although carbon disulphide was used as solvent. The hydrolysis product was reported as bis-hydroxyphenyl ether. Using a saturated solution of sulphur dioxide to hydrolyse the adducts from o- and p-cresol, Etard found that quinones were formed.

ii) Oxidation of poly-aromatics.

Like Carstanjen, Etard (21) obtained quinones from naphthalene and anthracene and reported that the products were difficult to isolate as they remained attached to the chromium. They also retained chlorine as was subsequently authenticated by Haller (40) who took special precautions to obtain chlorine free chromyl chloride.

Phenanthrene according to Cristol and Eilar (15) formed a 2:1 adduct if the reaction solution was warmed, but a 1:1 adduct at room temperature. The adducts gave phenanthraquinone on hydrolysis (46). A series of methyl substituted naphthalenes, anthracenes and phenanthracenes as well as the parent compounds were studied by Wheeler (112). In all cases quinones resulted accompanied in a few cases by aldehydes. Yields of the quinones varied from 12 to 70%. Wheeler also reported (113) that α and β tetralone resulted from tetralin, whilst indane gave low yields of α and β indanones.

Weiler (106,109) reported the customary two moles chromyl chloride addition product with p-p'-ditolyl. Hydrolysis gave mainly a resinous product although a small quantity of p-(p'-tolyl)benzaldehyde was also obtained.

Oxidation of 4-methyl-2-nitrodiphenyl and 4-methyl-4-nitrodiphenyl gave moderately good yields of the corresponding 4-aldehydes according to Grieve and Hey (38).

Weiler (108,109) reported that the methylene group of diphenyl methane was attacked by chromyl chloride and that on hydrolysis a quantitative yield of benzophenone was obtained. The adduct had the usual two mole chromyl chloride to one mole hydrocarbon constitution. Nenitzescu et al. (73) decomposed the diphenylmethane adduct with glacial acetic acid containing an excess of sodium azide. The products, identified by infra red spectroscopy, were reported as benzhydryl azide, benzophenone, benzhydrol and benzhydryl acetate. These workers also decomposed the diphenylmethane adduct, using a solution of SO_2 in acetic acid, reporting the products as benzophenone and benzhydrol. Wiberg and Eisenthal (119) considered the formation of the benzhydrol to be the result of reduction of the carbonyl compound by the SO_2, rather than the result of incomplete reaction. However the possibility of such a reduction was shown by Nenitzescu et al. (74) to be unlikely. They carried out the hydrolysis as before but with addition of carbon tetrachloride to remove the products as they formed. They still isolated alcohol.

Schafarik (86) and later Schiff (87) obtained an adduct from triphenylmethane containing one mole of chromyl chloride and one of hydrocarbon, but neither reported the hydrolysis product. Slack and Waters (91) also reported the adduct as a 1:1 addition compound. Recently, Nenitzescu et al. (74) reported that the adduct has a composition corresponding to, two moles of chromyl chloride and one of hydrocarbon, and that the product of hydrolysis is triphenycarbinol. They also reported that, on hydrolysis of the adduct using a concentrated solution of sodium azide, a 90% yield of triphenylmethylazide, with a small quantity of triphenylmethylcarbinol, was obtained. Sulima and Gragerov (99) oxidized triphenylmethane using one and one half equivalents of chromyl chloride obtaining a 90% yield of triphenylcarbinol. Thus, as stated by Wiberg, (120) only one equivalent of chromyl chloride is necessary, and the initial product appears to form a second compound by addition of a further mole of chromyl chloride, if the latter is in excess. Sulima and Gragerov also reported the regeneration of triphenylmethane if the adduct was decomposed with ether. Using water enriched with ^{18}O they also found that the adduct gave triphenylcarbinol with an increased ^{18}O content, indicating that 80% of the oxygen came from the water and only 20% from the oxidizing agent. This they considered showed that two adducts were formed, one giving triphenylcarbinol directly the other via hydrolysis of liberated triphenyl chloride. Gragerov and Ponomarchuk (37) showed that the analysis of the triphenylmethane adduct varied with various methods of preparation, but approximated a 1:1 adduct. They also showed, using a mixture of triphenylmethane and triphenyldeuteromethane, that the oxidation proceeded with a considerable isotope effect. These workers reported that triphenylchloromethane did not react with chromyl chloride. Nenitzescu et al. (74) confirmed that ether regenerated the hydrocarbon from the adduct and reported that the efficient hydride donor, cycloheptatriene, also caused this regeneration.

The main product from the oxidation of dibenzyl, according to Weiler (108,109) was the cleavage product, benzaldehyde, although reasonable yields of benzophenone, benzoic acid, benzyl chloride and benzal chloride were also obtained.

According to Weiler (108,109) p-benzyltoluene formed the customary two to one adduct which on hydrolysis gave a 62% yield of phenyl-p-tolyl ketone, as well as a smaller quantity of p-benzylbenzaldehyde.

iii) Oxidation of toluene and substituted toluenes.

As the solvent in the oxidation of toluene Etard (21) chose carbon disulphide. During the reaction a dark brown precipitate was obtained, which on hydrolysis gave benzaldehyde: no further hydrolysis products were detected. It has been reported subsequently (74) that under special solvolysis conditions, (using tert-butyl alcohol saturated with SO_2) up to 17% benzyl alcohol can be obtained. Etard found the adducts to be extremely hygroscopic and experienced difficulty in obtaining reliable analysis figures, but eventually found the composition of the complex to be $C_6H_5CH_3.2(CrO_2Cl_2)$. He reported that at 240-250° the adduct decomposed losing half its chlorine as hydrogen chloride, and that further heating resulted in the formation of an unidentified, volatile chloro-organic compound. Chromic oxide remained.

The compound obtained by the loss of the hydrogen chloride gave, on hydrolysis, benzaldehyde in high yield. Etard (21) also found that the original adduct was soluble in glacial acetic acid and ether, although Gibson, Robertson and Sword (36) later claimed that carefully dried ethyl ether had no effect. Etard reported that ethyl chloride as well as benzaldehyde was formed if the adduct was decomposed by the above mentioned solvents.

From the filtrate from the reaction with toluene, Etard isolated benzyl chloride which led him to believe that it was an intermediate in the formation of the toluene adduct. He therefore studied the reaction between chromyl chloride and benzyl chloride. However two factors made him realise that benzyl chloride could not be an intermediate in the oxidation of toluene. Firstly, the rate of reaction of the benzyl chloride was slower than with toluene, so much so that Etard had to concentrate the solution and maintain it at 30-40°. Secondly the benzyl chloride adduct analysed as $C_6H_5CH_2Cl.CrO_2Cl_2$, involving only one mole of chromyl chloride. However, hydrolysis of this adduct gave benzaldehyde. Heating to 170-180° expelled hydrogen chloride from the adduct and formed a compound analysing as $C_6H_5CHCl.CrO_2Cl$. Etard came to the conclusion that the benzyl chloride formed in the toluene reaction came from free chlorine in the chromyl chloride. Hartford and Darrin suggested accidental chlorination (42), possibly photochemically initiated.

Having studied a compound containing an α chlorine Etard next studied a compound containing a halogen in the ring (21), namely p-bromotoluene. No solvent was used and the composition of the adduct formed was found to be $C_6H_4brCH.2(CrO_2Cl)$ which Etard considered had formed from the expected adduct: $C_6H_4brCH_2.2(CrO_2Cl_2)$ by loss of hydrogen chloride, because of the heat of reaction. Hydrolysis gave mainly p-bromobenzoic acid and a lesser quantity of the bromoaldehyde. Stuart and Elliott (96) using a diluent obtained a 37% yield of the aldehyde. Wheeler (111) reported good yields of the aldehydes from p-fluoro, p-chloro, p-bromo and p-iodotoluenes. He also stated that, as the size of the halogeno atom increased the ease of oxidation decreased.

Wheeler reported a low yield of p-chloromethylbenzaldehyde from p-methylbenzyl chloride showing preferential attack of the methyl group.

Boon (7) reported a 50% yield of 2-nitroanisaldehyde from 4-methoxy-2-nitrotoluene.

Stuart and Elliott (96) studied the reaction between chromyl chloride and o-chloro, o-bromo, and o-iodotoluenes. The hydrolysis products were: from o-chlorotoluene, o-chlorobenzaldehyde; from o-bromotoluene a mixture of o-bromobenzaldehyde and o-bromo-benzal chloride; and from o-iodotoluene, almost exclusively o-iodobenzal chloride. This led these workers to suggest that the initial hydrolysis product was benzal chloride which was then converted to the aldehyde. However as Rohde (84) states this is unlikely since a temperature in the region of 140-170° is required to effect such a conversion. Wheeler (111) reported high yields of the aldehydes from o-chloro and o-bromotoluenes as well as a 14% yield of o-iodobenzaldehyde from the iodotoluene.

Etard (25,26) reported that, instead of the aldehyde, nitrotoluquinone was formed as the hydrolysis product when chromyl chloride was reacted with a mixture of o- and p-nitrotoluenes. The reaction was performed without a solvent, and at 200°. Ozone was reported to have been evolved. Later work by von Richter (80) showed the hydrolysis product to be p-nitrobenzoic acid. He also repeated the reaction using milder conditions obtaining the customary adduct, which gave the nitroaldehyde in 70% yield. Wheeler (111) also reported obtaining p-nitrobenzaldehyde from p-nitrotoluene. With o-nitrotoluene von Richter (80) obtained a two mole chromyl chloride addition product which gave on hydrolysis only a trace of the aldehyde, regenerating mainly o-nitrotoluene. Wheeler (111) repeated the oxidation obtaining a 7% yield of aldehyde. Other workers (37) have also obtained traces of o-nitrobenzoic acid.

According to von Richter (80) two nitro groups render the compound inert to oxidation, for instance no reaction occurred with m-dinitrotoluene.

Wheeler (111) obtained a small yield of unidentified organic material from p-cyanotoluene, and no reaction with p-methoxy, p-hydroxy, and p-mercaptotoluenes.

iv) Oxidation of higher arylalkanes.

According to Etard (29) xylenes formed the usual type of adduct, as well as an unidentified chloro-compound. Etard reported m-methyl benzaldehyde on hydrolysis of this adduct. Thus Etard claimed that the reaction could be used to separate the isomeric xylenes. Bornemann (8) and Weiler (108,109) have reported obtaining yields of 70-80% of o-tolualdehyde and m-tolualdehyde from o- and m-xylene respectively. Wheeler (111) found that the three isomeric xylenes reacted at similar rates and gave similar yields of aldehyde.

Etard (24) found that the usual adduct formed from mesitylene, and gave mesitylenealdehyde on hydrolysis. Higher methylated homologues also react, and, if unsymmetrical, yield mixed aldehydes.

Ethyl benzene and chromyl chloride, according to Etard (21) formed the characteristic adduct: $C_6H_5CH_2CH_3.2(CrO_2Cl_2)$. Evidence for phenylacetaldehyde and acetophenone as hydrolysis products was obtained. Miller and Rohde (70) also obtained a cleavage product (benzaldehyde) thus showing that chromyl chloride could attack either the methyl or methylene group, or both. However Wheeler could only isolate phenylacetaldehyde and acetophenone in almost equal yields (113).

Two moles of chromyl chloride were found to react with one of diethylbenzene according to Etard (21) and on hydrolysis of the adduct, unidentified aldehydes and ketones were obtained.

The reaction with n-propylbenzene gave an adduct analysing for $C6H_5CH_2CH_2CH.2(CrO_2Cl)$ considered by Etard (21) to have formed from the characteristic 2:1 adduct by loss of hydrogen chloride. On hydrolysis of this adduct hydrocinnamaldehyde was obtained. The chief products of this reaction were later reported as benzyl-methyl-ketone, propiophenone and benzaldehyde, together with a lesser quantity of benzal chloride and unidentified chloroketones by Dollfus (16) and von Miller and Rohde (70). An intensive study of this reaction was undertaken by Wiberg, Marshall and Foster (117). They confirmed, using n-propyl-D_2-benzene, that hydrogen migration occurred during the oxidation. Also they found that the concentrations of the reactants influenced the ratio of the ketonic products. A considerable quantity of 1-phenyl-chloropropane was isolated from the supernatant liquid as well as quantites of the ketones. Nenitzescu et al. (73) decomposed the n-propyl benzene adduct with a saturated aqueous solution of sulphur dioxide, obtaining as well as the already mentioned ketones, some 1-phenyl-1-propanol, and suggested a carbonium intermediate. The formation of such an intermediate was considered highly improbable by Wiberg and Eisenthal (119). A further study of this oxidation was undertaken by Nenitzescu et al. (79), who could not isolate any ketonic material from the supernatant liquid, and found all the 1-chloro-1-phenylpropane in the supernatant liquid. They thus suggested that the results of Wiberg et al. indicated that they, neither excluded moisture from their filtration nor washed the adduct adequatly. They found, however that the quantity of 1-chloro-1-phenylpropane varied from 1 to 30%. They isolated six hydrolysis products. Apart from the already mentioned products, 1-phenyl-2-chloro-1-propane, 1-phenyl-1-propene and 1-phenyl-1-chloro-2-propanone were isolated. When the hydrolysis was performed using a saturated solution of SO_2, 1-phenylpropan-1-ol was also obtained.

From cymene Etard found cumaldehyde as the hydrolysis product. However, subsequently von Miller and Rohde (70) showed that the main products were p-tolyl-methyl-ketone and p-methyl-hydratropaldehyde. This indicates preferential attack at the isopropyl group.

Although stating that p-amylmethylbenzene reacted normally Etard (30) did not identify the hydrolysis products.

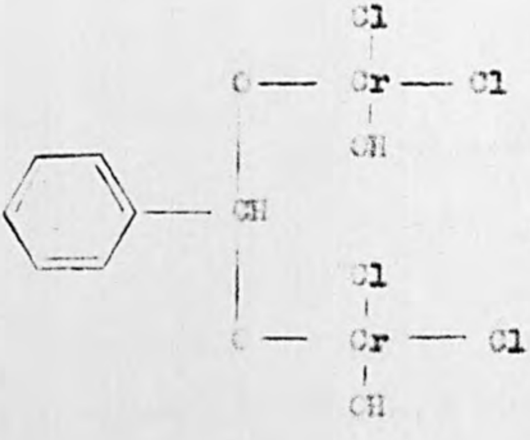
Etard reported that the hydrolysis products from cumene were hydratropaldehyde and acetophenone. This was confirmed by Wheeler (113) who obtained nearly equal quantities of the two products.

Tert-butylbenzene has been reported as inert towards chromyl chloride by many workers. Wheeler (113) reported finding weak carbonyl bands in the infra-red spectrum of the recovered tert-butylbenzene, though no precipitate formed with 2,4-dinitrophenylhydrazine.

b) Structure of the adducts.

It is accepted (73,113) that although many oxidations involving chromyl chloride have been studied especially in order to identify hydrolysis products, the structures of the intermediate adducts have not been completely elucidated. The following account has been arranged chronologically to demonstrate how the various theories of structure, have oscillated in popularity.

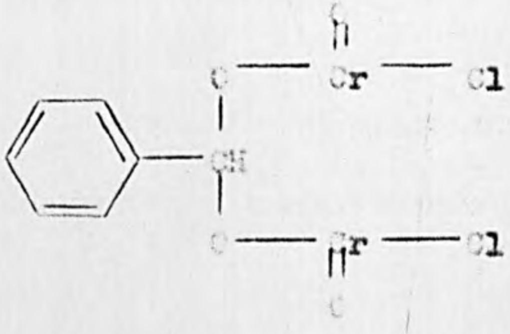
Etard (21), the first worker to obtain these adducts, postulated structure 1 for the adduct from toluene. No evidence was offered for this, however.



(1).

This structure contains two chromium atoms in an oxidation state of four. A stable solid containing chromium in this state, was a revolutionary idea. However intermediate valency states have since been detected during chromic acid oxidations by Westheimer (110) and many other workers (95,120). Also, solid compounds containing chromium in the oxidation states of four and five are now known, for instance, barium chromate IV, (89) and barium hypochromate (88).

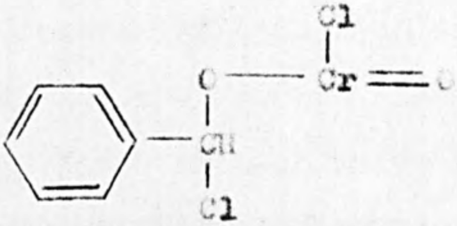
As already mentioned, on heating the adducts lose hydrogen chloride, and for the compound fromed from the toluene adduct Etard (21) assigned structure II, again containing two chromium atoms in a valency state of four, but again, for no sound reason.


(II).

Structures III and IV represent the corresponding adducts, in the case of benzyl chloride.


(III).

Then loss of hydrogen chloride to give:-

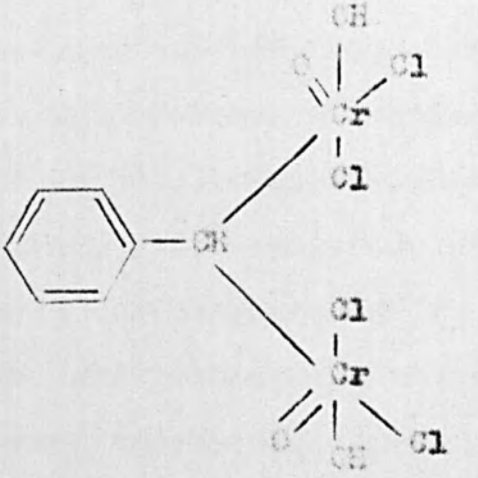


(IV).

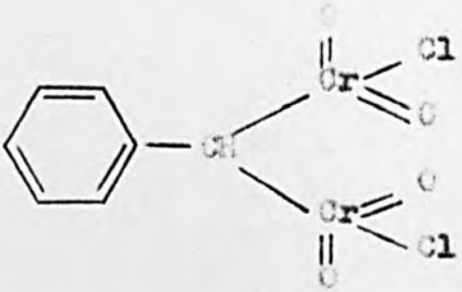
Etard formulated structures of the above form for all the cases that he studied.

No further attempt to assign structures was made until the review by Rohde (84), all Etard's contemporaries being content to study the hydrolysis products only.

Rohde believed the adducts to be organometallic, the toluene adduct having structure V.



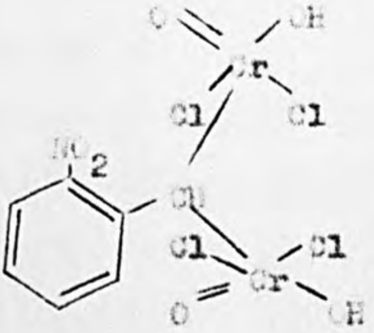
Here the chromium has a valency state of six. Rohde considered that this structure was more in keeping with the adduct's reaction with water, than was Etard's. He stated that the adducts instability towards water was because of the carbon-chromium bond. He then used his structure to demonstrate how the adducts were decomposed by ether and alcohol. For the compound obtained from the toluene adduct on heating, structure VI was proposed by Rohde.



(VI).

Rohde considered that the usual addition product formed during the reactions carried out by Carstanjen (13), but the excess acetic acid then caused the benzaldehyde to be liberated, and this was further oxidized, especially if the solution was not cooled, as was the case in Carstanjen's work.

The next mention of structure appears in a paper by Slack and Waters (91), forty years later. They concluded, after a consideration of results from chromic id, and chromyl chloride oxidations of 1:2 glycols, at the initial complex had the structure V, that oposed by Rohde, but then reacted further, so that the nal adduct had structure I proposed by Etard. Further, n the case of o-nitrotoluene, they considered the final duct to have a Rohde type structure VII. This assumption s based on the observation that o-nitrotoluene was leased on hydrolysis of the adduct.



(VII).

Slack and Waters postulated for this case at the strong electron with-drawing effect of the cinal nitro group, does not allow electron abstraction the chromium so that further rearrangement is inhibited.

In their review Hartford and Darrin (42) t forward six points which they considered any structure uld have to account for, namely;

). Usually two moles of the chromyl chloride unite with e mole of the organic compound, with considerable evolution of heat, and a change in colour.

b). Hydrolysis usually yields aldehydes and ketones, although chlorinated products, quinones, acids and other products may be formed.

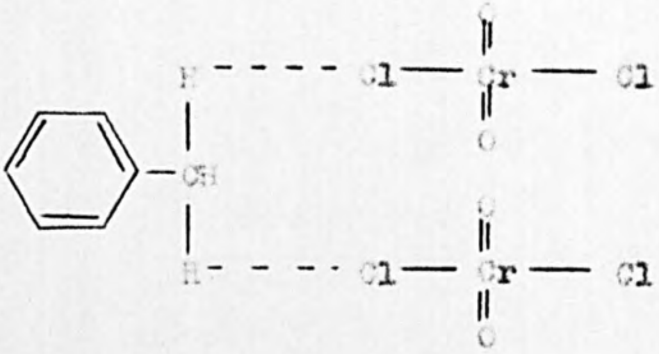
c). On heating the complex, half the chlorine is driven off as hydrogen chloride.

d). Certain materials, particularly nitro compounds, regenerate the original organic compound on hydrolysis.

e). With some compounds, particularly terpenes, rearrangement of structure occures.

f). Chromium (VI) possesses tetrahedrol co-ordination.

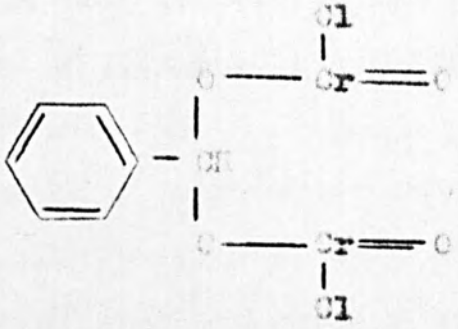
Hartford and Darrin dismissed Etard's structure I, because it could not explain the regeneration of nitro compounds on hydrolysis. They pointed out that a co-ordination number of five for chromium (VI), as required for Rohde's structure V, was unlikely. Hartford and Darrin also stated that the adducts are unlike the true organo-chromium compounds which have a π electron or sandwich structure (34,43,122). They postulated that the adducts are formed by utilization of hydrogen bonds. Two possibilities were considered, VIII and IX.



(VIII).

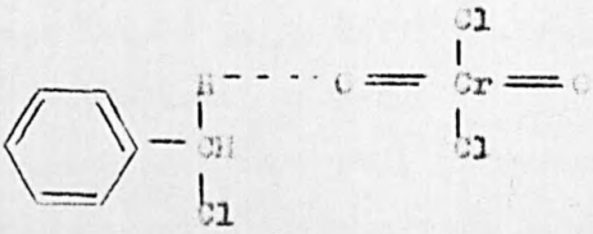
(IX).

Both formulae will explain the regeneration of the hydrocarbon on hydrolysis, and the tetrahedral co-ordination of chromium (VI) is retained in both. However on heating VIII would form a carbon-chromium bond, by loss of hydrogen chloride, hence Hartford and Darrin prefered structure IX, which on heating would lose half its chlorine as hydrogen chloride to form a compound X, having a carbon-oxygen-chromium chain.



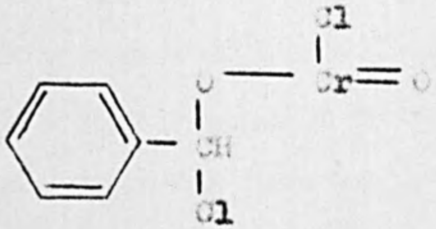
(X).

The corresponding structures according to Hartford and Darrin for the benzyl chloride case would be structures XI and XII



(XI).

XI on heating would give XII by loss of hydrogen chloride:



(XII).

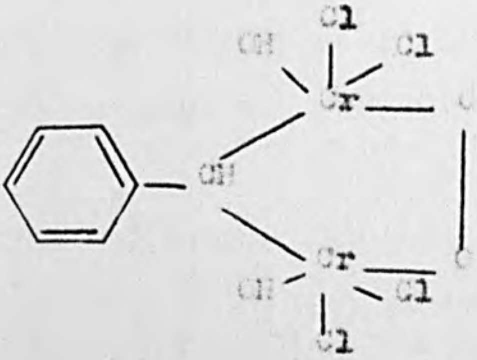
Hartford and Darrin pointed out the main objection to their structure was the high heat of formation of the adducts but suggested that electron displacement during bond formation might cause the oxygen to assume a partial single bond character and thus in effect produce chromium (V).

In the same year as the above review the first of the papers by Wheeler (111) was published. He reported the results of his studies with sixteen substituted toluenes and claimed to have obtained spectroscopic evidence for the rapid formation of a soluble complex during the oxidation. This he considered to be a σ or π complex between the aromatic ring and the chromyl chloride formed in an initial step, before precipitation of the usual adduct.

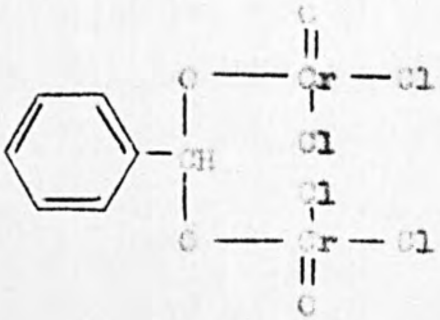
Sulima and Gragerov (99) treated a number of different adducts with heavy oxygen labeled water. In the case of the toluene adduct no conclusions could be reached because rapid exchange of the oxygen occurred, between the benzaldehyde formed and the labeled water, this was confirmed in a separate experiment. They considered however that their results were in agreement with the adduct having the structure suggested by Etard I. They disagreed with the structure suggested by Hartford and Darrin IA, because the formation of the proposed hydrogen bonds would not explain the heat of formation of the adducts. Hydrogen bonds they pointed out are more stable the greater the tendency of the hydrogen to ionise, thus complexes with nitrotoluenes, and especially dinitrotoluenes would be expected to form readily; this does not occur.

Sulima and Gragerov hydrolysed an o-nitrotoluene adduct with heavy hydrogen labeled water. They reported that no deuterium was incorporated into the o-nitrotoluene liberated, and therefore concluded that neither Etard's structure, nor the structure suggested by Slack and Waters VII, could explain this case.

In his second paper Wheeler (113) pointed out that the structures suggested by Rohde and by Hartford and Darrin, V and IX contained chromium VI, whilst those in the structure suggested by Etard I, were chromium IV. He also considered that the following two structures XIII and XIV, were possible, even though XIV was depleted in hydrogen. In both these structures the chromium atoms are chromium V.



(XIII).

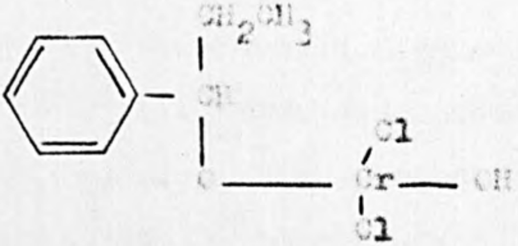


(XIV).

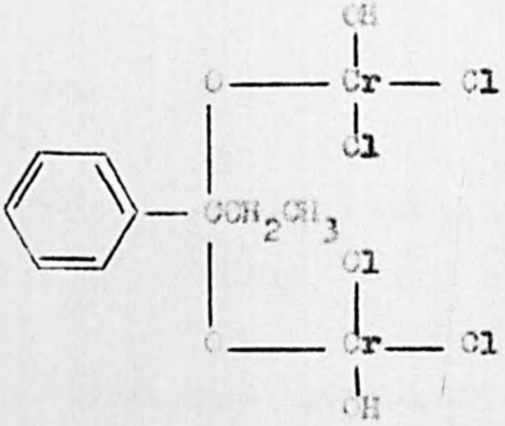
To differentiate between the structures, Wheeler determined the valency state of the chromium by the Gouy balance method, obtaining a value of 3·16 Bohr magnetons which corresponded to, two unshared electrons. Thus he considered the chromium to be tetravalent, and the correct structure to be given by I, the Etard structure.

Stairs (93) measured the rate of reaction of chromyl chloride and toluene in a number of solvents. Applying his results to equations by Hildeband (48) and Kirkwood (60), which correlate the influence of solvent on the rate of chemical reaction, Stairs concluded that the complex in Etard's reaction was more polar than the starting materials, but probably not polar enough to be ionic.

The oxidation of n-propylbenzene by chromyl chloride was studied by Wiberg, Marshall and Foster (117) who suggested that an intermediate XV initially formed, which, depending on the conditions, reverted wholly or partly to the normal Etard structure XVI.

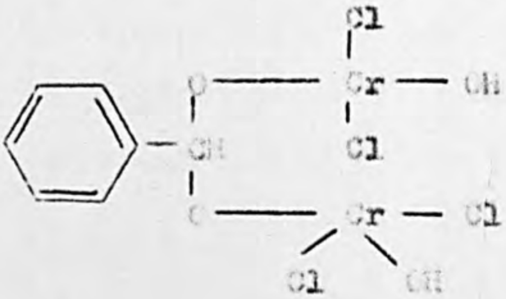


(XV).



(XVI).

Gragerov and Ponomarchuk (37) showed that the oxidation of toluene proceeded with a considerable isotope effect by studying the oxidation of a mixture of toluene and monodeuterated toluene. They came to the conclusion that the complex was not a single compound on the basis of their analysis figures. In a similar experiment, Gragerov and Ponomarchuk came to the conclusion that o-nitrotoluene and chromyl chloride formed two complexes of different structures, one giving o-nitrobenzaldehyde enriched in deuterium the other regenerating the o-nitrotoluene with mean isotopic composition. The latter adduct they considered, was either a σ or π complex which possibly reverted to the normal type of Etard structure XVII. This complex would then give the o-nitrobenzaldehyde on hydrolysis.

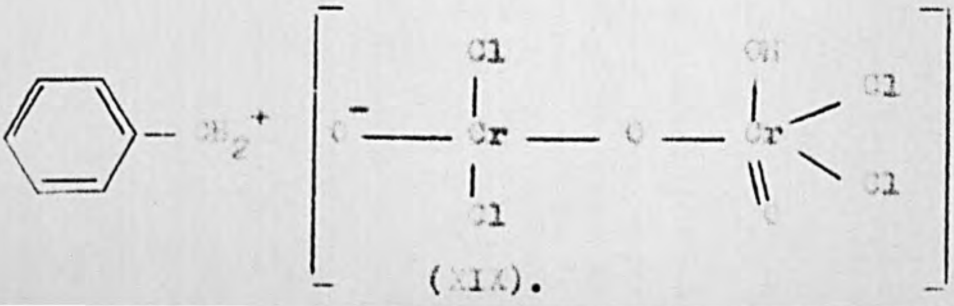


(XVII).

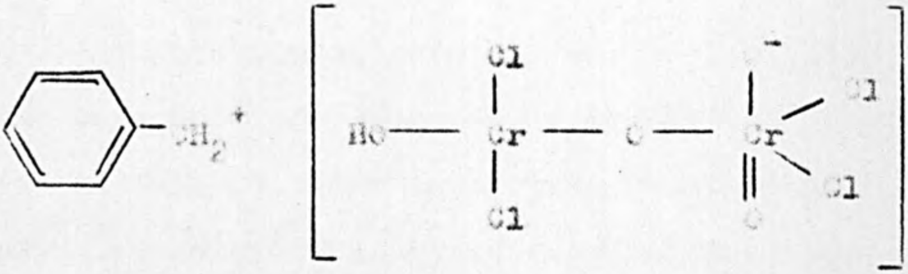
The nitrobenzyl chloride in the reaction solution was considerably enriched in deuterium.

The results of a study of the toluene adduct using E.S.R. was reported by Nenitzescu et al. (73). They reported that half the chromium atoms appeared to be paramagnetic and half diamagnetic and thus chromium (VI). They also attempted to measure the spectroscopic splitting factor, and thus determine the valency state of the paramagnetic chromium atoms. However they found that there was no difference between the splitting factor of tri and quadrivalent chromium, therefore E.S.R. could not be used to differentiate between the valency states. They also stated that, during the formation of the adducts, only one hydrogen was removed. This conclusion was based on a study of the decomposition of the adducts in the presence of sodium azide. They also thought that the primary hydrolysis products were alcohols which were then converted to the carbonyl product by oxidation during the course of the hydrolysis. These workers considered that the most likely state of the paramagnetic chromium to be four and the adduct best represented by structure XVIII or ion pairs XIX and XX.

(XVIII).

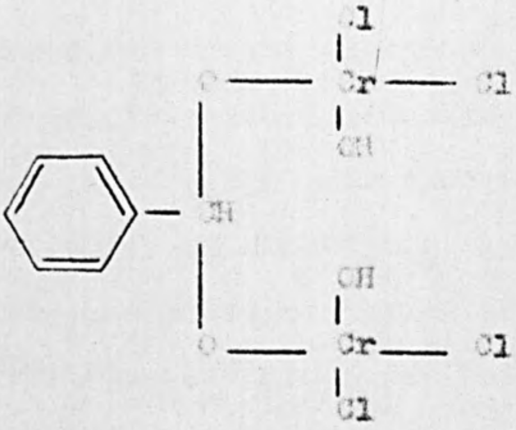


(XIX).



(XX).

Wiberg and Eisenthal (119) published a paper reviewing the evidence relating to chromyl chloride oxidations, with special reference to the foregoing paper of Nenitzescu et al. They recalculated the results of the E.S.R. experiment, and showed that they did in fact indicate that both chromium atoms are chromium (VI). Thus they considered that the adduct had the Etard structure I.



(I).

Unfortunately apaper by Wheeler (114), in which he reported the results of a reaction of chromyl chloride with α,α,α,trideuterotoluene which showed a considerable isotopic effect, was in the process of being published when the above paper by Wiberg appeared. Wheeler rescinded his earlier support of the Etard structure in favour of the structure proposed by Nenitzescu et al.

Further magnetic measurements were reported by Bartecki over a range of temperature; obtained using a Gouy balance. He also obtained the spectra of a number of reaction solutions. Bartecki (3,4) did not agree with Wheeler's claim for the initial formation of a σ or π complex, because the spectra he obtained contained a strong chromyl chloride absorption spectrum, practically identical to the spectrum of this compound, and not sufficiently different to be an indication of a σ or π complex. He also interpreted his spectra in terms of 'Ligand Field' theory, and considered that the results were in keeping with the adducts' having the Etard structure I. He emphatically disagreed with the hydrogen-bonded structure postulated by Hartford and Darrin.

A recent book (120) by Wiberg, confirms

his belief in the validity of Etard's structure.

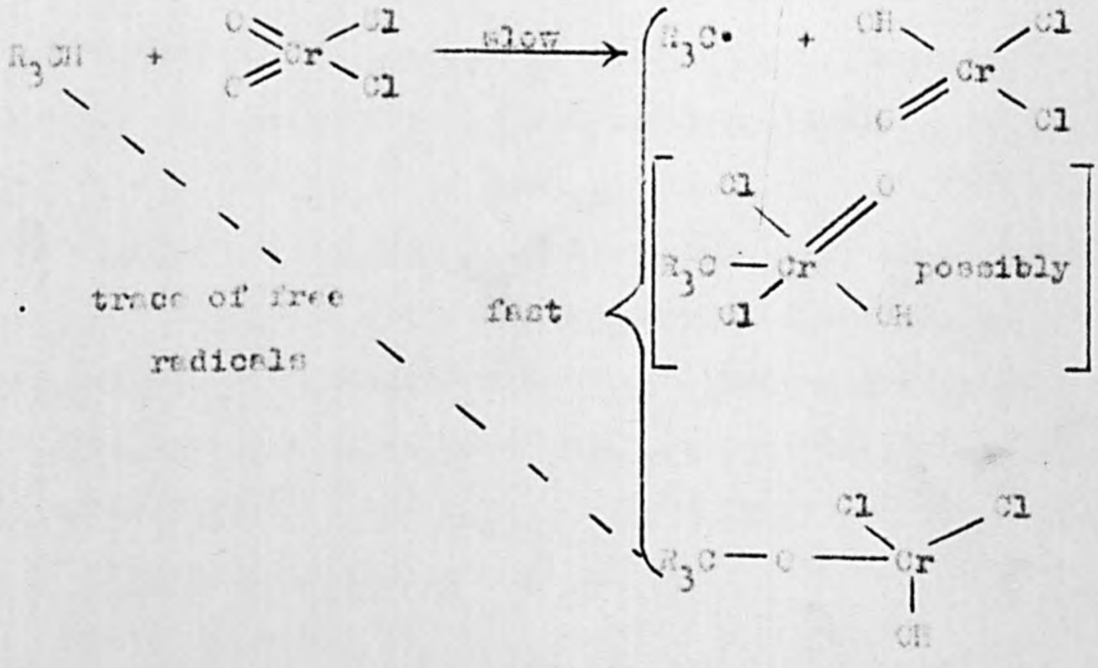
The critisms made by Wiberg and Eisenthal of the findings of Nenitzescu et al. (73) are considered by Nenitzescu et al in a later paper (74). They believe the arguments against their earlier findings to be inconclusive. This paper and one by similar authors (79) reaffirms their belief in their structures XVIII, XIX and XX.

In conclusion the situation can be aptly summarised by this quote from a paper by Nenitzescu (73), "Although the scope and limitations of the Etard reaction havebeen studies, the structure of the complexes formed from chromyl chloride with hydrocarbons in less known."

c). Mechanism.

This, the third and last section, has also been arranged chronologically so that it and the preceding section are complementary.

The first mechanistic scheme appears in the review by Hartford and Darrin (42). They adapted the results of a study of the oxidations of diphenylmethane and triphenylmethane by chromic acid, carried out by Slack and Waters (91), to chromyl chloride oxidations. The mechanism suggested is shown in the following sequence:



Hartford and Darrin however did not favour this free radical mechanism, but preferred hydrogen bonded intermediates.

Although not suggesting a mechanism, Wheeler (111) stated that the U.V. spectrum of the reaction solution during oxidation of toluene by chromyl chloride was evidence for the formation of a π complex, in which chromyl chloride acts as a Lewis acid, and the aromatic ring as the corresponding base.

The lack of kinetic or mechanistic information was noted by Stairs and Burns (92). They therefore decided to study the oxidations of toluene, diphenylmethane and triphenylmethane, by following the reactions iodimetrically. In this technique they determined residual oxidizing power and assumed all the chromium in the adduct to be in the oxidation state of (IV). They could not obtain normal second order curves, except in the case of diphenylmethane, so that they based their conclusions on initial rates. They found that the reactions were first order with respect to both components. For triphenylmethane they suggested that a free radical mechanism was operative, as shown:

$$CrO_2Cl_2 + Ph_3CH \longrightarrow Ph_3C\cdot + HOCrOCl_2$$

$$Ph_3C^\bullet + HOCrCl_2 \longrightarrow PhCOCrCl_2OH \text{ etc}$$

This mechanism, Stairs and Burns argued would be in agreement with the known stability of the triphenyl radical. They considered that ionic attack by Cl, as suggested for olefin oxidations, was unlikely, but thought the involvement of CrO_2Cl^+ possible, if the ionic dissociation:

$$2CrO_2Cl_2 \longrightarrow CrO_2Cl^+ + CrO_2Cl_2^-$$

was not rate determining.

The following two step process was suggested if this was so:

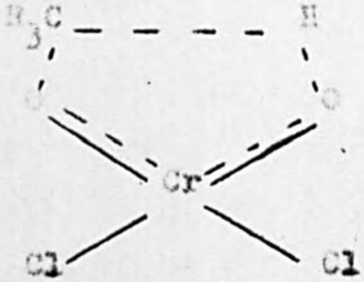
$$CrO_2Cl^+ + \text{hydrocarbon} \longrightarrow \text{complex I.}$$

$$\text{complex I} + CrO_2Cl_2 \longrightarrow \text{complex II.}$$

Stairs and Burns also conducted a single kinetic determination using benzyl chloride, and obtained a rate comparable with that of toluene. This they considered was at variance with both the ionic and free radical mechanisms, which they said would predict a faster reaction for the benzyl chloride. Finally they suggested two further possible mechanisms. The first involved attack by neutral chromyl chloride, so as to result in proton expulsion:

$$CrO_2Cl_2 \quad + \quad R_3CH \longrightarrow (R_3COCrOCl_2)^- \quad + \quad H^+$$

The second mechanism involved a four center activation complex:



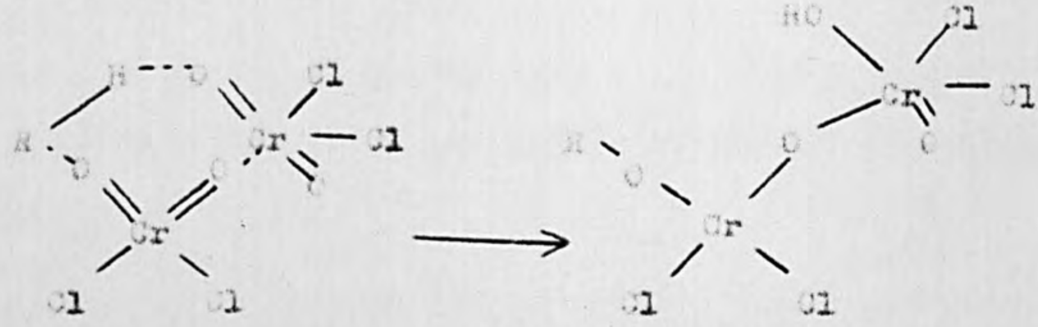
which could rearrange to $R_3COCrCl_2OH$ or if $R_3C\cdot$ was a stable radical, decompose by a homolytic route.

Gragerov and Ponomarchuk (37) reported a considerable isotopic effect in the oxidation of toluene. The exact magnitude of this effect could not be calculated because of side reactions, however the results proved that the rate determining step was the breaking of a carbon-hydrogen bond.

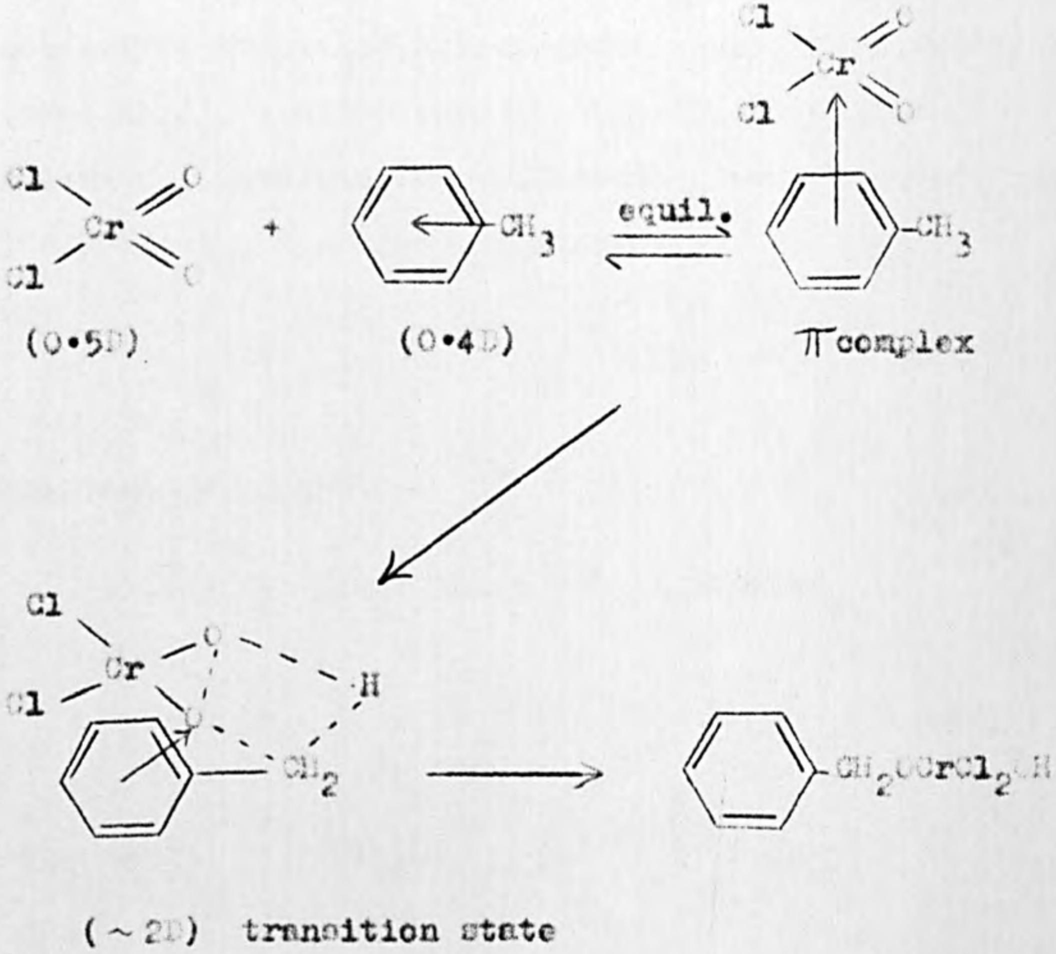
Nenitzescu et al (7[illegible]), reviewed the mechanisms postulated for oxidations with chromic acid and interpreted chromyl chloride oxidations using the conclusions from the review. They concluded that hydride ion transfer was favoured by the existing data. The chromium (VI), they considered, acted as a strong electrophilic reagent and the first step could be represented by:

$$R_3CH \quad + \quad Cr(VI) \longrightarrow R_3C^+ \quad + \quad (HCr(IV))^-$$

They emphasized that the above only represented the electron transfer in the first step and gave no information about the more or less free state of the carbonium ion. For oxidations involving chromyl chloride Nenitzescu et al (37), considered that the facts could best be explained by the formation of a cyclic transition state involving oxidative hydride abstraction as shown:



This would, of course be termolecular. A kinetic study involving a number of m- and p-substituted toluenes was reported by Stairs (94). He interpreted his results using Hammett's relation, obtaining the following values for ρ : $-3{\cdot}94$ at 1°, $-2{\cdot}06$ at 25° and $-1{\cdot}58$ at 40°. These results, Stairs stated, were compatible with the known electrophilic nature of chromyl chloride and a fortiori of species such as CrO_2Cl^+. Stairs explained the rather large value obtained for $\partial \Delta S^{*}/\partial \rho$ as evidence for π complex formation. Stairs (93) had earlier concluded, from a kinetic study of the oxidation of toluene in a number of solvents having differing dielectric constants, that the activation complex did not involve a large change in polarity. He stated that the results of his second kinetic study, might appear to be at variance with this conclusion. He explains the ambiguity in terms of the dipole moment of toluene which he stated would reverse in direction, during the approach of the electrophilic species, thus allowing fairly large movement of electrons with only a moderate increase in dipole moment. He therefore suggested the following scheme in which the arrows and numbers represent the dipole moments.



The paper by Nenitzescu (73) prompted Wiberg and Eisenthal (119) to review again the oxidations involving chromic acid and chromyl chloride, because they considered that the paper by Nenitzescu contained a number of inconsistencies. In both cases Wiberg and Eisenthal considered that hydrogen atom abstraction was the initial step. As they considered cyclic intermediates did not form with chromic acid, they though that it was unlikely that cyclic intermediates would form with the structurally similar chromyl chloride. Results of oxidations involving chromyl acetate were invoked, and the following mechanism suggested:

$$R_3CH \quad + \quad CrO_2Cl_2 \longrightarrow R_3C\cdot \quad + \quad HOCrOCl_2$$

Followed by either:

$$\text{a).} \quad R_3C\cdot \quad + \quad HOCrOCl_2 \longrightarrow R_3COCr(OH)Cl_2$$

$$\text{or} \qquad \longrightarrow R_3CCl \quad + \quad HOCrOCl$$

$$\text{b).} \quad R_3C\cdot \quad + \quad CrO_2Cl_2 \longrightarrow R_3COCrOCl_2$$

$$\text{or} \qquad \longrightarrow R_3CCl \quad + \quad CrO_2Cl\cdot$$

and then:

$$R_3COCrOCl_2 \quad + \quad R_3CH \longrightarrow R_3COCr(OH)Cl_2 \quad + \quad R_3C\cdot$$

or

$$CrO_2Cl\cdot \quad + \quad R_3CH \longrightarrow R_3C\cdot \quad + \quad HOCrOCl$$

In either case they concluded that the first moderately stable intermediate would be:

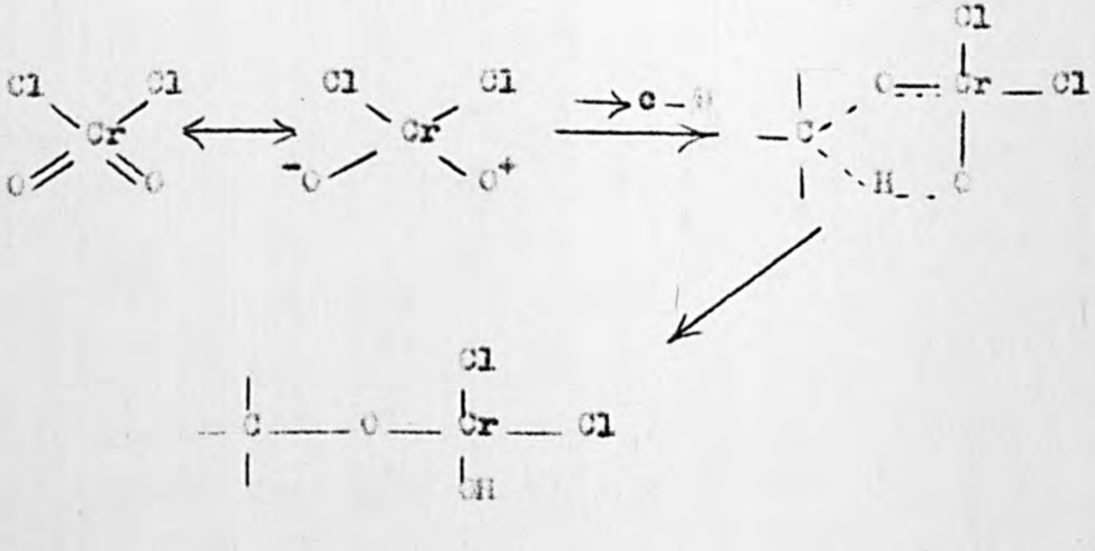
$$R_3C-O-Cr(OH)Cl_2$$

An identical mechanism is given by Wiberg in a recently published book (120).

The conclusion that the rate determining step in the chromyl chloride oxidation of toluene involves the breaking of a carbon-hydrogen bond, was confirmed by Wheeler (114) who obtained a value of 2·4 for k_H / k_D using α,α,α,trideuterotoluene.

Bartecki (3,4) disagreed with Wheeler's claim for the initial formation of a π complex during the oxidations. He argued that the spectrum reported by Wheeler (112) was almost identical to that of chromyl chloride, and differed widely from the spectra that he had obtained for the adducts.

The latest paper published,(22) which was published during the course of this investigation, is by Nenitzescu et al. (22). In this they reiterate their claim that the initial step involves hydride transfer, and include their objections to Wiberg's theory of homolytic fission. They consider that the participation of the 'd' orbitals in the metal oxygen bond, allows one of the oxygens of the chromyl chloride to act as an electrophile, and the other as a nucleophile, during the transition from chromium (VI) to chromium (IV). During the reaction to form the ester intermediate, two new bonds, C=O and O-H are formed, and they consider that the formation of these proceeds simultaneously with the breaking of the carbon-hydrogen bond, through a cyclic transition state as shown. Formally a hydride ion, is transferred from the organic compound to the oxidant.



Nenitzescu et al. also considered that the mechanism of Wiberg was untenable, as it required the free radicals to be retained in solvent cages. This they thought unlikely.

The foregoing historical survey clearly shows, that many inconsistencies exist in the field of chromyl chloride oxidations, and that there is considerable scope for further investigation.

CHAPTER III

DISCUSSION

III. DISCUSSION

a). Structure of the adducts

i). General

The historical survey clearly shows that although the products from various oxidations have been well investigated, there are conflicting theories regarding the structure of the intermediate adducts and the mechanism involved in their production.

The elucidation of the structure of the adducts is, clearly, of prime importance to a study of mechanisms. For instance, if the hydrogen bonded structure postulated by Hartford and Darrin (42) is correct no bond fission would occur until hydrolysis. Alternatively, if the alkoxy structure of Nenitzescu (73,74,79) is correct, one carbon hydrogen bond has been broken at the adduct stage. The Etard structure predicts that two carbon-hydrogen bonds are broken at the adduct stage. The investigation of the structure of the adduct, was therefore made the initial task. The adducts formed from toluene and benzyl chloride, both of which yield benzaldehyde on hydrolysis, were chosen for study. This choice depended on the facts that:

a). toluene presents the simplest possible case, in that only one type of bond is available for reaction, namely a carbon-hydrogen bond; that of a methyl group, attached to a relatively very unreactive benzene ring.
b). the related benzyl chloride forms only a 1:1 adduct, so that all the chromium atoms should be in the same oxidation state.

ii). Search for a solvent

So that physical techniques, for instance U.V. spectroscopy, which had yielded pertinent information in similar problems (121), and N.M.R. spectroscopy, which require a solution of the material under investigation could be used in the investigation, an attempt was made initially to find a suitable solvent for the adducts. Earlier attempts by other workers had met with only partial success. Indeed in a recent paper, Nenitzescu et al. stated;"The determination of the structure of Etard complexes meets with considerable difficulties since owing to their complete insolubility in unreactive solvents, the usual purification methods are not applicable." As the adduct, formed from toluene, has a composition corresponding approximately to two moles of chromyl chloride to one of toluene whereas the benzyl chloride adduct has a chromyl chloride hydrocarbon ratio of one to one, the latter adduct was studied initially, as it was thought that it was probably of simpler structure and therefore was more likely to be soluble.

Because of the conflicting evidence in the literature concerning the effect of diethyl ether, (21,36) this was studied first. It was found that only approximately half the adduct was soluble even in very dry ether, and on distilling the excess ether from the soluble portion, a dark green solid was obtained, which gave ether and benzaldehyde on hydrolysis. Subsequently, pyridine, tetrahydrofuran (T.H.F.) dimethylsulphoxide and dioxane were found to dissolve the adduct. All the above solvents except diethyl ether were found to liberate benzaldehyde from the adducts in the cold. This is evident from the following considerations:

a). The original adduct could not be recovered from any of the solvents used.

b). Reduced pressure distillation of dioxane solutions yielded dark green, voluminous solids from which benzaldehyde and solvent molecules were liberated on hydrolysis; as proved by gas chromatography and infra red spectroscopy. Final fractions of distillate contained large quantities of benzaldehyde. Analysis of residues were indefinite.

c). Infra red spectra of solutions, though complex, were consistent with the presence of dissolved benzaldehyde.

d). Upon standing, the solutions of T.H.F. and dioxane precipitated crystals, purple from the former and green from the latter. This precipitation could be facilitated by addition of carbon tetrachloride. The crystals from T.H.F. were recrystallized from T.H.F. and were found to analysis for; $(T.H.F.)_2CrCl_3.H_2O$. On hydrolysis of these crystals only T.H.F. was detected chromatographically. A similar compound has been reported by Kern, who showed that the T.H.F. was co-ordinated to the chromic chloride, through the oxygen. The $(T.H.F.)_2CrCl_3.H_2O$ was found to have the same infra red spectrum as that reported by Kern (47,58) for his complex, with additional bands from the water. The liberation of benzaldehyde from adducts when treated with pyridine was particularly relevant, because it proved that the carbonyl oxygen, under these conditions at least, must originate from the oxidant, a fact that the isotopic study of Sulima and Gragerov (99) was unable to prove.

iii). Evidence for co-ordination

Concurrently the infra red spectra of the adducts were obtained. Both the adducts gave good infra red spectra as nujol mulls. The only previously recorded spectrum is of the toluene adduct. This was reported by Wheeler (113) who described it as being rather ill defined but showing a hydroxyl group. As can be seen from table 14, and figs. 22 and 23, the infra red spectra obtained from the toluene and benzyl chloride adducts are very similar. As the infra red spectrum of such compounds is predominately associated with the organic component this result suggested that the adducts possessed a common organic constituent. This is inconsistent with any of the postulated structures but accords with the fact that, both the adducts give benzaldehyde, in more than 90% yield on hydrolysis.

The infra red evidence coupled with the fact that the benzaldehyde is liberated from the adducts by strong co-ordination solvents and that the oxygen must come from the chromyl chloride, suggested that the benzaldehyde was already formed, though co-ordinated to the inorganic nucleus at the adduct stage. If this were so, it was reasoned, that other compounds which oxidise

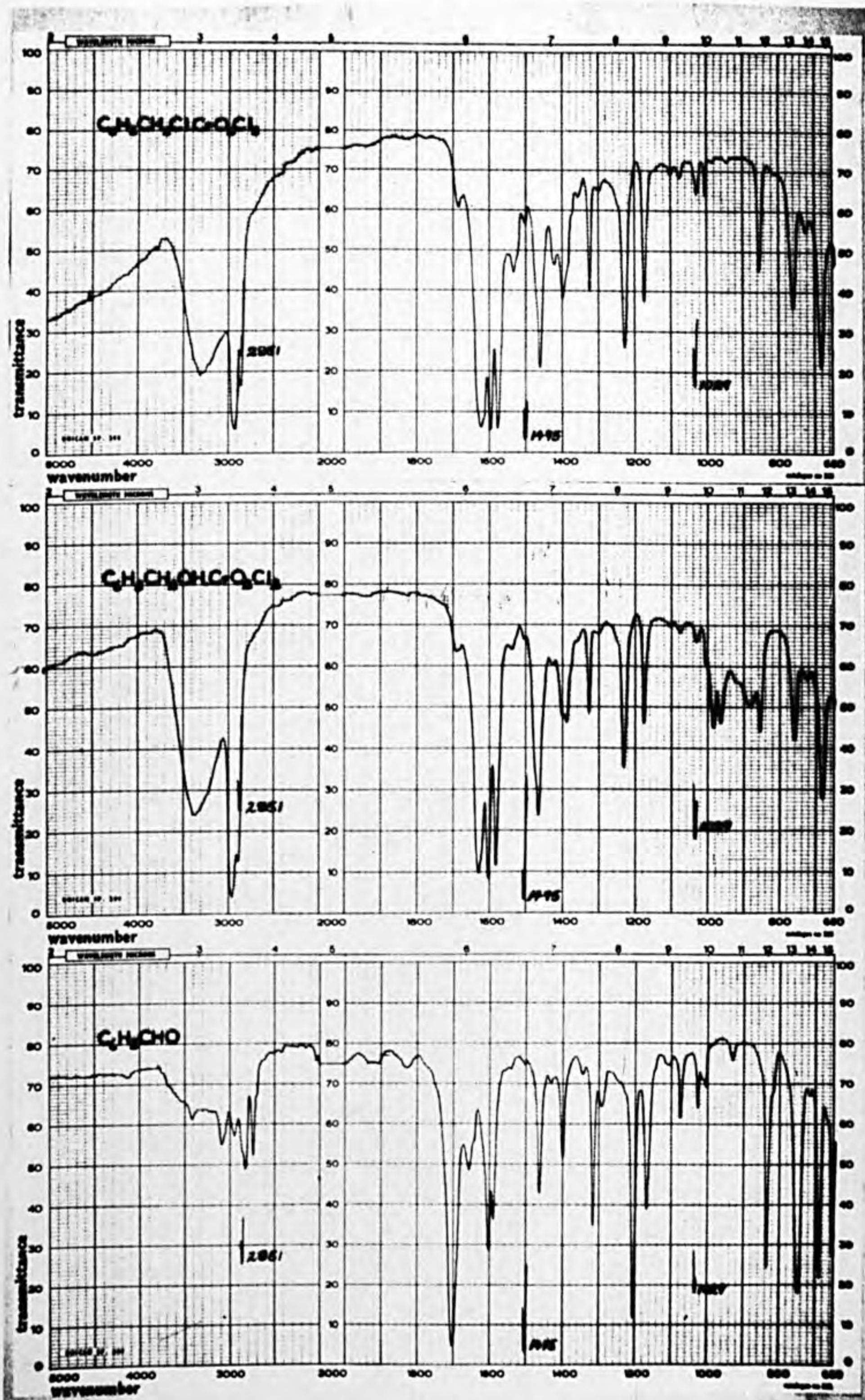

$C_6H_5CH_2ClC=O_2Cl_3$
$C_6H_5CH_2OHC=O_2Cl_3$
C_6H_5CHO
transmittance
wavenumber
wavelength microns
2851
1495
1028
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
0
10
20
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
9
10
11
12
13
14
15

fig. 22.

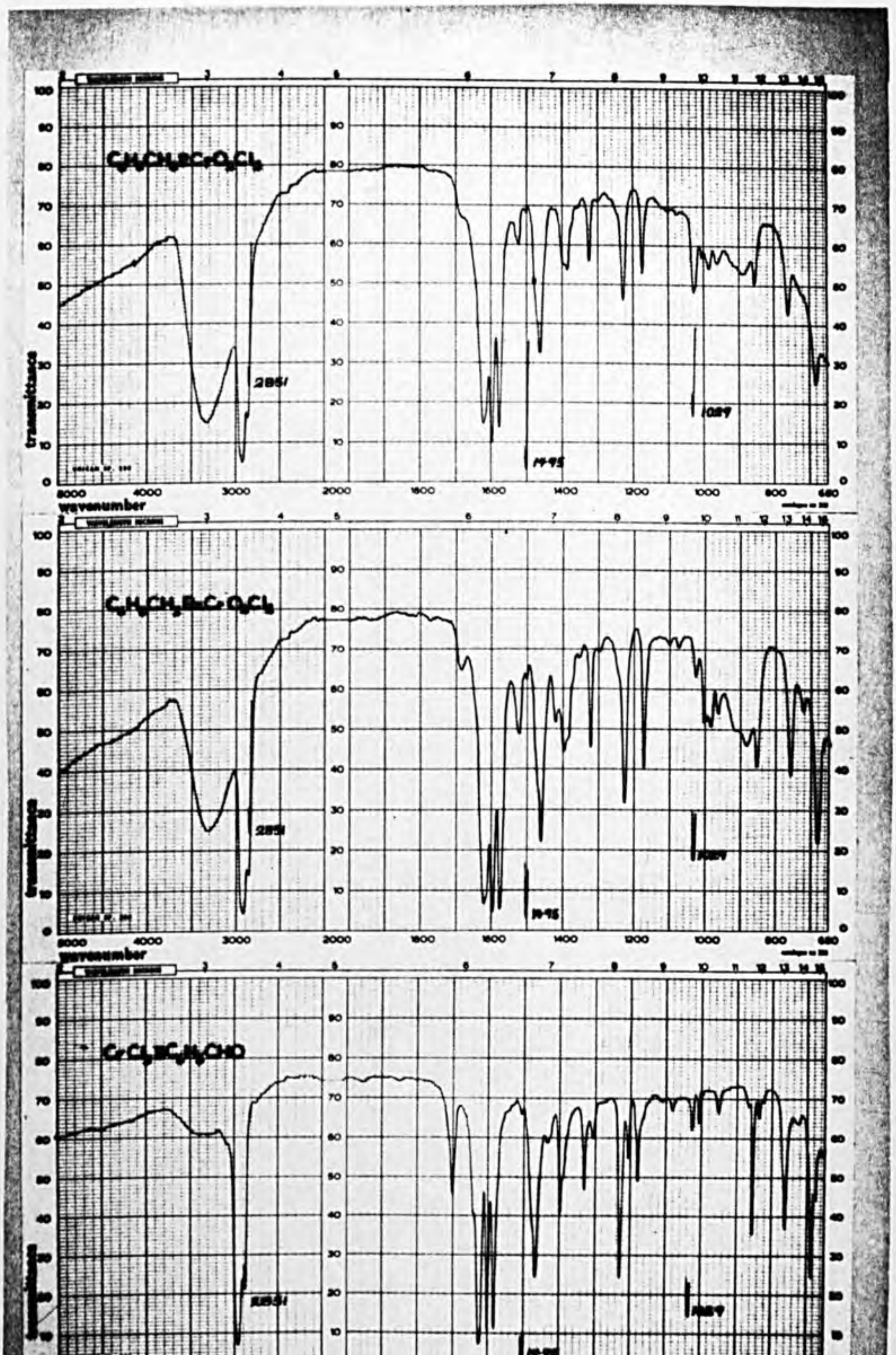

$C_6H_5CH_3 \cdot 2CrO_2Cl_2$
2851
1495
1029
$C_6H_5CH_3 \cdot 2CrO_2Cl_2$
2851
1495
1029
$CrCl_3 \cdot 3C_6H_5CHO$
2851
1495
1029
transmittance
wavenumber
8000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
0
10
20
30
40
50
60
70
80
90
100
2
3
4
5
6
7
8
9
10
11
12
13
14
15

fig. 23.

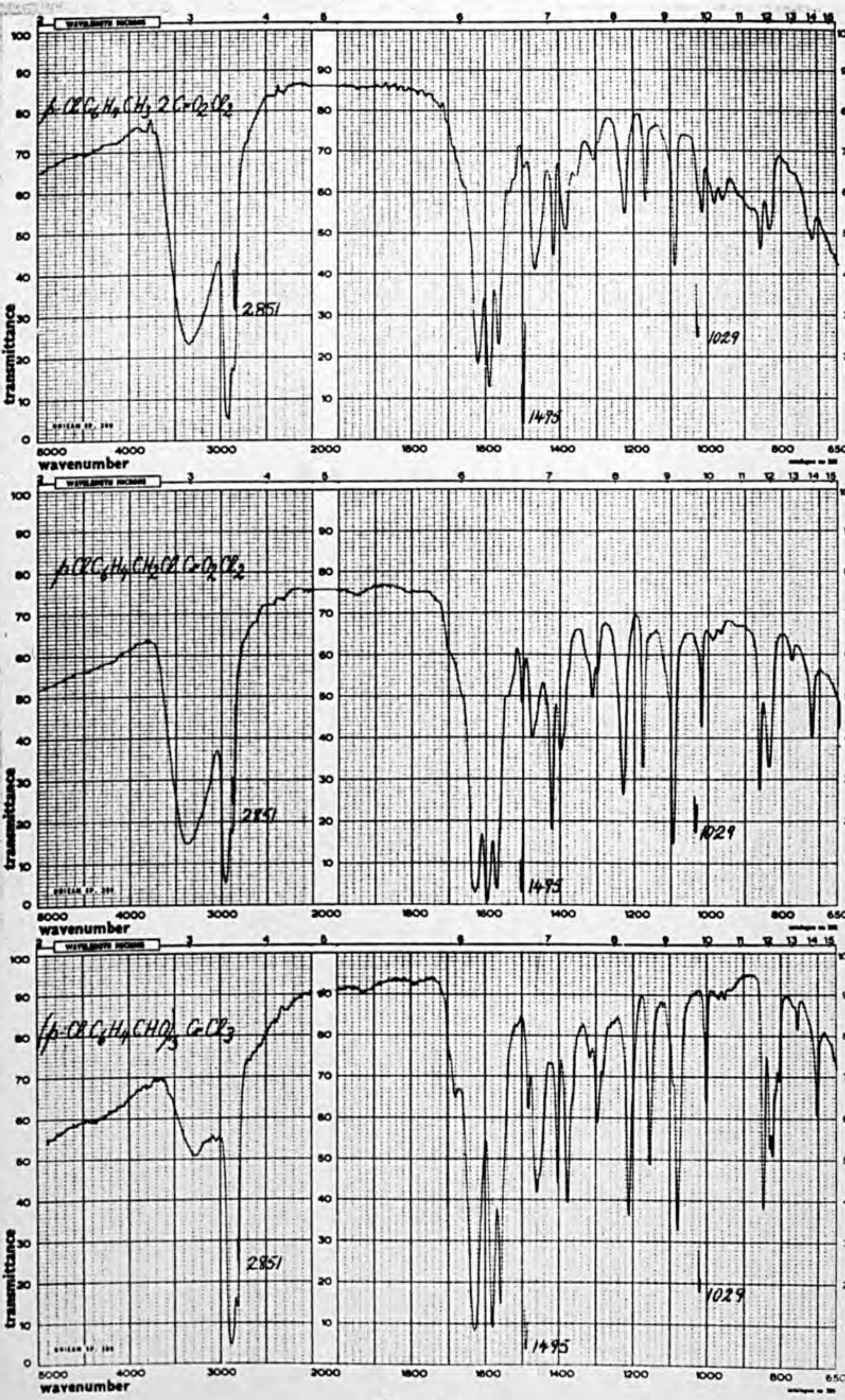

p-ClC6H4CH3 2CrO2Cl2
2851
1495
1029
p-ClC6H4CH2Cl CrO2Cl2
2851
1495
1029
[p-ClC6H4CHO]3 CrCl3
2851
1495
1029
transmittance
wavenumber
WAVELENGTH MICRONS
UNICAM SP. 200
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650

fig 24

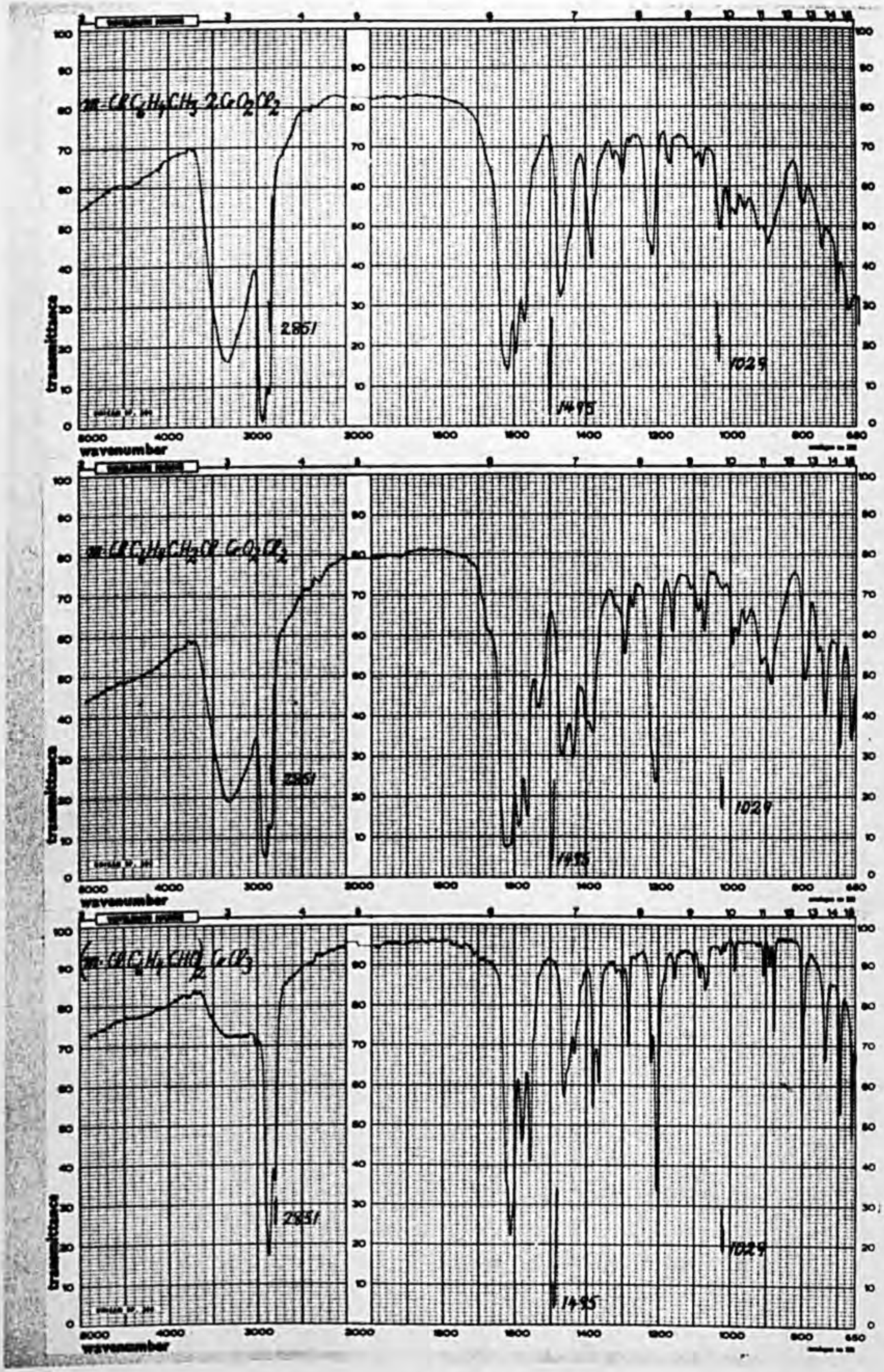

m-ClC6H4CH3·2CrO2Cl2
2851
1495
1029
m-ClC6H4CH2Cl·CrO2Cl2
2851
1495
1029
(m-ClC6H4CHO)2CrCl3
2851
1495
1029
transmittance
wavenumber
0
10
20
30
40
50
60
70
80
90
100
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
2
3
4
5
6
7
8
9
10
11
12
13
14
15

fig 25

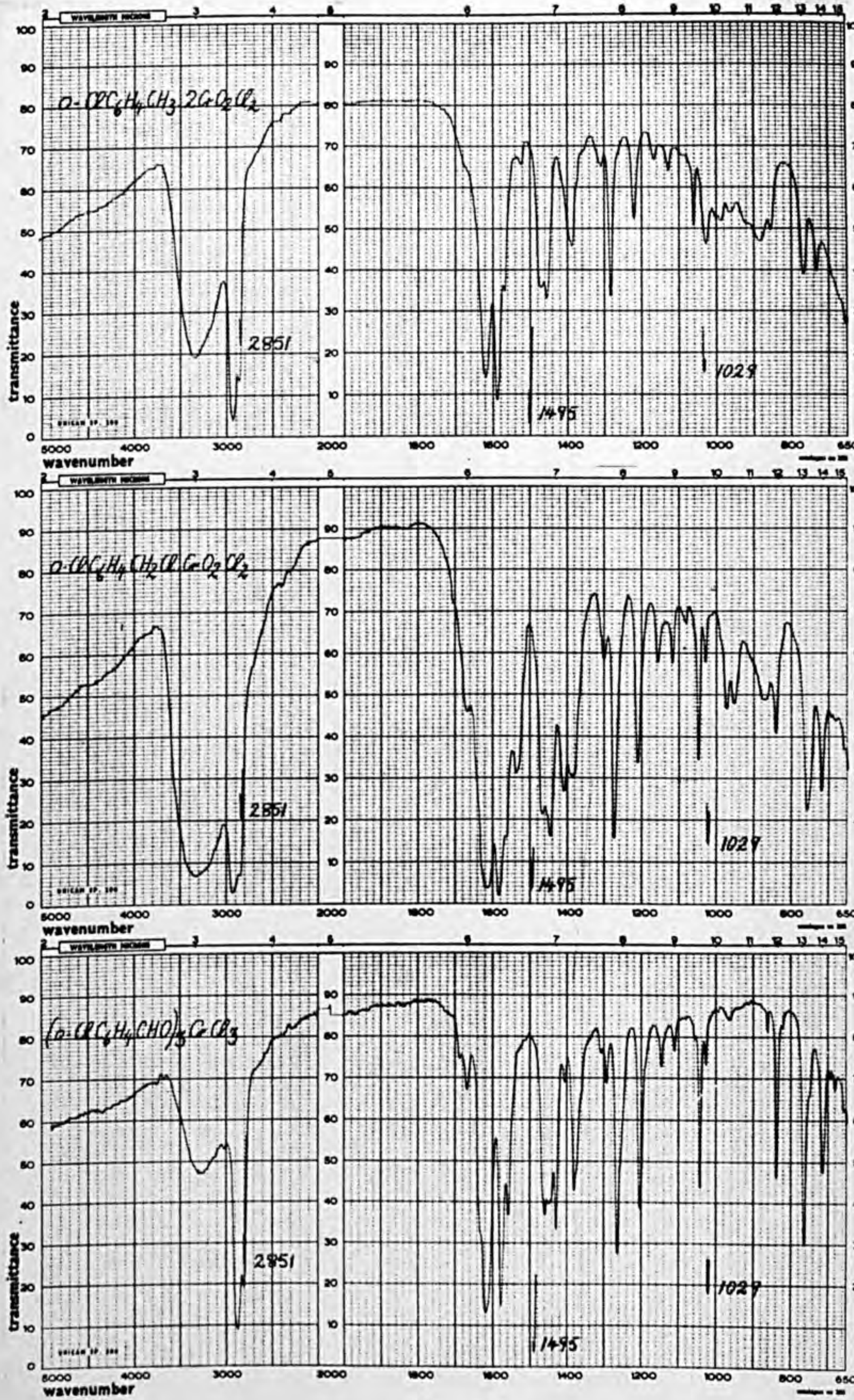

o-ClC6H4CH3 2CrO2Cl2
o-ClC6H4CH2Cl CrO2Cl2
(o-ClC6H4CHO)3 CrCl3
2851
1495
1029
WAVELENGTH MICRONS
2
3
4
5
6
7
8
9
10
11
12
13
14
15
transmittance
0
10
20
30
40
50
60
70
80
90
100
wavenumber
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
UNICAM SP. 200

fig 26

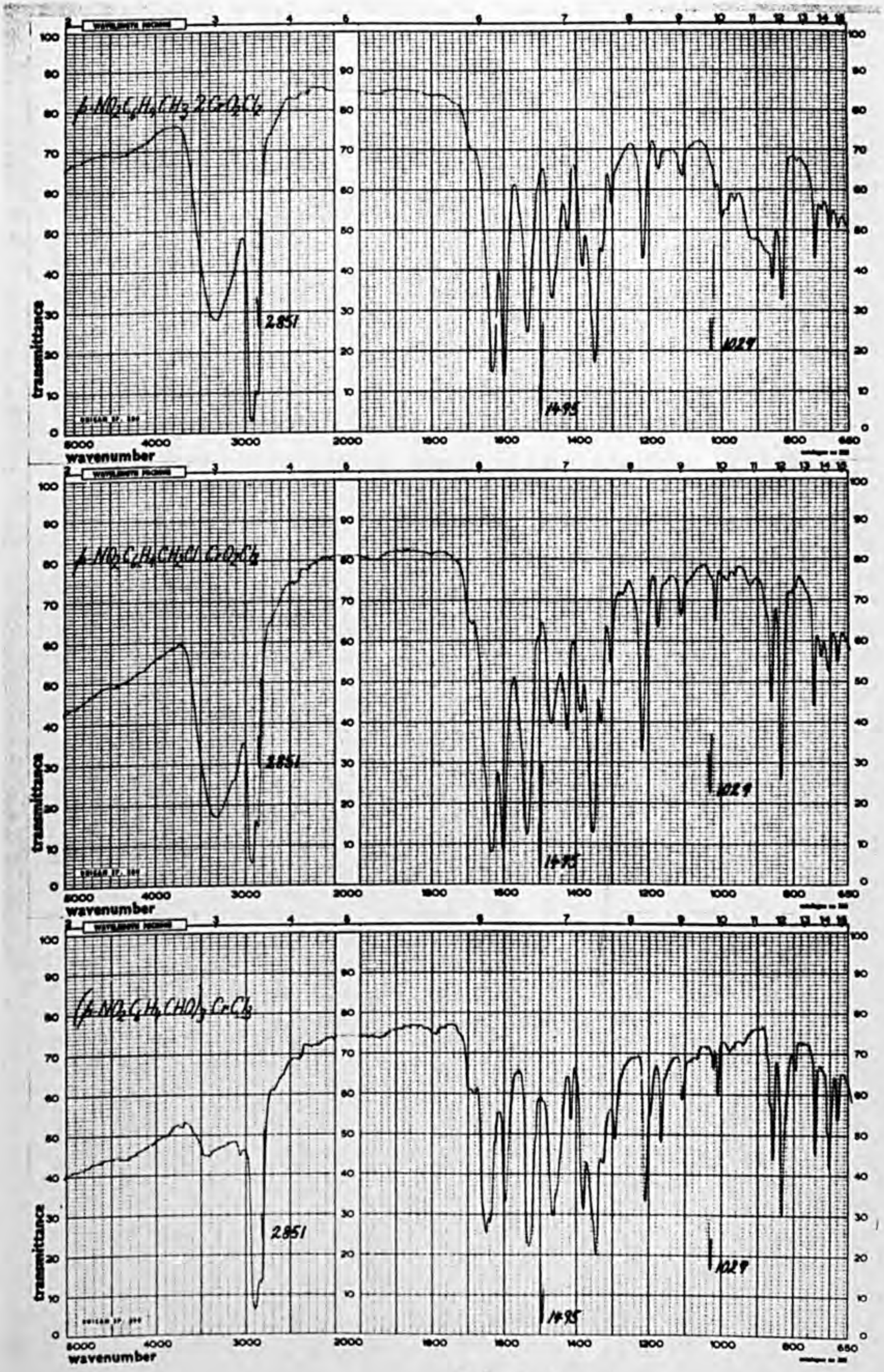

p-NO₂C₆H₄CH₃ 2CrO₂Cl₂
2851
1495
1029
p-NO₂C₆H₄CH₂Cl CrO₂Cl₂
2851
1495
1029
(p-NO₂C₆H₄CHO)₃ CrCl₃
2851
1495
1029
WAVELENGTH MICRONS
transmittance
wavenumber
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
0
10
20
30
40
50
60
70
80
90
100

fig 27

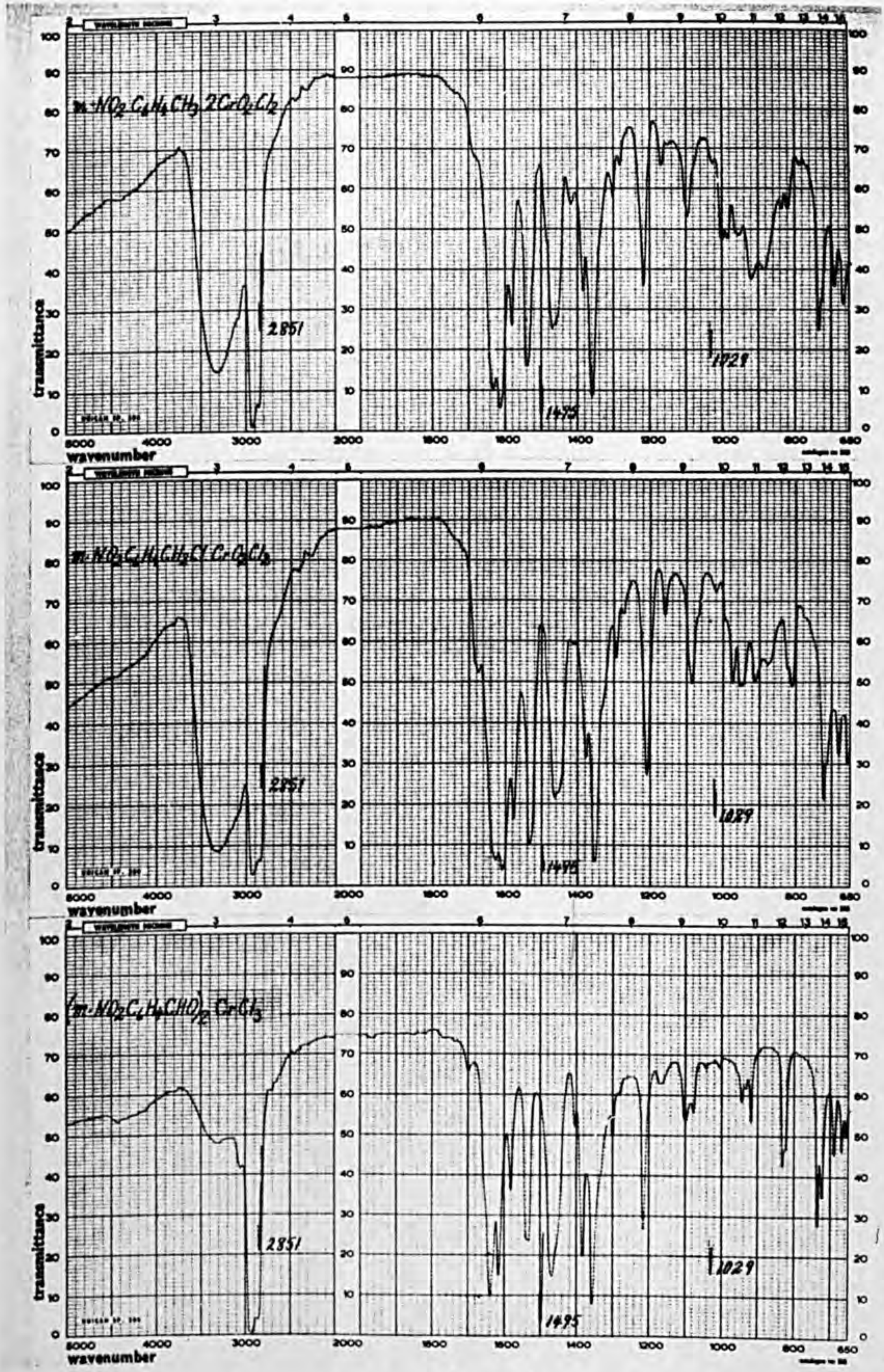
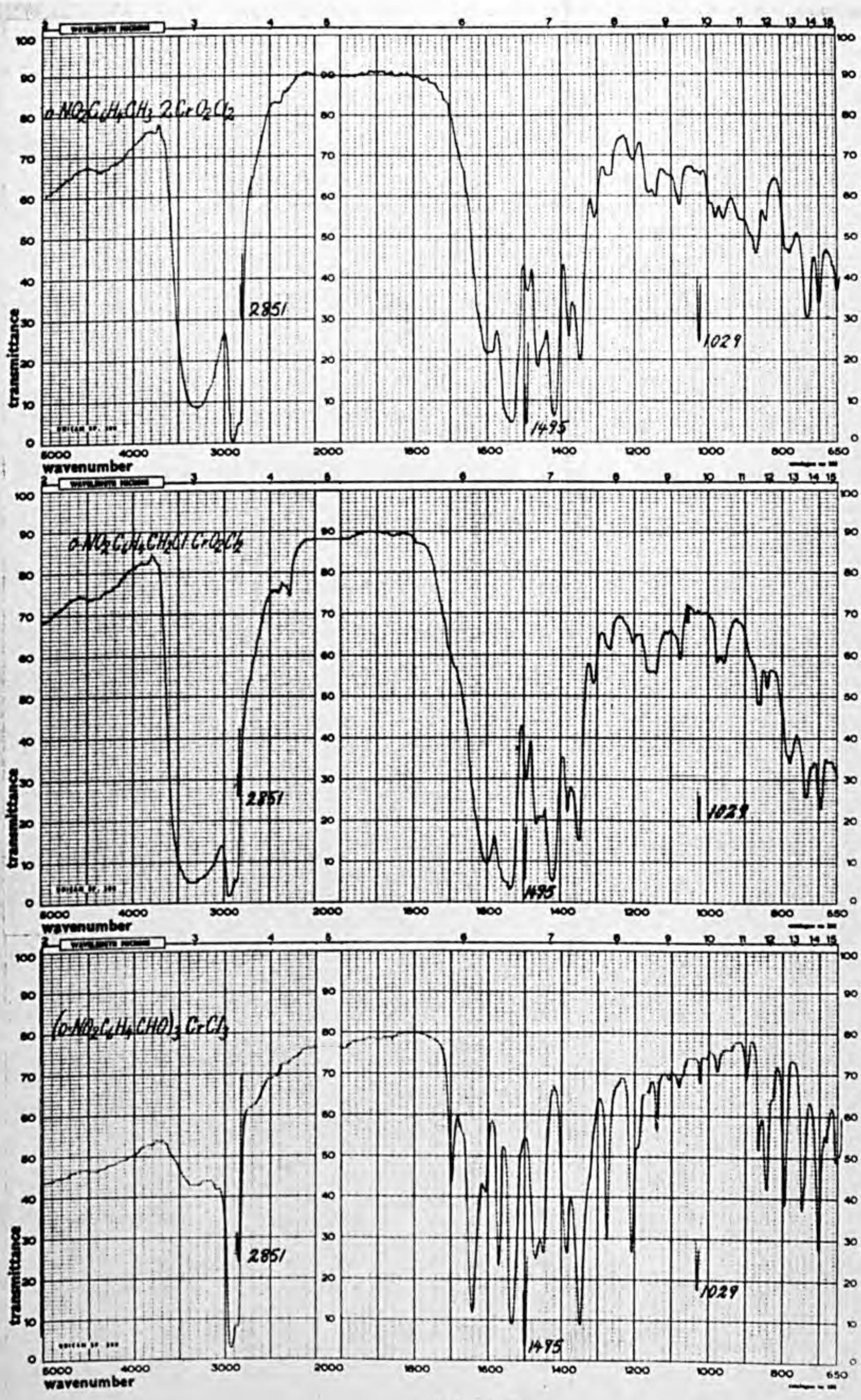

m-$NO_2C_6H_4CH_3$ $2CrO_2Cl_2$
m-$NO_2C_6H_4CH_2Cl$ CrO_2Cl_2
(m-$NO_2C_6H_4CHO)_2$ $CrCl_3$
2851
1495
1029
transmittance
wavenumber
5000
4000
3000
2000
1800
1600
1400
1200
1000
800
650
2
3
4
5
6
7
8
9
10
11
12
13
14
15
0
10
20
30
40
50
60
70
80
90
100

fig 28



WAVELENGTH MICRONS
2 3 4 5 6 7 8 9 10 11 12 13 14 15
$o\,NO_2C_6H_4CH_3\,2CrO_2Cl_2$
2851
1495
1029
o-$NO_2C_6H_4CH_2Cl\,CrO_2Cl_2$
2851
1495
1029
$(o$-$NO_2C_6H_4CHO)_3\,CrCl_3$
2851
1495
1029
transmittance
0 10 20 30 40 50 60 70 80 90 100
wavenumber
5000 4000 3000 2000 1800 1600 1400 1200 1000 800 650

fig 29.

to benzaldehyde should yield similar spectra. When benzyl bromide and benzyl alcohol were oxidized with chromyl chloride the adducts as predicted, were found to have similar infra red spectra to the toluene and benzyl chloride adducts. Table 16, and figs. 22and 23 show the similarity. Both of these adducts also give benzaldehyde in high yield on hydrolysis. However it was found necessary to maintain a large excess of chromyl chloride in the oxidation of benzyl alcohol, otherwise a greenish compound from which benzyl alcohol and benzoic acid were liberated by hydrolysis, was formed. Again, this suggested that, the benzaldehyde was initially co-ordinated to the reduced chromium, so that subsequent displacement by the stronger co-ordination alcohol permitted oxidation to the acid, by the excess chromyl chloride. It is interesting to note, that alcohols have been used since Etard's time to liberate the products of oxidation from the adducts, though no explanation for such solvolysis has been offered previously.

As the evidence indicated that the adducts were co-ordination complexes, an attempt was made to synthesis authentic complexes of this type, for comparisons.

No reference could be found to complexes formed between benzaldehyde and chromium compounds, although complexes between benzaldehyde and a number of other metal halides were known (77). A complex between chromic chloride and benzaldehyde was prepared as described in the experimental section k. As can be seen from comparing the infra red spectrum of this complex table 29, it corresponds with those of the above mentioned adducts.

The adducts obtained by the oxidation of m-, p- and o- chloro and nitro toluenes and m-, p- and o- chloro and nitro benzyl chlorides were compared in a similar manner with the corresponding co-ordination complexes, formed between the substituted benzaldehydes and chromic chloride. The infra red spectra obtained are contained in tables 16 and 29. This evidence is also collected in figs. 24 to 29, where the spectra of the toluene and benzyl chloride adducts and the co-ordination complex are shown together for each substituted species. The similarity in the spectra of any set of spectra, with the exception of the o-nitro case, is evident immediately. In all cases, with the exception, significantly of the o-nitro adducts, high yields of aldehyde were obtained on hydrolysis of the adducts and complexes.

Reference has already been made to complexes of benzaldehyde with metals other than chromium. It was of interest to compare the infra red spectrum of a well known benzaldehyde complex since this might have provided confirmatory evidence. One such complex has been reported between stannic chloride and benzaldehyde: $SnCl_4 . 2(C_6H_5CHO)$. Following Pfeifer (77) this complex was prepared and its infra red spectrum obtained. Once again, the spectrum table 30, closely resembles the spectrum from the benzaldehyde chromic chloride complex as well as the spectra of the adducts which hydrolyses to benzaldehyde.

If it was accepted that the benzaldehyde was attached to the chromium in the adducts, the mode of such attachment is of interest. An obvious possibility is co-ordination between the lone pair electrons of the carbonyl oxygen and the chromium. However for completeness other structures must also be considered, for instance, complex formation between the electrons of the aromatic ring and the metal (97,9), even though this might seem unlikely as such complexing normally occurs with metals in low oxidation states. Lappert (59) has shown that, for acyl oxygen donation in co-ordination complexes, a shortening in the carbonyl frequency of 50-150 cm^{-1} is required. He used this method to differentiate between three possible structures for ethyl acetate-Lewis acid complexes. The above π complexing would only fractionary reduce the carbonyl frequency. The similarity of the spectra of the adducts with that of benzaldehyde is evident from tables 14 and 31, the major difference, apart from the absence of hydroxyl absorption being an apparent shift of the carbonyl band from 1701 cm^{-1} to 1640-1615 cm^{-1} that is a shift of 61-86 cm^{-1}, which is of the order required by Lappert's criterion for co-ordination between the carbonyl oxygen and the metal.

It is believed that the evidence quoted above is strongly in favour of the theory that Etard adducts are co-ordination complexes formed between the carbonyl compound, produced by oxidation of the hydrocarbon, and the product of reduction of the chromyl chloride. It is also pertinent to mention that this theory offers a ready explanation of apparent anomalies in the literature as will be seen later. Thus the adducts can be considered as of the form shown in fig. 30.

This work has already been published and a copy of the paper is appended.

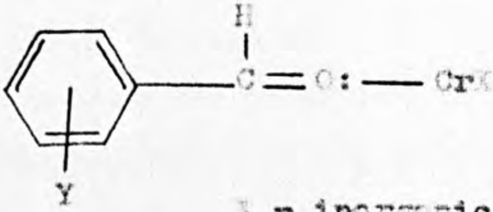


fig.30

X = inorganic residue.

It is relevant that similar compounds, involving co-ordination between aldehydes and various Lewis acids, are isolated as intermediates in other reactions conducted under similar conditions. Such reactions involve anhydrous materials and non-polar solvents. For instance both the Friedel Crafts acylation and the Gattermann Koch reaction are considered to involve co-ordination complexes (14,17). A number of patents (108) have been taken out, where synthesised aldehyde co-ordination complexes are added in the latter reaction to promote it.

Following this work, evidence of complexing in other oxidations with chromyl chloride has been reported. The first case is the oxidation of phenols, (97,9) where the adducts have been shown to involve co-ordinated quinones. The second case is the oxidation of primary and secondary alcohols, (62) where the adducts have been shown to consist of ketones and esters co-ordinated to the reduced chromyl chloride. Using the method out lined in this thesis, the former workers have obtained complexes between chromic chloride and quinones. The latter workers obtained complexes between, chromic chloride, and ketones and esters.

In contrast a consideration of tables 14,15 and 29 shows that although the infra red spectra of the o-nitrotoluene and o-nitrobenzyl chloride adducts are similar, they bear little resemblance to the o-nitrobenzaldehyde chromic chloride complex. This is hardly surprising since little aldehyde is obtained on hydrolysis of these adducts (42), the apparent product being the hydrocarbon itself. The writer obtained a yield of 11% of the aldehyde and approximately 30% of the nitrotoluene, as well as a quantity of the nitro acid, in a typical experiment. An exhaustive investigation showed that a considerable quantity of acid remained attached to the chromium (a similar result for quinones has been referred to in the historical survey, page 11). Even precipitation of the chromium by ammonium hydroxide did not release the o-nitrobenzoic acid, which however was shown to be present by C / H combustion analysis and infra red spectroscopy on the precipitated, hydrated chromic oxide .

Up to 11% carbon was found to be present in such precipitates and the infra red spectrum was compared with that of the chromium precipitate obtained in the presence of authentic acid and found to be similar. In addition, it was found that the benzyl chloride adduct was significantly soluble in nitrobenzene and o-nitro toluene. Further, when an oxidation was performed in neat o-nitrotoluene the solution rapidly turned dark brown and became viscous, but no precipitation occurred. If however carbon disulphide, or carbon tetrachloride was added precipitation occurred immediately. It was concluded that the intermediate was soluble because of the co-ordinating properties, albeit weak, of the nitro group. Co-ordination between nitro-hydrocarbons and certain acceptors, has long been known, and these compounds have been used as derivatives (99) for identification.

Bearing in mind the above, the o-nitrotoluene and o-nitrobenzyl chloride oxidations can be explained within the overall pattern as follows. The chromyl chloride and the nitro-hydrocarbon initially react to form the usual aldehyde co-ordination compound. However because of the co-ordinating power of the nitro group and the long reaction time, the aldehyde is displaced and subsequently oxidized to the carboxylic acid. The acid then strongly co-ordinates with the chromium resisting attempts to displace it. However, insufficient acid is present to saturate the chromium species, so that some of the excess o-nitro compound is brought down with the precipitate. On hydrolysis the nitro compound is readily detectable, in contrast to the carboxylic acid, so that it can easily be mistaken for the major product. This theory explains why in the isotopic investigation of Sulima and Gragerov (99) they reported that the o-nitrotoluene isolated from their adduct did not contain excess deuterium. Ponomarchuk and Gragerov (37) also reported no isotopic effect associated with the liberated o-nitrotoluene from the adduct. Sulima and Gregerov (99) reported that ether gave a regeneration of o-nitrotoluene from the adduct, again this can now be explained in terms of the stronger co-ordinating solvent, ether, displacing the weakly held nitro hydrocarbon. It could be asked why the m- and p-nitrohydrocarbons do not react similarly, high yields of the aldehyde being obtained in these oxidations. The difference could be that the proximity of the nitro group to the chromium, when the aldehyde is co-ordinated allows the nitro group to easily displace the aldehyde, although the possibility of chelating in such a system and hence increased stability might appear possible. However this would require a seven membered ring which might be difficult to form because of steric crowding. Alternatively the nitro group in the o-nitro hydrocarbon could weaken the donor properties of the carbonyl group by electron withdrawal more than in the caseof the other two isomers.

The above theory may also explain why, carbonyl compounds are the ultimate oxidation products. The carbonyl group, being co-ordinated is probably protected from further oxidation, especially since it is removed from solution as formed.

The work of Carstanjen (13) can also be explained using the co-ordination theory. It is assumed that the usual adduct forms but is soluble in the acetic acid (as mentioned in the historical survey, acetic acid has been used to liberate the oxidation products). The carbonyl compound would then be liberated by the more powerful donor, acetic acid, and subsequently oxidized by the excess chromyl chloride. This explains why acids were normally isolated by Carstanjen.

A further example of the liberation of the carbonyl compound and subsequent oxidation is provided by the work of Bartecki (3). He used chromyl acetate, in a solvent of carbon tetrachloride, as the oxidizing agent and found that, no matter which hydrocarbon was oxidized, the adduct isolated was always of the same composition and contained no oxidation product. Bartecki did not attempt to isolate any product from the solutions. If the co-ordination theory is accepted, the hydrocarbon would be expected to be oxidized to the carbonyl compound which would then be displaced by the acetate groups, either intra of intermolecularly and would then be subsequently oxidized. The adducts would therefore all be identical, since they would all contain reduced chromyl acetate. The product of oxidation, presumably the carboxylic acid, would be found in the supernatent liquid. To test this theory a sample of chromyl acetate was prepared by the writer, and used to oxidize benzyl chloride. The isolated adduct contained no oxidation product, and a large yield of benzoic acid, the expected product from subsequent oxidation of the benzaldehyde, was isolated from the supernatent liquid.

Of the various structures suggested prior to the writing of this thesis, the two which had not been refuted, were those suggested by Etard 1, and Nenitzescu et al. XVIII, XIX and XX.

The following are some of the objections to Etard's structure:

a). Such a structure could not be formed by reaction between benzaldehyde and anhydrous chromic chloride.

b). Structures of this type do not explain why the oxidation product is liberated simply by treatment with co-ordinating solvents.

c). The results of Bartecki and Carstanjen are not then explicable.

d). The structures suggested by Etard for toluene I, and Benzyl chloride III would not have identical infra red spectra, as has been found.

e). It would be difficult to explain the similarly of the infra red spectra of the adducts and the well authenticated co-ordination complex of benzaldehyde.

Nenitzescu et al. (73,74,79) base their structures on their observation that, under special conditions, alcohols, in addition to aldehydes are liberated on hydrolysis. They postulated therefore that the initial hydrolysis products were alcohols which were subsequently, rapidly oxidised by the second mole of chromyl chloride. However Nenitzescu's structure does not account for the five points set out above any better than does Etard's. Although many oxidations have been performed by this author between chromyl chloride and toluene, or benzyl chloride, no alcohols have ever been isolated, although careful attempts to isolate them were made. Solutions used during the course of this work were always dilute, and it could be argued that in more concentrated solutions, the rapid precipitation of the adduct could trap small quantities of the initially formed chromium ester, page 97, which would then remain in the adduct to yield alcohol on hydrolysis.

All the evidence at present available in the opinion of the writer is in keeping with the above theory of co-ordinated oxidation products.

Since strongly co-ordination compounds such as T.H.F. and dioxane, had been shown to displace the oxidation products from the adducts, it was thought that these ethers might be used as solvents to effect oxidations under homogeneous conditions. They were therefore examined under normal conditions. However with chromyl chloride was formed the usual adducts. The oxidations were carried out in carbon disulphide and the adducts were found to form rapidly.

The hydrolysis products were not isolated although they were shown to possess carbonyl groups. As would be expected since excess ether was employed a quantity of the product was isolated from the solution. Obviously this theory could be applied to all the other oxidations involving chromyl chloride, the first compounds to study might well be the phenylmethanes, although the adducts from oxidations of olefins, alcolols, aliphatic hydrocarbons and ethers would also repay investigation.

b). Mechanism

Having shown that the adducts were co-ordination compounds a study of the mechanism operative during the oxidation was commenced.

The rate determining step during the oxidation of toluene by chromyl chloride has been shown, by the isotopic investigations of Wheeler (114) and Gragerov and Ponomarchuk (37), to involve carbon-hydrogen bond fission.

Stairs and Burns (92) reported that the reaction of toluene and chromyl chloride was second order overall and first order with respect to each component. They obtained this result from varying the initial concentrations of the reactants. This writer has also measured the rate of the toluene oxidation, table 7, and obtained a variation comparable to that reported by Stairs and Burns.

Assuming chromyl chloride's electrophilic nature there are then, three possibilities for the rate determining step:

i). Hydrogen atom abstraction.

ii). Hydride ion abstraction.

III). A cyclic transition state leading to single state substitution.

The following mechanisms can, therefore be postulated for the initial stage of the oxidation of toluene and related compounds:

a).

$$ArCH_2H + CrO_2Cl_2 \longrightarrow (ArCH_2 \cdot HCrO_2Cl_2)$$

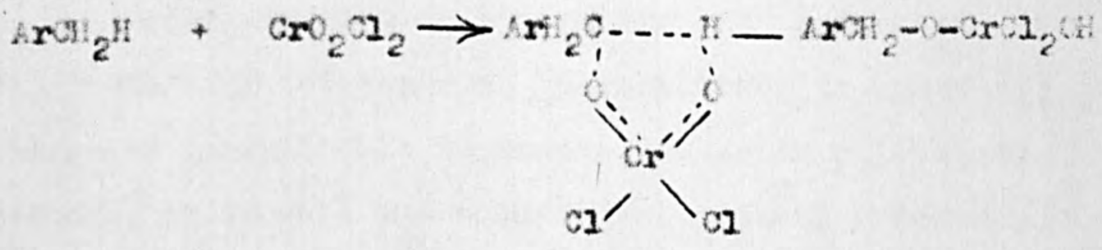
$$(ArCH_2 \cdot HCrO_2Cl_2) \longrightarrow ArCH_2{-}O{-}Cr(OH)Cl_2$$

b).

$$ArCH_2H + CrO_2Cl_2 \longrightarrow ArCH_2 \cdot + HCrO_2Cl_2$$

$$ArCH_2 \cdot + CrO_2Cl_2 \longrightarrow ArCH_2{-}O{-}CrOCl_2$$

c).



$$ArCH_2H + CrO_2Cl_2 \longrightarrow ArH_2C{-}{-}{-}{-}H \text{ — } ArCH_2{-}O{-}CrCl_2OH$$

d).

$$ArCH_2H + CrO_2Cl_2 \longrightarrow ArCH_2^{+} + HCrO_2Cl_2^{-}$$

$$ArCH_2^{+} + HCrO_2Cl_2^{-} \longrightarrow ArCH_2O{-}O{-}Cr(OH)Cl_2$$

Schemes a) and b) involve free radicals

and the initial formation of chromium (V). Scheme a) required the free radical and complementary chromium (V) to remain in a solvent cage and subsequently react. Whereas scheme b) allows for the possibility of reaction of the free radical with another species. Scheme c) postulates a cyclic intermediate, and scheme d) the generation of a carbonium ion. All four cases lead to an ester intermediate similar to those postulated during chromic acid and permanganate oxidations, and normally accepted as the first relatively stable intermediate (120). All the above schemes of mechanisms have been suggested at some time (120). However no single mechanism has been universally accepted.

Many standard methods which have been used for differentiating between such possibilities in other reactions, are inapplicable to chromyl chloride oxidations. For instance, it is well known that free radical reactions can be initiated and inhibited. However, because of the reactivity of chromyl chloride, any added initiator or inhibitor would be unlikely to be inert to this oxidant. For the same reason appropriate olefins would not be expected to polymerise even if radicals were present. Similarly it has been suggested (120) that dimers would be unlikely, as further reaction of the free radical with a chromium species would occur before dimerisation. Thus the absence of dimers, Wiberg has stated, does not oppose the formation of free radicals, particularly in the case of scheme a) which involves the trapping of the free radical and chromium (V) in a solvent cage. It is interesting to note however that dimers have been isolated from certain chromic acid oxidations (1), which have been interpreted as proceeding via free radical formation. Free radical reactions are often associated with oxygen uptake, there has been no report of any oxygen absorption during toluene oxidations with chromyl chloride. The phenomenon of induced oxidation (120) has been widely used in studies of transition metal oxidations and has led to many useful results and conclusions. The usual compounds that are added to the reaction solution to produce induced oxidations are salts of transition metals. Although, having wide applicability in aqueous media, the use of non-polar solvents for chromyl chloride oxidations limits their usefulness. Various physical techniques have also been used with success in similar investigations. As already mentioned U.V. spectroscopy has been used to study chromic acid oxidations. However as the chromyl chloride oxidations are not homogeneous, its use would be difficult in this case. Electron spin resonance is used to prove the existence of free radicals. However in a system involving various oxidation states of chromium, which would also be contributing absorption bands, this method is fraught with difficulties.

There remains one major method which can be used to study the mechanism of these reactions, kinetics.

A kinetic study of the oxidations by chromyl chloride of a series of substituted toluenes and benzyl chlorides was therefore undertaken in an attempt to obtain mechanistic information.

The method commonly used to follow oxidations involving transition oxidants is to perform redox titrations on the reaction solution and then to calculate the quantity of oxidant that has reacted. Stairs reported (94) a kinetic study of the reaction between substituted toluenes and chromyl chloride, using the above method during the course of this investigation. He made a correction to each reading on the basis that the adduct contained two moles of chromium (IV). Simple reaction curves were not obtained, and conclusions were therefore based on initial rates.

During the earlier investigation of the structure of the adducts, we found that the chromium need not be present as chromium (IV), and that in extreme cases the chromium appeared in the adducts as chromium (III). The majority of adducts were found to contain sufficient oxidizing power for the average value of the chromiums to be between chromium (III) and chromium (IV), (see page 122). Due to the uncertainty of any correction involving residual oxidising power another method, involving following the reaction directly by measuring the amount of adduct produced, was developed.

The kinetic results were investigated by applying the Hammett equation. The Hammett equation (41), basically a linear free energy relationship, has been extensively used in mechanistic problems. The relationship is most commonly written as:

$$\log_{10} \frac{k}{k_o} = \sigma \rho$$

where: k, is the rate constant for a substituted species.

k_o, is the rate constant for the unsubstituted species.

σ, the substituent constant.

ρ, the polar effect of the reaction.

A plot of $\log_{10} k / k_o$ or $\log_{10} k$ against the substituent constant σ allows a value of ρ to be calculated, which is a quantitative measure of the polar effect in the reaction of the given m- or p- substituent, relative to the hydrogen atom. The σ values are obtained from the effect of substituents on the acidity of substituted benzoic acids ($\sigma = \log_{10} K / K_o$ for benzoic acids where K is the equilibrium constant). There exists a further set of substituent constants, termed σ^+ values which are relevant to reactions in which mesomeric interactions are involved. The σ^+ values are obtained for example from rates of hydrolysis of dimethylbenzyl halides.

It has been pointed out by Russell (85) that in certain free radical reactions, in particular those in which considerable bond breaking occurs, σ^+ values are more pertinent. These latter σ^+ values, it has been suggested, should be used if a highly electronegative free radical of relatively low reactivity is implicated, for instance the trichloromethyl radical. It appears reasonable to conclude that if chromyl chloride should function in a one electron process it would be of this form.

The ρ and ρ^+ values, were therefore calculated from the respective graphs, using σ and σ^+ values reported by Brown and Okamoto (12). The results of twelve rate determinations at 40° were used to obtain the following values of ρ and ρ^+.

ρ for substitued toluenes at 40°c = $-2{\cdot}28 \pm 0{\cdot}08$
ρ^+ for substitued toluenes at 40°c = $-2{\cdot}20 \pm 0{\cdot}08$

The values obtained for ρ and ρ^+ do not allow a ready differentiation between the two possibilities, and substituents which have markedly different σ and σ^+ values such as $-OCH_3$ and $-CN$ cannot be used. The former causes ring oxidation (98) and both, owing to their strong co-ordinating power, would tend to displace the co-ordinated product, which would undergo further oxidation.

Values of σ^+ were used throughout the remainder of the investigation as it has been claimed that they correlate carbonium ions or free radicals of the form that are likely in this study, better than σ values.

Now: $\Delta G^* = \Delta H^* - T\Delta S^*$

where ΔH^*, ΔS^* and ΔG^* are the enthalpy, entropy and free energy of activation respectively.

Differentiating with respect to temperature:

$$\frac{\partial \Delta G^*}{\partial T} = \frac{\partial \Delta H^*}{\partial T} - \frac{T\partial \Delta S^*}{\partial T} - \Delta S^*$$

But ΔH^* and ΔS^* are normally taken to be independent of temperature for small ΔT.

$$\therefore \quad \frac{\partial \Delta G^*}{\partial T} = -\Delta S^*$$

for substituents s_1 and s_2, the equation becomes:

$$\left(\frac{\partial \Delta G^*}{\partial T}\right)_{s_1} - \left(\frac{\partial \Delta G^*}{\partial T}\right)_{s_2} = \Delta S^*_{s_2} - \Delta S^*_{s_1}$$

or
$$\frac{\partial\left(\frac{\partial \Delta G^*}{\partial \sigma}\right)}{\partial T} = \frac{\partial \Delta S^*}{\partial \sigma}$$

Hammett (41) originally assumed that ΔS^*, was independent of substituent, that is $\partial \Delta S^* / \partial \sigma = 0$. This is reasonable since his equation applies only to m- and p- substituents. Thus since the substituents are remote from the reaction site steric effects should be small. Under these circumstances:

$$\frac{\partial \left(\frac{\partial \Delta G^*}{\partial \sigma} \right)}{\partial T} = 0$$

or $\partial \Delta G^* / \partial \sigma$ is independent of temperature. Then from the 'transition state' theory of reaction rates:

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}}$$

or: $\log_e k = \log_e \frac{RT}{Nh} - \frac{\Delta G^*}{RT}$

but: $\log_{10} k - \log_{10} k_o = 2.303 \rho \sigma$

$$\frac{\partial \log_e k}{\partial \sigma} = 2{\cdot}303 \rho$$

Thus:
$$\frac{\partial \Delta G^*}{\partial \sigma} = -2{\cdot}303\ RT\rho$$

$$\left(\frac{\partial \Delta G^*}{\partial \sigma}\right)_{T_1} - \left(\frac{\partial \Delta G^*}{\partial \sigma}\right)_{T_2} = 0 = -2{\cdot}303R(T_1\rho_1 - T_2\rho_2)$$

$$\frac{\rho_1}{\rho_2} = \frac{T_2}{T_1}$$

Thus, variation of ρ within the temperature range normally used for kinetic measurements is small and predictable, and comparisons of the value, at one temperature only, with values for other reactions are justified. However, Leffler (63) pointed out that $\partial \Delta S^* / \partial \sigma$ need not be zero, but that ΔH^* and ΔS^* need only be linearly related by the equation:

$$\Delta H^* = \Delta H_0^* + \beta \Delta S^*$$

if a linear plot of $\log_{10}$ k against   is to be obtained, then:

$$\Delta G^* = \Delta H_0^* - (T - \beta)\Delta S^*$$

and $$-2{\cdot}303R(T_1\rho_1 - T_2\rho_2) = \frac{\partial \Delta S^*}{\partial \sigma}$$

The value of ρ at one temperature is now no longer predictable from that at another temperature. In fact if β, termed the isokinetic temperature by Leffler, is within the experimentally accessible temperature range ρ^{+}, $(\partial \Delta G^{*} / \partial \sigma^{+} = -2{\cdot}303RT\rho^{+})$ can change sign with consequent ambiguity in interpretation in terms of reaction mechanism.

Hence the rates were also determined at 25°, the value of ρ^{+} obtained being:

ρ^{+} for substituted toluenes at 25°c = $-2{\cdot}32 \pm 0{\cdot}10$

The variation of ρ^{+} from $-2{\cdot}32$ to $-2{\cdot}20$ represents a lowering of selectivity at the higher temperature, as would be expected. As already stated the expression $\rho^{+}_{1} / \rho^{+}_{2} = T_{1} / T_{2}$ is normally approximately followed. Then using the value found at 25°, $(-2{\cdot}32)$ the calculated value for ρ^{+} at 40° is $-2{\cdot}21$ which agrees well with the experimental value, and therefore the use of a single value to draw mechanistic conclusions is justified. The graph of log k against σ^{+} at the two temperatures is shown in fig. 8. Jaffe (57) has taken a medium precision of 15% to embrace reactions following the Hammett equation, our results follow the relationship with a minimum precision of 4%, although it is admitted that groups such as CH_3O- are not included.

As a negative value of ρ^+ was obtained this indicates that the reaction is facilitated by electron releasing groups, this is analogous to chromic acid oxidation of hydrocarbons. Therefore the chromyl chloride must be acting as an electrophilic reagent as expected. The magnitude of ρ^+ obtained, can be used for mechanistic interpretation, as different processes are correlated by differing values of ρ^+, which reflect the electron requirement at the reaction centre.

The value of ρ^+ obtained is too low to accommodate a carbonium ion mechanism for which + has been shown to lie between -3 and -5 (116).

The values of ρ^+ obtained for free radical reactions are normally considered to be within the range -0·75 to -1·5 (85). Highly reactive, electronegative radicals, which involve little bond breaking in the transition state, are correlated with low negative + values. Conversely relatively unreactive electronegative radicals, show marked selectivity, because they are susceptible to polar effects, because of the high degree

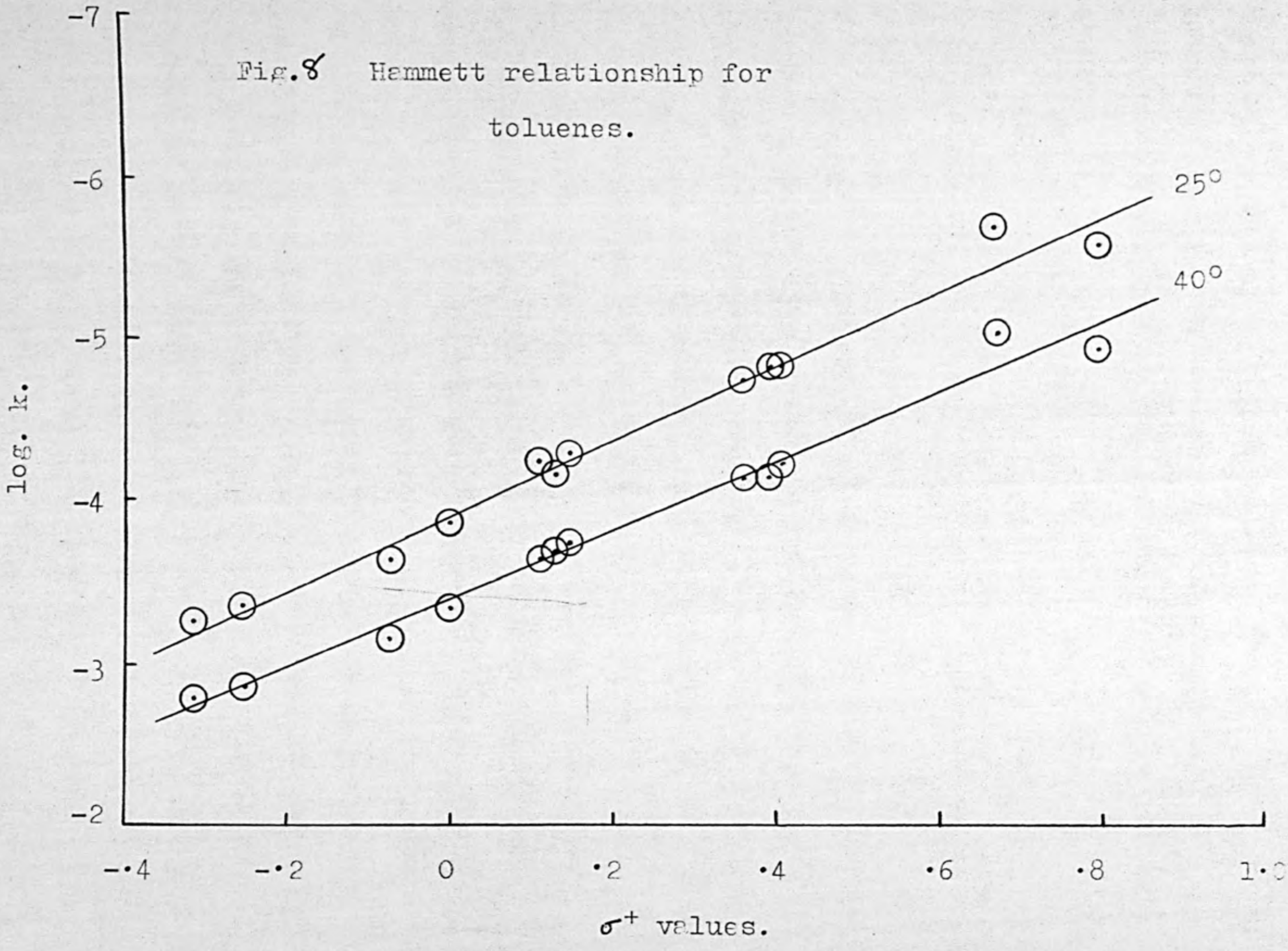


Fig. 8 Hammett relationship for toluenes.

of bond breaking during the transition state. The following canonical structures have been suggested for the transition states (85), involved in free radical reactions.

$$\underset{\text{I}}{R{:}HX} \longleftrightarrow RH + {\cdot}X \longleftrightarrow \underset{\text{II}}{R^{+}{\cdot}\,H\ \ {:}X^{-}}$$

Then the structure I represents the transition state for reactive free radicals, and II, where charge separation is considerable, for relatively unreactive radicals. That is, a radical such as chlorine would have a low negative ρ^{+} value, for although highly electronegative it is also highly reactive. Conversely radicals such as trichloromethyl or bromine atoms, have values of ρ^{+} of -1·46 and -1·05 (51,104), respectively, because of their low reactivity and high electronegativity. It should be stressed that only radicals of high electronegativity can be influenced by polar effects in bonds, and hence follow the Hammett relationship, radicals such as methyl or phenyl would not be expected to show this tendency, and radical stability becomes dominant. It could be argued that chromyl chloride might be less reactive than trichloromethyl, as a radical, and certainly would be electronegative, therefore a larger negative value for ρ^{+} would be expected. However a value over -2 for ρ^{+} is probably too high even for such a radical, especially when chromic acid oxidations of a number of substituted toluenes (76) have been correlated with a value of -1·12.

As the value found for ρ^{+} for the chromyl chloride oxidation of substituted toluenes is intermediate between the values accepted for free radicals and carbonium ions, this would suggest that the cyclic mechanism correlates the facts most satisfactory.

There appears to be a paucity of information on ρ^{+} values, for cyclic transition states. However the following two cases although not identical are analogous in involving intermediate charge development. The first is the well known Sn2 mechanism invoked for the solvolysis of benzyl halides. If the attacking water molecule is considered to represent the nucleophilic oxygen of chromyl chloride (fig. 31) so that carbon-oxygen bond formation is occuring in both cases, and the breaking of the carbon-chlorine bond is considered to represent the breaking of the carbon-hydrogen bond of the toluene then the two systems are seen to be similar.

Accepting the differences in solvents, the fact that the hydrolysis of benzyl chlorides are correlated with a ρ^+ of $-2{\cdot}18$ (116) is significant.

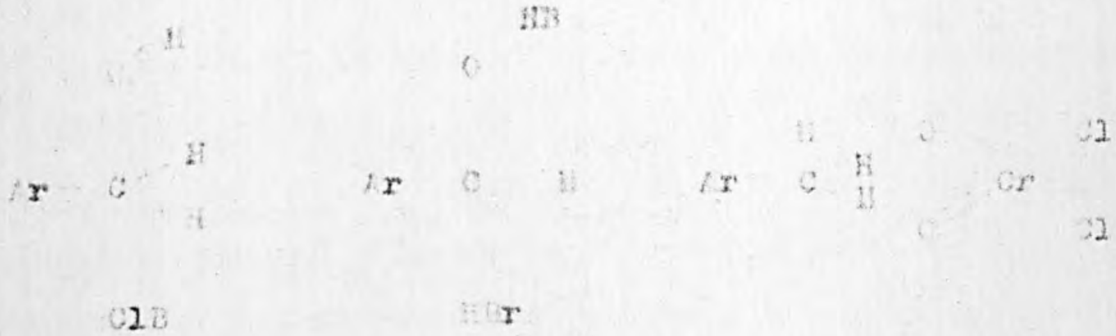
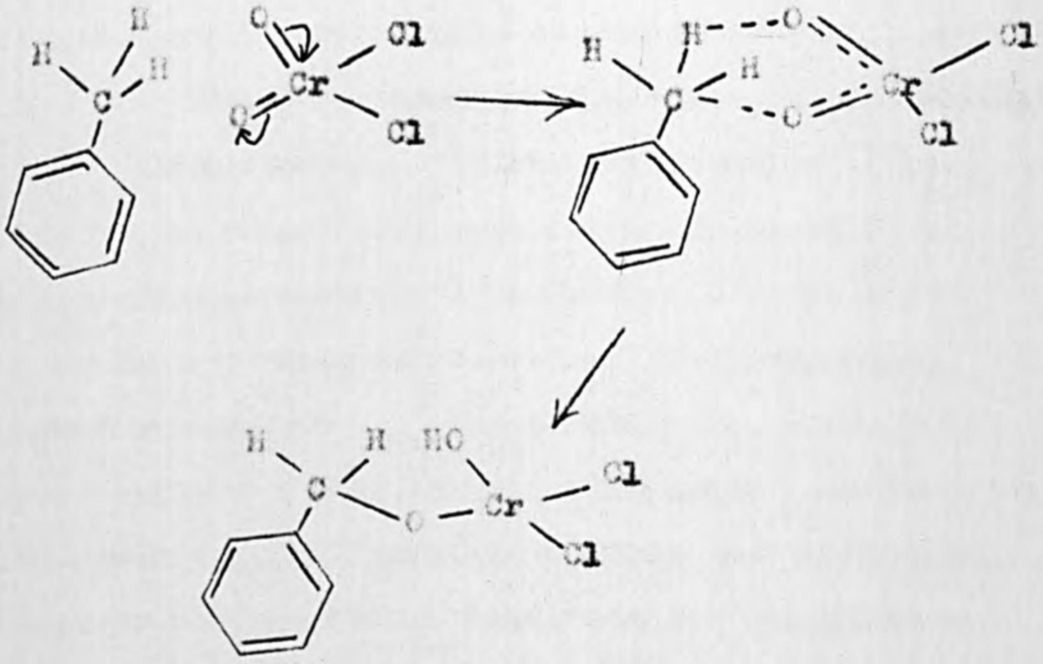


fig. 31.

The second case is the oxidation of benzyl alcohol to benzaldehyde by bromine water in aqueous acetic acid. The reaction has been found to give a value for ρ of $-2{\cdot}29$ at 25° (2). The mechanism of this oxidation requires hydride transfer and synchronous removal of hydroxylic proton by base. So once again the transition state involves intermediate charge development.

Other transition metal oxidations of toluene for which ρ or ρ^+ values have been reported, apart from the already mentioned chromic acid oxidation, are the following reported by Murti and Pati (71,72), recently. They obtained a ρ value of $-3{\cdot}75$ for the oxidation of substituted toluenes by vanadium (V), which is an unambiguous two electron transfer. They have also measured ρ in a similar experiment using cerium (IV) as the oxidant and claimed that the value of $-1{\cdot}7$ indicated one electron transfer, however in this latter case their conclusions are open to debate.

It is therefore concluded that oxidation of toluene by chromyl chloride most probably proceeds through a cyclic stage as shown. The electrophilic oxygen is produced by the utilisation of the 'd' orbitals of the chromium.



Whether the cyclic stage involves a simultaneous two electron transfer, or a step wise two electron transfer is not clear. As stated by Rocek (82), "Once we accept the cyclic model .... the differences between various modes of breaking of the carbon-hydrogen bond become much less clearly defined."

It is interesting to note, that a limiting case of this cyclic transition stage could be considered to be the transition stage favoured by Wiberg, namely the trapping of the radical and chromium (V) species together in a solvent cage and subsequent reaction. Similarlythe hydride transfer suggested by Nenitzescu during the cyclic stage would be the other limit.

The above conclusions, based on the magnitude of the ρ^+ value assume that the magnitude of ρ^+ is a direct consequence of the polar requirements of the reaction centre. However it is known (118) that if a reaction occurs prior to the rate determining step, ambiguous results for ρ^+ can be obtained. Indeed it has been suggested (111) that π complexing occurs prior to bond breaking. If this was so then the values could be composite values, which would require modification before any attempt was made at mechanistic implications. Although De La Mare and Ridd (69) have argued that if complexing occurred to a significant level the reaction would no longer be second order, as is found. However as π complexing has been suggested an attempt was made to determine whether or not complex formation occurs. The rate of the toluene reaction was measured in benzene solution. The rate obtained after correcting for slight solvent reaction, did not differ markedly from the rate as measured in carbon disulphide, table 6. The variation is in fact less than that observed in the investigation of Stairs (93) in which the reaction was carried out in a number of aliphatic solvents of differing dipole moments. If π complexing occurred, then the use of benzene to which the chromyl chloride would be expected to complex, should have radically altered the rate. Thus I must, like Bartecki (3), whose conclusions were based on spectroscopic evidence, disagree with Wheeler's claim for π complex formation.

There is evidence (91) to suggest that certain solvents can influence free radical reactions. Carbon disulphide has been reported as doing this in certain circumstances. Therefore the oxidations of toluene and p-nitrotoluene were performed in carbon tetrachloride. The rates obtained are shown in table 6, and clearly do not differ significantly from the rates obtained in carbon disulphide. The conclusions relating to ρ^{+} are therefore valid and π complexing is shown not to occur.

A cyclic transition state would be expected to be influenced markedly by steric effects. In this context the results of the rate constants obtained for the ortho substituted toluenes are informative.

Taft (100) has suggested that the ortho steric effect of a substituent, is given by : log. k_o / k_p where k_o and k_p are the rate constants for the o- and p-substituents respectively. Where steric interaction is minimal the effect of ortho and para substituents should be similar. The results of this investigation show that the ortho steric effect is high, depressing the rates of the ortho substituted toluenes to lower values than were obtained for the respective meta-substituted toluenes. Such a large ortho effect would not be consistent with any mechanism not requiring high steric order, such as the initial production of an unencumbered free radical.

According to Taft's values of Es (steric substituent constants) the nitro group should have a larger steric effect than the chloro substituent in the ortho position, as long as the nitro group is coplanar with the benzene ring. The converse is true if the nitro group is perpendicular. This investigation gives the following values for the ortho effect of chloro and nitro groups:

$$\log.\frac{k_o}{k_p} \text{ for nitro substitution } = -0{\cdot}35 \text{ at } 25^\circ$$
$$-0{\cdot}35 \text{ at } 40^\circ$$

$$\log.\frac{k_o}{k_p} \text{ for chloro substitution } = -0{\cdot}51 \text{ at } 25^\circ$$
$$-0{\cdot}52 \text{ at } 40^\circ$$

The above values indicate that during chromyl chloride oxidation, the nitro group is perpendicular to the aromatic ring. As a coplanar position is favoured for resonance interaction, the relative positions of the meta and para nitro toluenes fig. 8, might be the result of this effect.

A similar effect of the ortho substituent depressing the rate constants to a value below that of the meta substituent has been noted in chromic acid oxidation of aldehydes (64 to 68), where a cyclic stage has been suggested. The fact that chromic acid oxidations of hydrocarbons and alcohols, assumed free radical reactions, do not show this effect is noteworthy.

As already mentioned, a report of a similar kinetic study (94) appeared during this investigation. However the methos used to follow thd kinetics is suspect, and the fact that good secind order curves were obtained in this investigation, which Stairs was unable to do indicates that the method and results of this investigation, are likely to be superior. The values of ρ obtained by Stairs gave an isokinetic temperature in the vicinity of 340°K. This unusually low and Exner (33) has stated that it can be assumed, that the isokinetic temperature is always far from experimental temperatures. A similar determination using the ρ^+ values obtained in this investigation leads to value of 730°K, which is of expected magnitude. Stairs also reported values of $\partial\Delta S^*/\partial\sigma$, $\partial\Delta G^*/\partial\sigma$ and $\partial\Delta H^*/\partial\sigma$. The large value of $\partial\Delta H^*/\partial\sigma$ (25 k.cal), Stairs stated, indicated a substantial electron demand at the reaction site. He also explains the large value of $\partial\Delta S^*/\partial\sigma$ (72 cal/deg), as evidence for initial π complexing. Stairs earlier work indicated that the adduct had little polar character, and to account for these conflicting results he suggested a mechanism involving dipole interactions. The values of $\partial \Delta H^* / \partial \sigma$ and $\partial \Delta S^* / \partial \sigma$ obtained from this investigation are 6·0 k.cal and 9·3 cal/deg, respectively, which are of normal magnitude, and would agree with Stairs earlier conclusion regarding the polarity of the adducts, but which would be in variance with π complexing.

A similar kinetic study was also conducted on a series of substituted benzyl chlorides. The adducts from benzyl chlorides are of 1:1 molar ratio in hydrocarbon and chromyl chloride, in contrast to the 2:1 toluene adducts. Good second order curves were obtained, and the rate constants at 25° and 40°, correlated by means of the Hammett relationship, are shown in fig. 9. The values found for the parameter ρ^+ are:

ρ^+ for substituted benzyl chlorides at 25° = $-1{\cdot}71 \pm 0{\cdot}16$
ρ^+ for substituted benzyl chlorides at 40° = $-1{\cdot}68 \pm 0{\cdot}16$

giving a medium precision of 9%. The individual rate constant for any substituent was depressed relative to the corresponding toluene. This is in agreement with Etard's (10) qualitative assessment, but conflicts with Stairs and Burns (92) who reported a rate constant for

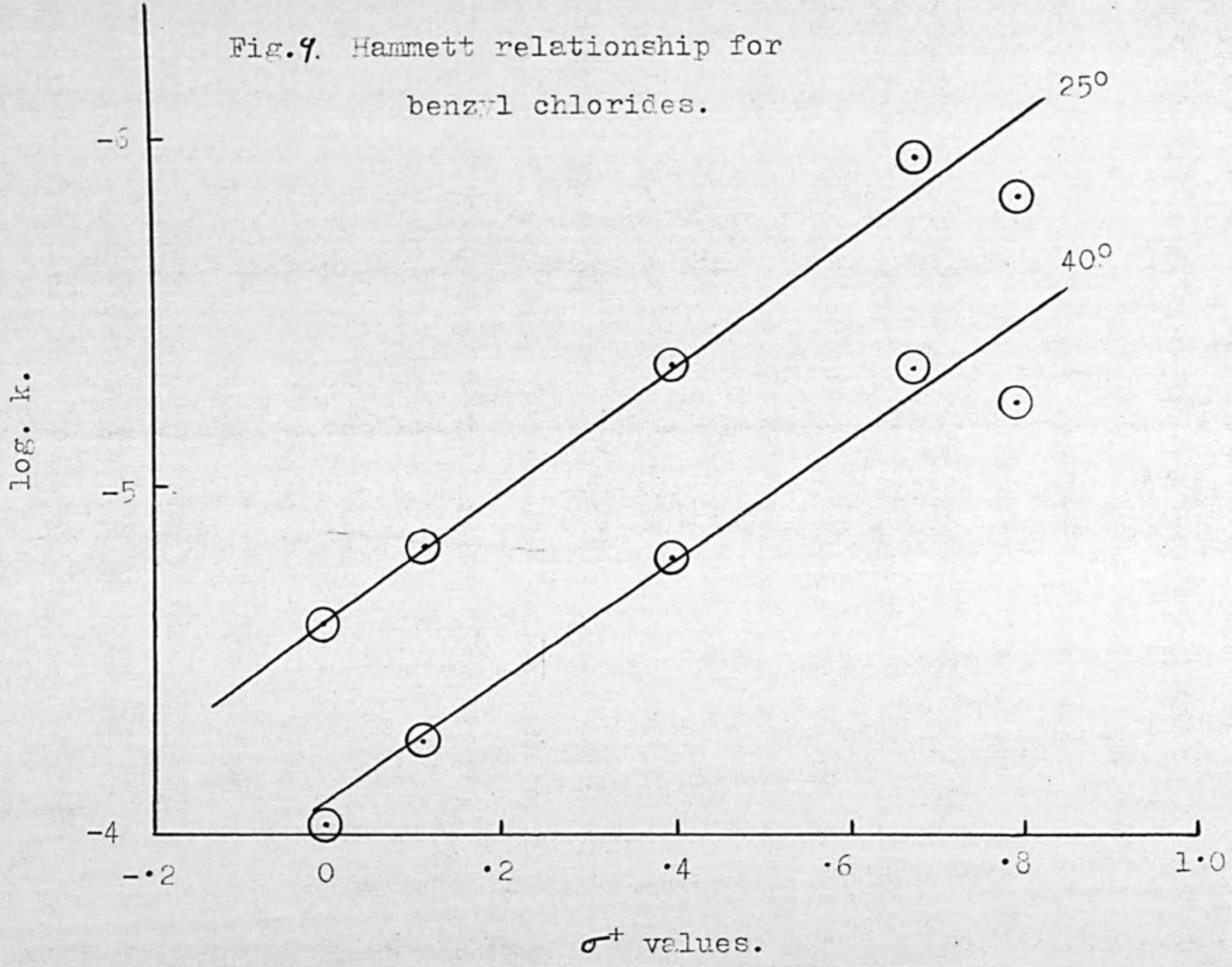


Fig.9. Hammett relationship for benzyl chlorides.

benzyl chloride comparable to that of toluene.

The kinetic results therefore show that an α chlorine atom has the effect of lowering reactivity and selectivity, that is, it reduces the effect of nuclear substitution. The electronic effects of a nuclear chlorine have been shown, in the case of toluene, to reduce the rate, as expected by analogy with electrophilic substitution. Unfortunately the effect of α substitution is not predictable. The α chlorine would be expected to lower the electron density at the reaction site inductively, but its resonance contribution might well be expected to be greater, relative to the nuclear chlorine, for both radical and carbonium ion formation. However the observed effect is not at variance with the proposed cyclic transition state.

The single determination using benzyl bromide shows a further reduction in rate. Therefore the substitution of an α bromo for an α chloro reduces the rate. Taft (100) has reported that the values of σ^* (polar effect of substituents) indicate that an α chloro has a greater polar effect than an α bromo; a similar result can be obtained from Roberts and Moreland's (81) σ' values. On this basis it would be expected that benzyl chloride would react slower and not faster than benzyl bromide. However the Es values (steric effect of substituents) are reversed, an α bromo substituent having a larger steric effect than an α chloro group.

Since the α bromo substituent has been found to reduce the rate of oxidation with chromyl chloride relative to benzyl chloride, a considerable steric effect must be operative.

Although the ρ^+ values for the benzyl chlorides are lower than those for the toluenes and approach those quoted for free radical reactions, they have not fallen below the maximum value so far obtained, for free radical reactions. A strict comparison with the range of values introduced earlier for the various mechanisms is not justified, as they were obtained for hydrogen abstraction from a methyl group and not a monochloromethyl group. The magnitude of the ρ^+ values most likely require modification. The fact, however, that the ρ^+ values for benzyl chlorides have not reached the values for free radical reactions, must indicate strongly that a similar mechanism to the toluene case is operative. The values of $\partial\Delta H^* / \partial\sigma^+$ and $\partial\Delta S^* / \partial\sigma^+$ are 1.36 k.cal and 5.52 cal/deg, respectively for benzyl chloride oxidation. These values allow the same conclusions to be drawn as for the toluene values.

Analogously to the case of chromyl chloride oxidation of toluenes, the ortho substituted benzyl chlorides have a marked Taft ortho steric effect, which reduces the rate for an ortho substituted benzyl chloride to a value lower than that of the corresponding meta substituted compound, see table 8.

Knowledge of the influence of α substitution on free radical reactions is somewhat meagre. However it is known that halogeno substitution can have a large effect on subsequent reaction if the free radical has a high electronegativity and is therefore capable of responding to polar effects in the carbon-hydrogen bond of the hydrocarbon. For instance, the photo-chlorination of methane is known (91) to be slightly enhanced by α mono chloro substitution but retarded by further chloro substitution. Presumably the polar effects of the first chloro substituent is less than its stabilizing effect on the incipient free radical, whereas the effects are reversed for di and tri chloro substitution. In bromination (91) a hydrogen attached to carbon directly bonded to halogen can be much more readily substituted than if the halogen was absent. However, it has also been reported (50) that trichloromethyl radicals preferentially attack the methyl group of α bromo-p-xylene. Thus if chromyl chloride were to function as a free radical there are two possibilities. If it reacted in a similar manner to chlorine and bromine atoms, then the oxidation of benzyl chloride should have been more facile than the oxidation of toluene, which was not found. This unfortunately cannot be taken as evidence against the possible free radical nature of chromyl chloride because if chromyl chloride were to function as a radical in a similar manner to trichloromethyl radicals, then the introduction of an halogen would retard the oxidation, as was found. It seems probable that if chromyl chloride were to function as a radical then it would tend to be similar to the trichloromethyl radicals, because their selectivity and electronegativity should be more comparable, than with the halogens.

A study of the oxidation of benzal chloride in which there are two α halogens was undertaken as it was thought that it might yield an interesting result of mechanistic importance. The literature stated (42) that no reaction occurred. However a reaction was found to occur with the evolution of hydrogen chloride. The adduct obtained corresponded to $C_6H_5CCl.CrO_2Cl_2$, (found: C,·30·0; H, 2·2; Cr, 18·7; Cl, 38·1%. $C_7H_5Cl_3CrO_2$ requires C, 30·0; H, 2·2; Cr, 18·6; Cl, 38·0%). That is a 1:1 molar ratio depleted by one mole of hydrogen chloride. The hydrolysis product was found to be benzoic acid. The ratio of the rates; toluene, benzyl chloride and benzal chloride was found to be 93:20:1 at 40° and 76:14:1 at 25°. The low relative rate of the benzal chloride indicates that the transition state has been extensively influenced through dichloro substitution. This is in keeping with the cyclic intermediate of the form postulated, which would be highly sterically influenced in this case. For comparison the relative selections; as favoured by Tedder (91) are 31:10:1 at 40° and 25:7:1 at 25°.

The value of ΔS^* obtained for a reaction can be considered (115) as an indication of the steric requirements of a reaction, as long as they pertain to the rate determining step, that is, there are no prior stages. The ΔS^* values calculated from the results of this kinetic study are -25·6 and -21·1 cal/deg, for toluene and benzyl chloride respectively. These are values which would be expected for a bimolecular process involving reasonabley complex molecules. However the value calculated for benzal chloride is -43·4 cal/deg, which is considerably higher and indicates a highly ordered transition state, as would be expected for a cyclic transition state but definitely not for the linear transition states, as are postulated for free radical or carbonium ion production.

Therefore it is concluded that the kinetic information presented here is best accommodated on the assumption that the reaction proceeds through a cyclic transition state.

The majority of the kinetic investigation discussed above has been published in two papers, which are appended.

c). Further investigation of the kinetic results

The Hammett equation can be considered as a linear entropy/enthalpy relationship, although Hammett proved his equation for constant entropy cases. Various attempts have been made to extend the information that can be obtained from kinetic results, by studying directly the variation in entropy and enthalpy.

One of the first reports, by R.F.Brown (11) recognised the existence of families of compounds, whose entropy and enthalpy are linear related by the equation:

$$\Delta H^* = \Delta H^*_0 + \beta_0 \Delta S^*$$

Where β_0 was considered to be a universal constant of approximately 300°, or multiples of 300°, and termed the isokinetic temperature. Fig. 17 shows the entropy and enthalpy values obtained in this investigation for the substituted toluenes. It is possible to obtain a number of families, one such being shown (dotted line A-A) between the para halogens. The slope of this line approximates 300°. Brown used his families to suggest extensions, especially as regards the values of ΔH^*_0.

Linear entropy/enthalpy relationships were

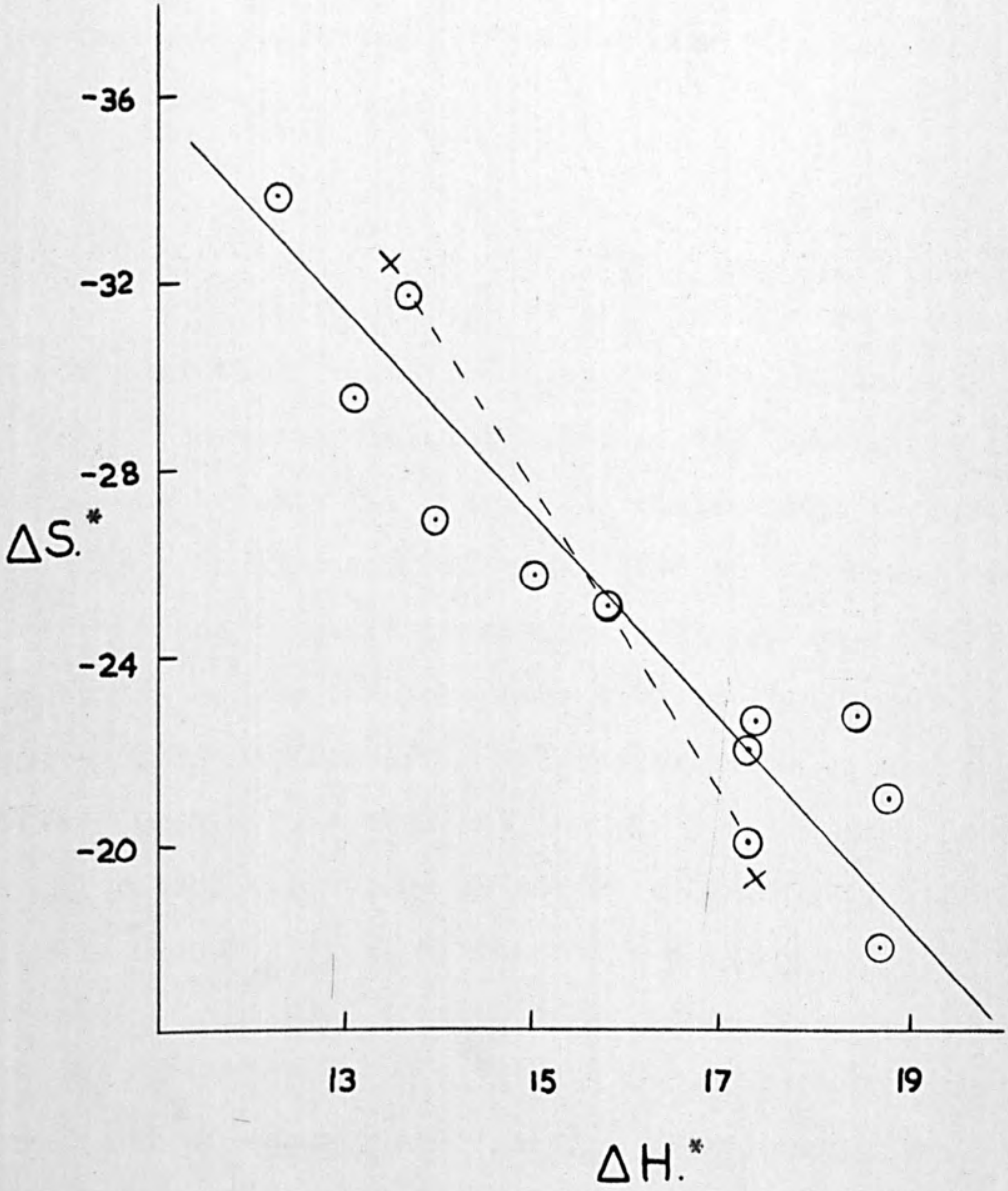


Fig. 17. Values of ΔH^* and ΔS^* obtained for the substituted toluenes.

reviewed by Leffler, (63) who, as has already been stated, derived the following expression involving the isokinetic temperature β.

$$\Delta G^* = \Delta H^*_0 - (T - \beta)\Delta S^*$$

Leffler reported that great care was required in interpreting reactions which had β approximating T' the average temperature, because of the possibility of erroneous results for a trivial mathematical reason. This is seen if one considers a case in which the reaction rates at one temperature are nearly the same. This might be because the independent variable (structure or solvent) is negligible at all temperatures. Then ΔG^* will approximate a constant and ΔH^*, determined from the small random variations in the rate constants, will be a linear function of ΔS^*, the slope β being equal to the average of the experimental temperature range.

Following this a rigorous mathematical treatment of entropy and enthalpy relationships was reported by Exner (81). He came to the conclusion that in a number of cases, families of the form reported by Brown are merely manifestations of the error involved and are in fact error slopes. These lines have slopes corresponding to the average temperature of the determinations, and as most determinations are carried out at temperatures in the range 20° to 40°, the slope would be approximately 300, as found by Brown. Exner concluded that relationships between entropy and enthalpy should be looked for indirectly, by ploting log.k_1 against log.k_2, so that no distortion of errors occurs, rather than directly by investigation of ΔS^*, ΔH^* plots. The plots of log.k_{313} against log.k_{298} for the toluenes and benzyl chlorides are shown in figs. 18 and 19, respectively. According to Exner's criterion a straight line plot, as found to occur for the toluenes and benzyl chlorides, demonstrates the existence of linear free energy relationships.

When the broken line from fig. 17 is mapped back onto fig. 18 (broken line X-X) in the manner recommended by Exner, the lack of a linear relationship becomes evident.

Exner showed that the slopes, λ , of log.k_1-log.k_2 graphs were related to β by the expression:

$$\beta = \frac{T_2(T_1\lambda - T_1)}{T_1\lambda - T_2}$$

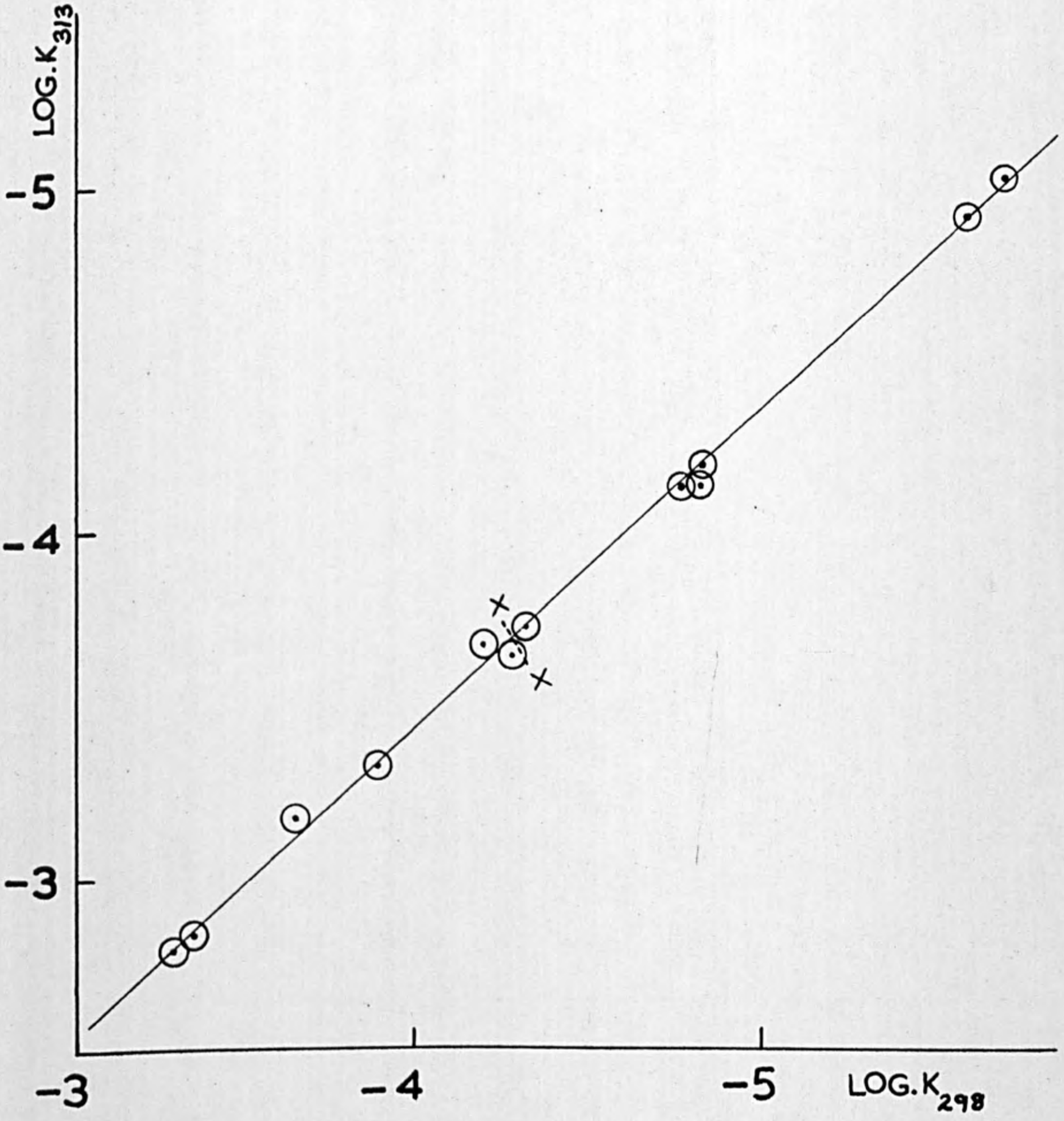


Fig. 18. Rate constants for substituted toluenes.

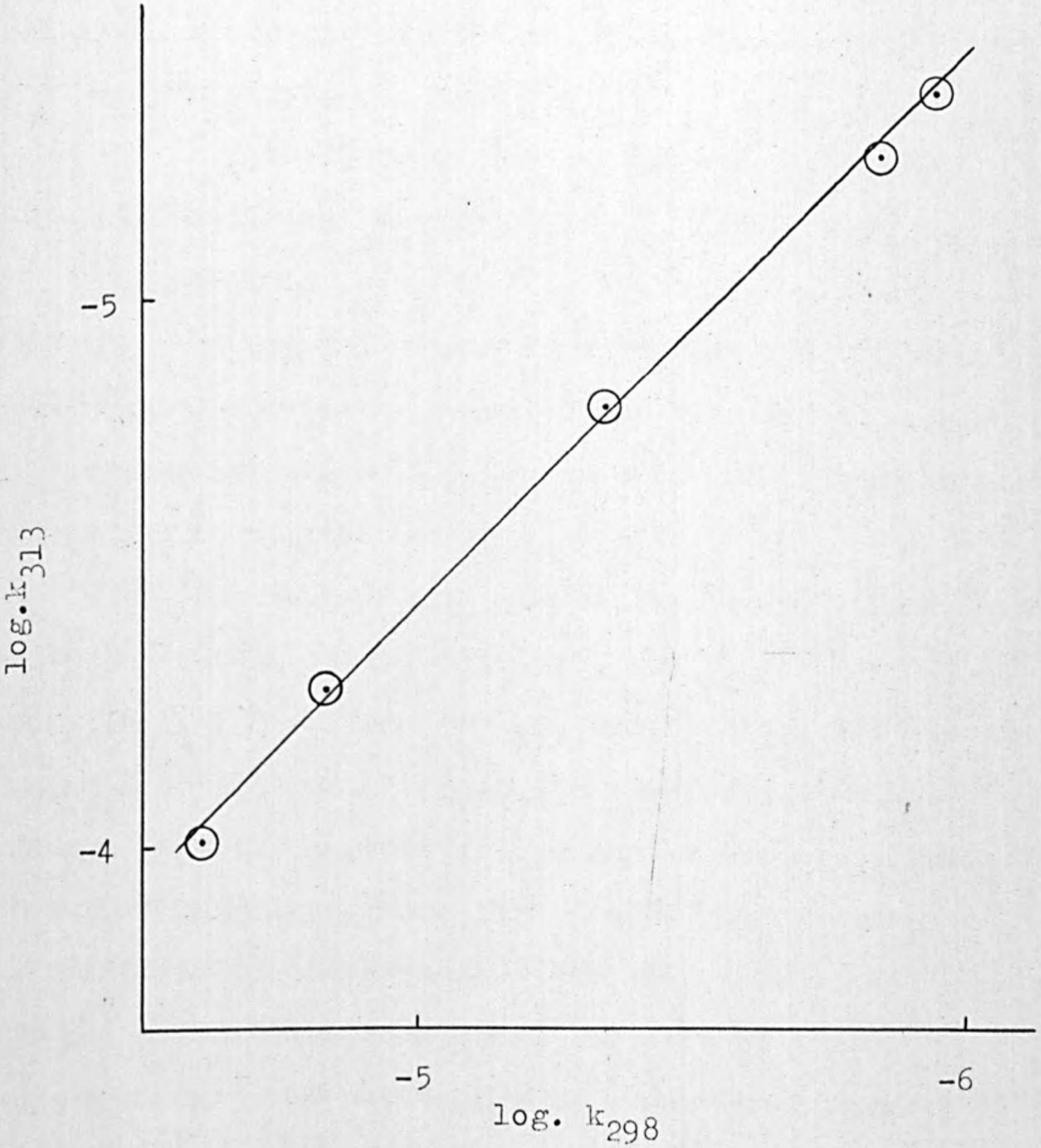


Fig. 19. Rate constants for substituted benzyl chlorides.

He then considered four possible cases embracing all the possible values of β. The various possibilities are differentiated by the values obtained for β and T_2 / T_1.

In the case of the substituted toluenes $\lambda = 0{\cdot}915 \pm 0{\cdot}012$ and $\beta = 730 \pm 140^{\circ}K$. As $T_2 / T_1 = 0{\cdot}95$, then for this case, $T_2 / T_1 > \lambda$ and $\beta > T_1$, so that this reaction falls into Exner's category 3a, namely the most common category. This indicates that H.C.Brown's compensation law holds (10), changes in ΔH^* partially compensate for changes in ΔS^*.

However in the case of the benzyl chlorides $\lambda = 0{\cdot}986 \pm 0{\cdot}017$, $\beta = -124 \pm 206$ and $T_2 / T_1 = 0{\cdot}95$. Thus, $T_2 / T_1 < \lambda < 1$ and $\beta < 0$, which places the reaction in Exner's category 4. The implication of this classification is that compensation no longer occurs. Exner states that this latter inference could not be drawn from relationships between ΔS^* and ΔH^*, and the existence of this category shows that the postulation that compensation of parameters is a universal natural law, must be considered fallacious.

The conclusions which can be drawn on the basis of Exner's classification are not clear, and no report of its interpretation has as yet been reported.

Similarly it is not known why the introduction of an α chloro, as in the present study, should cause a change from compensation to non-compensation, or whether this is a general phenomenon.

As already mentioned many of the conventional aids which have been used in the elucidation of similar problems are inapplicable to this system. However although the facts are best correlated by a cyclic transition state, the mode of transfer of the electrons is not clear and further kinetic work on the systems used in this investigation appears unlikely to clarify the situation. Therefore a kinetic study involving systems in which the differences between hydride ion and free radical mechanisms would be expected to manifest themselves is a possible extension. Such systems might be the diphenylmethane and triphenylmethane cases.

Extensions

Throughout the course of this discussion, where applicable, for convenience references hav been made to possible extensions. Apart from those already mentioned the following two possibilities are worth considering. Firstly, it has recently been reported (83) that chromic acid effects an induced oxidation of cyclohexanone. This has been claimed as the first reported induced oxidation involving a simple organic compound. It is only the second involving an organic compound of any description the other being the induced oxidation of indigo (90). The presence of succinic and adipic acids was taken as evidence of oxidation by chromium (V). No report has as yet been published on the reaction of chromyl chloride and cyclohexanone. The second possible extension would be a study of the reaction between chromyl chloride and triphenylacetaldehyde. It has been argued (82,120) that, depending on the nature of the reaction triphenylcarbinol and carbon monoxide or triphenyacetic acid will be formed. For instance oxidation by ceric ion; a one electron transfer, gave triphenylcarbinol and carbon monoxide (82) whereas oxidation by permanganate, a presumed two electron process, gave only triphenylacetic acid.

Whether either of the above suggestions would resolve the problem is not certain. Indeed they are both fraught with difficulties, the first involves very small quantities of induced oxidation products.

Whilst, as it has been pointed out (120), triphenyacetaldehyde may well be an atypical aldehyde, and whether conclusions reached on the basis of aldehyde oxidations must necessary be applicable to hydrocarbon oxidations must be debatable.

In conclusion it can be seen from the discussion that the reactions of chromyl chloride, which are carried out in non-polar solvents may often be very different from the similar oxidations carried out in polar solvents, by oxidants such as chromic acid or chromyl acetate. Therefore it would appear inadvisable to draw conclusions regarding the possible reactions of chromyl chloride on results obtained from chromic acid or chromyl acetate oxidations, as has been done in the past (73,119).

d). Oxidation state of the chromium in the adducts

Although the two problems of structure and mechanism have been most extensively studied, there are other aspects of interest associated with the Etard reaction. For instance the nature of the chromium in the final adduct.

In the oxidations of chromium (VI) in polar solvents, the final state of the chromium is chromium (III) although in some cases a chromium (III)-chromium (VI) complex has been isolated (91) from oxidations in acetic acid. However chromium (III) is not necessarily the final state during oxidations involving chromyl chloride. Although chromium (V) and chromium (IV) are known (120) to be unstable in aqueous solution, the use of a non-polar solvent and the precipitation of the adducts during chromyl chloride oxidations of the hydrocarbons allows for the possibility that intermediate oxidation states will be present in the adducts.

If a simple two electron transfer had occurred the chromium (VI) would have been reduced to chromium (IV). The presence of the chromium (IV) could have been detected by suitable redox titrations, and physical techniques for determining oxidation states, such as E.S.R. or the Gouy magnetic susceptibility method. Nenitzescu et al (73) used the technique of E.S.R. and concluded that half the chromium in the toluene adduct was paramagnetic, and half diamagnetic, hence sexivalent. They were unable to differentiate between the lower oxidation states, but considered the most likely state to be four, however Wiberg and Eisenthal (119) reinterpted Nenitzescu's results and claimed that they were in fact in agreement with the conclusion that both chromiums are in oxidation state four. Wheeler (113) had already measured the magnetic susceptibility of the toluene adduct, obtaining a value of 3•16 Bohr magnetons per chromium atom. This, he concluded, demonstrated that both chromium atoms were in oxidation state four (see table 13). We have found that it is more convenient to measure the average oxidation state by means of simple redox titrations. As the benzyl chloride adducts contain only one chromium atom, initial determinations were carried out on them. Results of Gouy determinations varied from 3•2 to 3•64 B.M., depending on the method used to prepare the adduct. Whilst redox titrations indicated between 3 and 96% oxidizing power. A low Gouy value should, of course, indicate a high oxidizing power and vice versa. For instance the benzyl chloride adduct prepared using no solvent at 0°, but with rapid isolation had the values 3•2 B.M. and 96% oxidizing power. It was found that at high temperature (45°) and in carbon disulphide rather than carbon tetrachloride solution lower oxidizing powers resulted. Oxidizing power was found to alter throughout a kinetic run, for instance a run done under the normal kinetic conditions in carbon disulphide had an oxidizing power of 13•6% after 48 hr., 8•5% after 126 hr., and 5•3% after 517 hr., for comparison the reaction had proceeded to 75% completion after 96 hr. A benzyl chloride adduct prepared in carbon tetrachloride had an oxidizing power of 44•6% whereas one prepared in carbon disulphide at 45° had an oxidizing power of 3•8%. The normal value obtained for the benzyl chloride adducts from the kinetic runs was between 10 and 20%. A similar effect was noted in the case of toluene adducts, except that the oxidation value was normally between 40 and 100%. Generally adducts which had low oxidizing power assumed a light purple colour, rather than the usual browns. It is therefore clear that the oxidizing power of an adduct is not a standard quantity and conclusions are not justified if based on this assumption.

The benzyl chloride adduct having 96%

oxidizing power was subjected to a differential thermal analysis. An exothermic peak was obtained at approximately 100° followed by endothermic peaks, fig. 20. Once a sample of the adduct had produced the exothermic peak subsequent cooling and rescanning, did not produce the peak again. A similar analysis was carried out on an adduct containing negligible oxidizing power. No exothermic peak was obtained. It seemed therefore that the exothermic peak was associated with the reduction of the chromium (IV) (or any variation, i.e., chromium (V) plus chromium (III)), and indeed it was shown that the high oxidizing power adduct, contained no oxidizing power after being heated to 100°. It's analysis however had not varied considerable. Analysis of adduct before exothermic reaction C, 28·0; H, 2·3; Cr, 21·7, and Cl, 35·5%. After C, 29·8; H, 2·3; Cr, 21·7, and Cl, 31·5%. A possible explenation of these results is that a quantity of the co-ordinated benzaldehyde had been oxidized to benzoic acid by the chromium (IV). Certainly the quantity of benzaldehyde was less after heating (approximately 40%), however the quantity of benzoic acid formed could not be determined accurately. This was because of the fact (page 74) that the benzoic acid attached itself strongly to the chromium and defied all

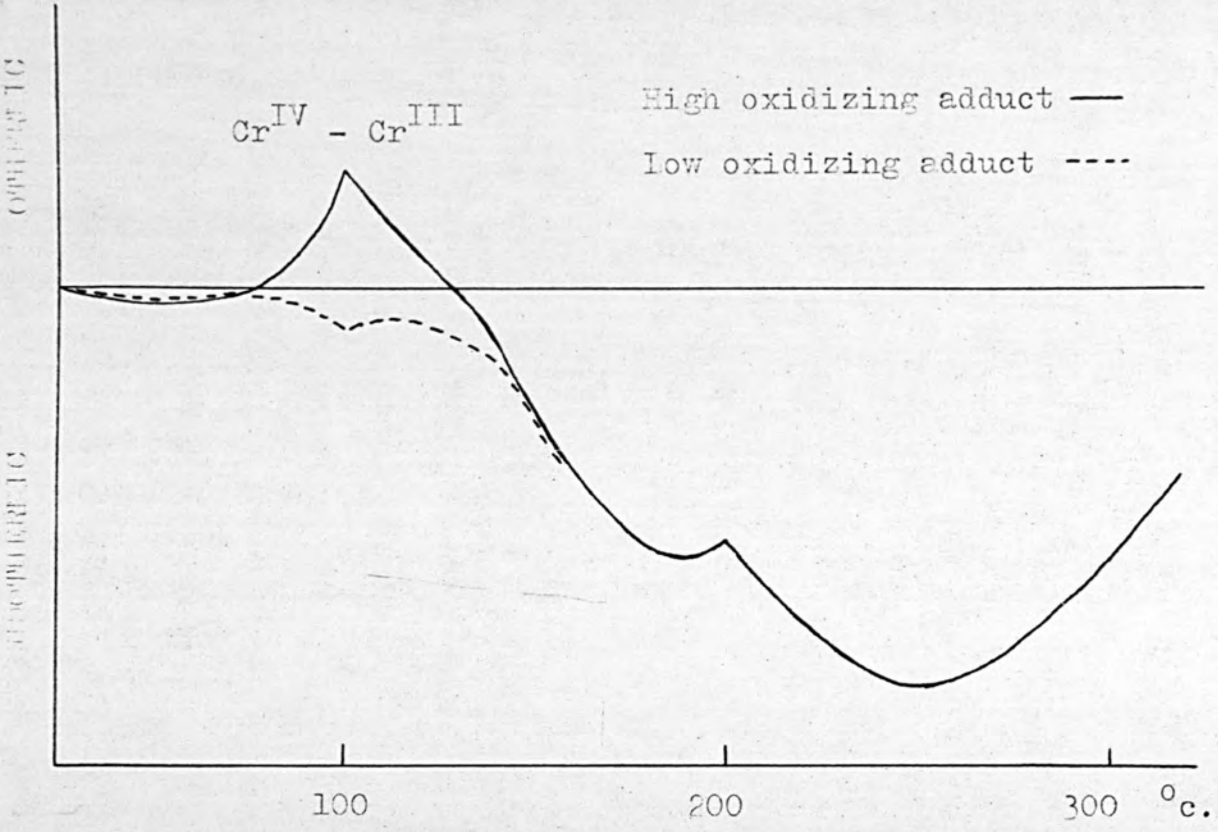
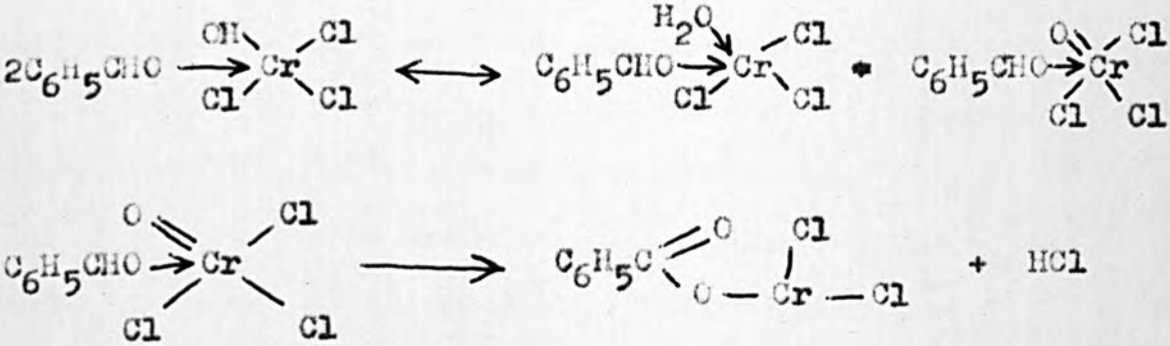


Fig. 20 Differential thermal analysis spectra

attempts to quantitatively detach it, although a considerable quantity was indicated by C / H analysis. During the thermal analysis the adduct lost 4·3% by weight. The following sequence would account for the observed facts:



The theoretical weight lose and final quantity of benzaldehyde are 6·5% and 50% which are in reasonable agreement with the experimental results.

The later endothermic peaks, fig. 20, are presumably associated with the lose of hydrogen chloride which has been reported previously (42).

e). The chlorinated product.

It is well known (42) that during the oxidations of chromyl chloride quantities of chlorinated products are formed, which remain in the reaction solution. The chlorinated products from the oxidations of toluene and benzyl chloride being benzyl chloride and benzal chloride respectively, no other products were found. The role of these compounds, is not understood, most workers suggesting either accidental chlorination (42) or an independant side reaction (74). It was known however that even if chlorine free chromyl chloride was used, chlorination still occurred (40).

No attempt had been made to follow the growth of the chlorinated species or to determine the effect of varying the starting materials. It was important to know how much chlorinated product was formed in order to correct the kinetic results if necessary. The growth of benzal chloride during an oxidation of benzyl chloride was therefore followed, using the technique of gas liquid chromatography. The resulting curve is shown in fig. 21. The plot of the relationship between the molar concentration of benzal chloride and the molar concentration of adduct formed is also shown. The resulting straight line indicates that the two reactions are not independant, but rather bear a constant ratio to each other. This ratio has the value 0·196. Thus using the rate found for benzyl chloride oxidation at 25°, ($2{\cdot}45.10^{-5}$ l.mole^{-1}.sec^{-1}.) the rate of formation of the benzal chloride is, $4{\cdot}8.10^{-6}$ l.mole^{-1}.sec^{-1}. The quantity of benzal chloride formed was found to be independant of the initial concentrations of benzyl chloride as long as the hydrocarbon remained in excess. A similar parallelism of rates has been demonstrated (19) in the case of toluene oxidation and benzyl chloride formation. A comparison of the two reactions reveals the interesting fact that the ratio: mole chlorinated hydrocarbon to mole of chromyl chloride reacted is the same within experimental error.

The production of the chlorinated compounds must contribute to the loss of oxidizing power from the adducts, as could the already discussed formation of benzoic acid, but it has as yet not been possible to determine the exact involvement of these possibilities. A recent paper by Nenitzescu et al. (74) has reported that the ratio between the products formed by oxidation and chlorination may vary considerabley. They also stated that the proportion of chlorinated products was not

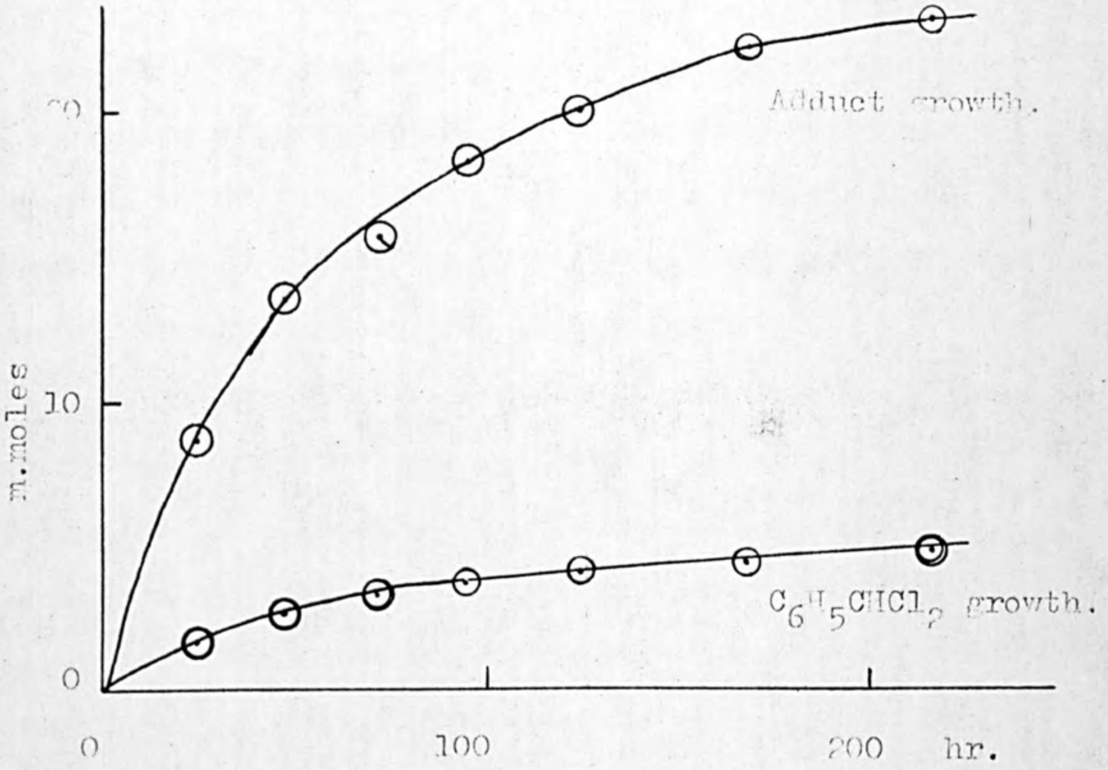

20
10
0
m.moles
Adduct growth.
$C_6H_5CHCl_2$ growth.
0
100
200
hr.

Fig. 21.

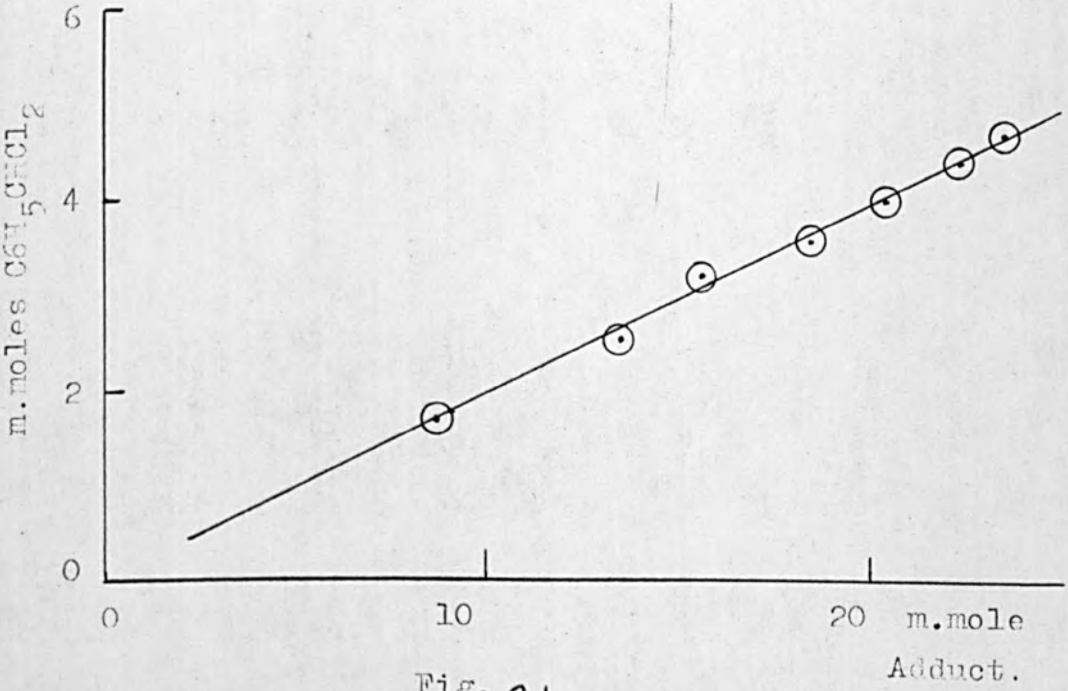

6
4
2
0
m.moles $C_6H_5CHCl_2$
0
10
20
m.mole
Adduct.

Fig. 21.

influenced by the initial concentration of reactants and remained approximately the same with or without traces of water, and in the presence or absence of oxygen. They concluded that oxidation and chlorination occurred simultaneously but independently.

The effect of variation of the initial concentration of reactants, effect of temperature, effect of substitution on the production of the chlorinated product, should all be investigated in an attempt to determine the role of the chlorinated species in the reaction. It is conceivable that this aspect could yield much useful information.

f). Effect of chlorinated products on kinetic results

As already mentioned the ratio: mole chlorinated hydrocarbon to mole of chromyl chloride reacted is 0·196, this will be approximated to 0·2 during the following discussion.

a). The toluene case.

The uncorrected rate expression for this case is:

$$\frac{dx}{dt} = k.(A - x')(B - 2x')$$

however the hydrocarbon is being used at a higher rate because of the formation of the chlorinated species. As two moles of chromyl chloride are involved the expression becomes:

$$\frac{dx}{dt} = k.(A - 1{\cdot}4x')(B - 2x')$$

which on integration gives:

$$k. = \frac{2.2{\cdot}303}{t.5.(2A - 1{\cdot}4B)} \log_{10} \frac{1{\cdot}4B}{2A}\left(\frac{\frac{2A}{1{\cdot}4} - x}{B - x}\right)$$

x' are the moles of reactants used at time t, and the other symbols have the meanings given on page 152.

A toluene run done at 40° and giving a rate constant of $4{\cdot}58.10^{-4}$ was corrected to $4{\cdot}91.10^{-4}$ on applying the foregoing rate expression.

b). The benzyl chloride case.

As only one mole of chromyl chloride is being involved in this case, the rate expression is:

$$\frac{dx}{dt} = k.(A - 1{\cdot}2x)(B - x)$$

this gives on integration:

$$k. = \frac{2{\cdot}303}{(A - 1{\cdot}2B)} \log_{10} \frac{1{\cdot}2B}{A} \left(\frac{\frac{A}{1{\cdot}2} - x}{B - x} \right).$$

The benzyl chloride run giving an uncorrected rate value of $2{\cdot}31.10^{-5}$ at 25° was corrected to $2{\cdot}68.10^{-5}$ on applying the foregoing rate expression.

As can be seen the results are slightly modified but not sufficiently to annul the conclusions, especially those conclusions based on relative rates which would be modified by a constant factor. Hence it is concluded that although the production of the chlorinated species does modify the rate expressions, conclusions based on uncorrected rate constants are still applicable.

CHAPTER IV

EXPERIMENTAL

EXPERIMENTAL AND RESULTS

Section a, reagents

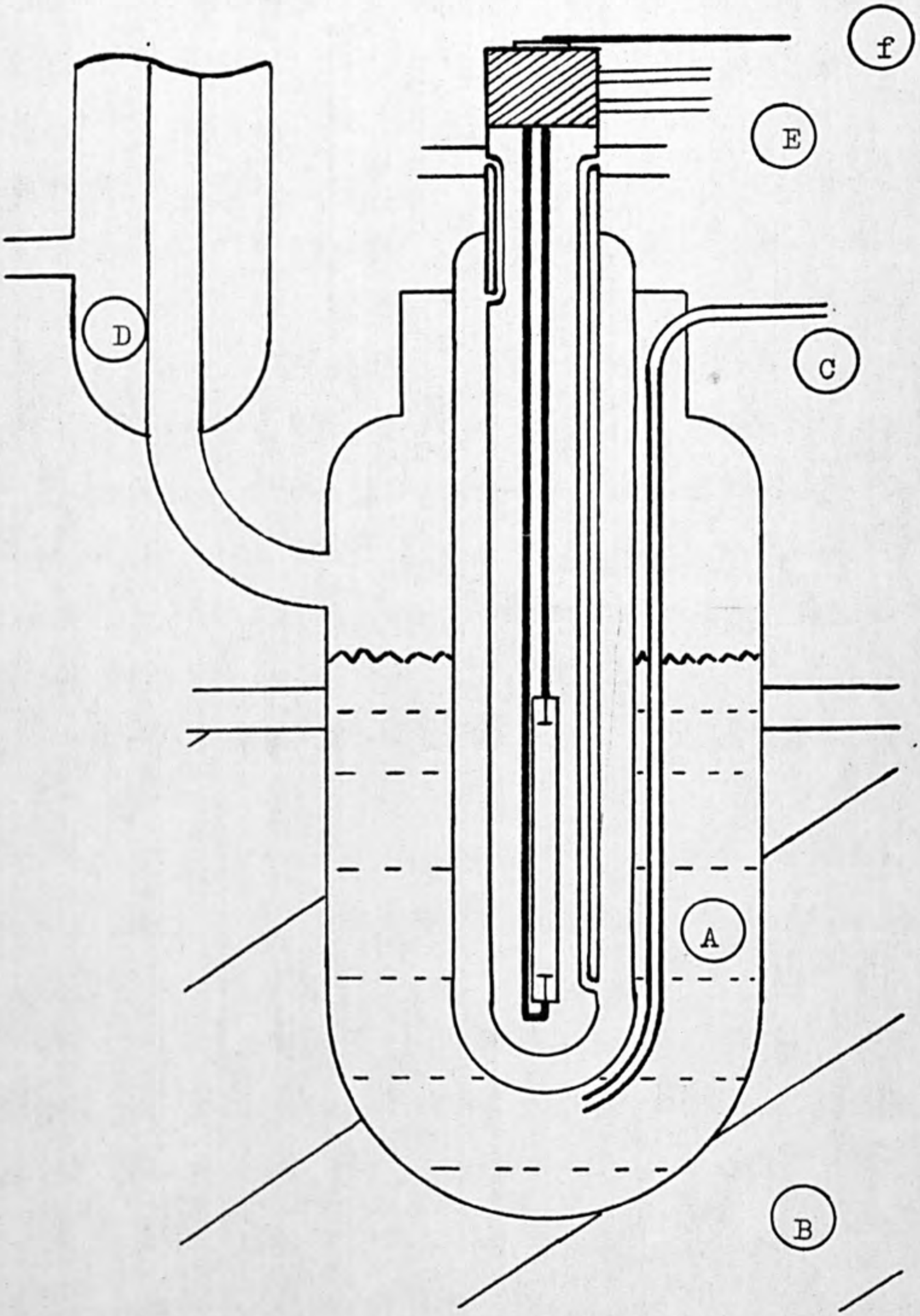
All the reagents were commercially available with the exception of the anhydrous chromic chloride and four of the benzyl chlorides.

The solvents used in the oxidations (carbon disulphide and carbon tetrachloride) were used after drying with anhydrous calcium chloride and then fractionally distilled twice. The carbon tetrachloride fraction boiling at 77° at 760 mm of Hg., and the carbon disulphide fraction boiling at 46° at 760 mm of Hg., were collected.

The toluenes were dried by standing over anhydrous calcium chloride and used without further treatment.

The p-nitro and p-chlorobenzyl chlorides were treated in similar manner to the toluenes. The m- and o-chloro and m- and o-nitrobenzyl chlorides were prepared by photo-chlorination of the corresponding toluene (approx. 200 ml.) was contained in the outer vessel A, fig. 1, and maintained between 150-200° by the heating mantle B chlorine was introduced from a cylinder via C and excess chlorine and hydrogen chloride

Fig. 1.



escaped through the condenser B. The source of ultra violet light was a 'Hanovia' immersion lamp contained in a quartz tube, inside a quartz cooling jacket. Air was contimuously circulated, via E, round the cooling jacket from an oil pump. The lamp was connected, P to a transformer working off the mains. The reaction was taken to approx. half convertion which required a reaction time between 30 and 50 hours, depending on the toluene.

The chlorobenzyl chlorides, (liquids) were obtained from the reaction solution by vacuum distillation and purified by fractional vacuum distillation. The m-chlorobenzyl chloride fraction boiling at 95-96° at approx. 2 mm of Hg and the o-chlorobenzyl chloride fraction boiling at 105° at approx. 2 mm of Hg, were collected.

The m-nitrobenzyl chloride crystallised from the reaction solution on cooling. It was recrystallised three times from 60/80 pet. ether, as well as being twice refluxed with charcoal. The compound was obtained as cream plates.

The o-nitrobenzyl chloride did not recrystallise from the reaction solution. When an attempt was made to remove the excess toluene by vacuum distillation, the solution rapidly darkened and decomposition occurred suddenly, though without explosion. The o-nitrobenzyl chloride was extracted from this solution by repeated extractions with 60/80 pet. ether. The excess pet. ether was removed by distillation, leaving an oil. This oil was purified by two charcoal treatments and seven recrystallizations from 60/80 pet. ether. The o-nitrobenzyl chloride was finally obtained as yellow crystals.

The o-nitrobenzyl chloride was unpleasant to handle, causing severe skin irration as well as being extremely lachrymatory. The analysis of these compounds is summarized in table 1.

Table 1

Compound	Analysis				M.P.	
	Found,		theory		found	theory
	C	H	C	H		
o-chloro	52·0	3·7	52·2	3·7		
m-chloro	52·1	3·8	52·2	3·7		
o-nitro	48·7	3·7	49·0	3·5	47–47·5	48–49 (16)
m-nitro	49·9	3·7	49·0	3·5	44–45	45–47 (16)

The aldehydes were used without further treatment.

The dioxan was purified in the following manner. 500 ml were refluxed with dilute hydrochloric acid with a stream of nitrogen for two days. Following the addition of a small quantity of stannous chloride the solution was firstly refluxed for a further eight hours, and then an aqueous layer was salted out by addition of sodium hydroxide pellets, this layer was rejected. The dioxan was then distilled from sodium, the fraction boiling between 100-101° at 760 mm of Hg., was collected.

Purification of the tetrahydrofuran was effected by refluxing with potassium hydroxide pellets and a small quantity of stannous chloride for a few hours. When the mixture had cooled the tetrahydrofuran was decanted, and lithium aluminium hydride added till effervescence ceased. The tetrahydrofuran was then distilled from an excess of lithium aluminium hydride the fraction boiling at 64° at 760 mm of Hg., was collected.

Anhydrous ether was kept over sodium wire and used without further treatment.

Anhydrous ether was kept over sodium wire

Anhydrous chromic chloride was prepared from 'Analar' chromic chloride hexahydrate by refluxing with thionyl chloride until no further evolution of hydrochloric acid occurred. The chromic chloride was found to be deficent in both chlorine and chromium; Cr, 30·5; Cl, 65·3%, $CrCl_3$ requires Cr, 32·8; Cl, 67·2%. This is consistent with the results of Frey who instigated this method of preparation and who obtained (78) analysis of; Cr, 31·5; Cl, 64·5%. In an attempt to obtain a pure sample, a quantity of chromic chloride obtained from the above preparation was introduced into a silica tube. The tube was closed and chlorine passed through while the chromic chloride was sublimed along the tube by means of external heating. The chromic chloride was allowed to cool in the chlorine and was then collected, (see section k).

The chromyl chloride was purified by distillation, the fraction boiling between 115-116° at 760 mm of Hg., being collected. Great care being taken to exclude any moisture. The distillation was facilitated by using a slow stream of dry nitrogen. When small quantities (approx. 5 ml) were required for the kinetic runs the chromyl chloride was redistilled immediately before use by utilizing the apparatus shown in Fig. 2.

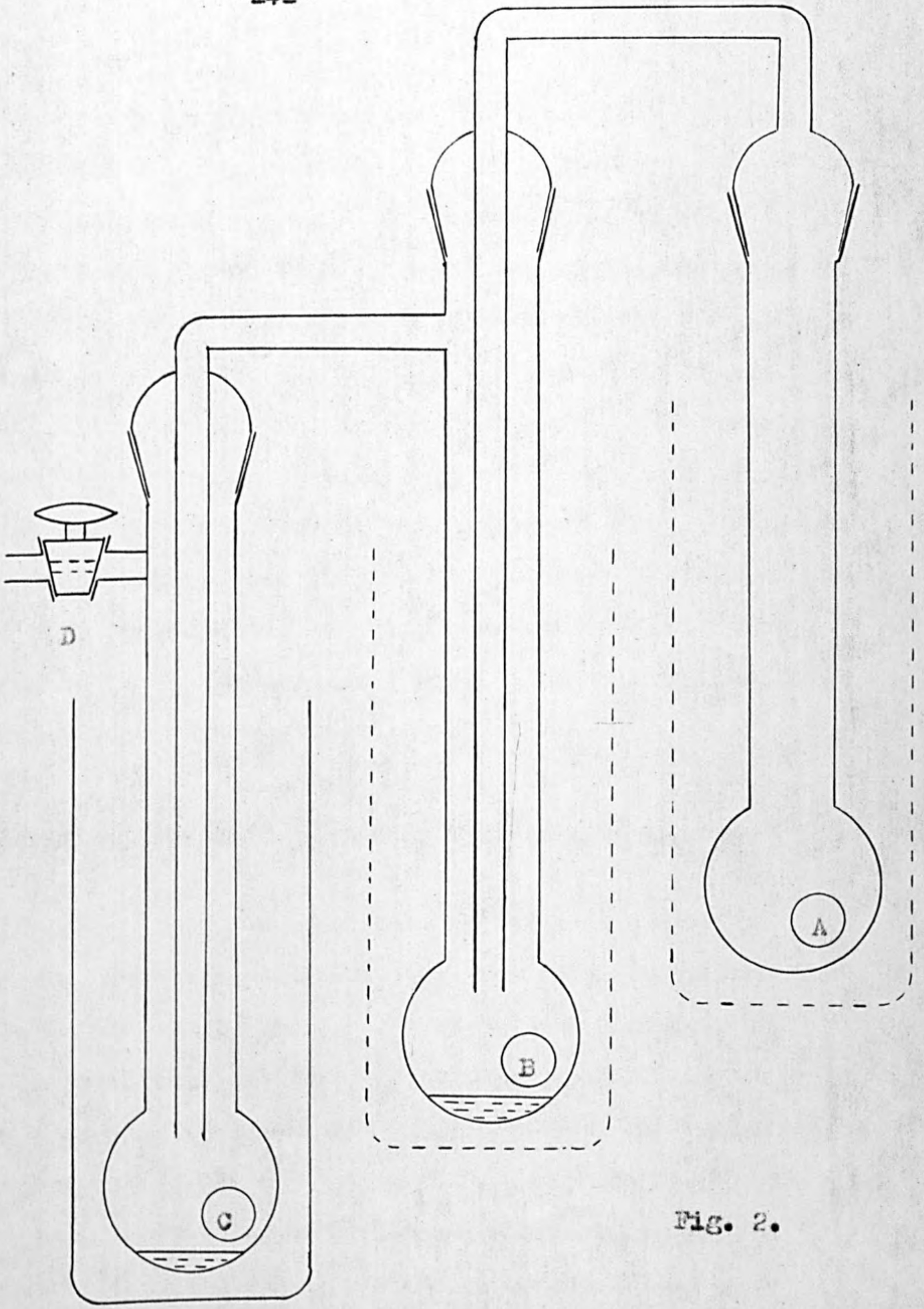


Fig. 2.

A sample of chromyl chloride was pipetted into the flask A, and cooled by surrounding the flask with a 'Dewar flask' containing a mixture of methanol and solid CO_2. The whole system was then pumped down and the stopcock [illegible] closed. The 'Dewar flask' was moved to surround flask B, thus causing the chromyl chloride to distil from A to B. The procedure was repeated so that the chromyl chloride was finally distilled into flask C. The 'Dewar flask' was then removed and the apparatus allowed to attain room temperature, when an atmosphere of air, dried by passage through sulphuric acid and a calcium chloride tube, was introduced. The required quantity of chromyl chloride was then directly pipetted from flask C.

Section b, Preparation and handling of the adducts.

The general method of preparation of the adducts involved the addition of the chromyl chloride in an inert solvent of either carbon tetrachloride or carbon disulphide to the hydrocarbon dissolved in the same solvent. It was found that if carbon tetrachloride was used as the solvent it was impossible to remove it from the adduct even on prolonged vacuum treatment. The spectra of adducts prepared in carbon tetrachloride always contained a peak at 800 cm^{-1} due to carbon tetrachloride which was never present in adducts prepared in carbon disulphide. Indeed 8% of the hydrolysis product of a toluene adduct was found to be carbon tetrachloride by G.L.C., although the adduct had been subjected to a prolonged vacuum treatment. A similar result has been reported of occlusion of carbon tetrachloride (49). Therefore it is concluded that the purest adducts are those prepared in carbon disulphide. The reaction solution was stirred and externally cooled in ice during the addition of the chromyl chloride. The chromyl chloride was added from a dropping funnel and both this and the reaction flask were protected from moisture by calcium chloride guard tubes. Every effort was made to preclude moisture at every stage of the preparation. In some cases modifications of the above procedure were undertaken. For instance in some preparation, no solvent was used and in others the hydrocarbon solution was added to the chromyl chloride solution. The following section illustrates the various preparations and where applicable variations are cited. All yields were calculated on the reagent which was not in excess.

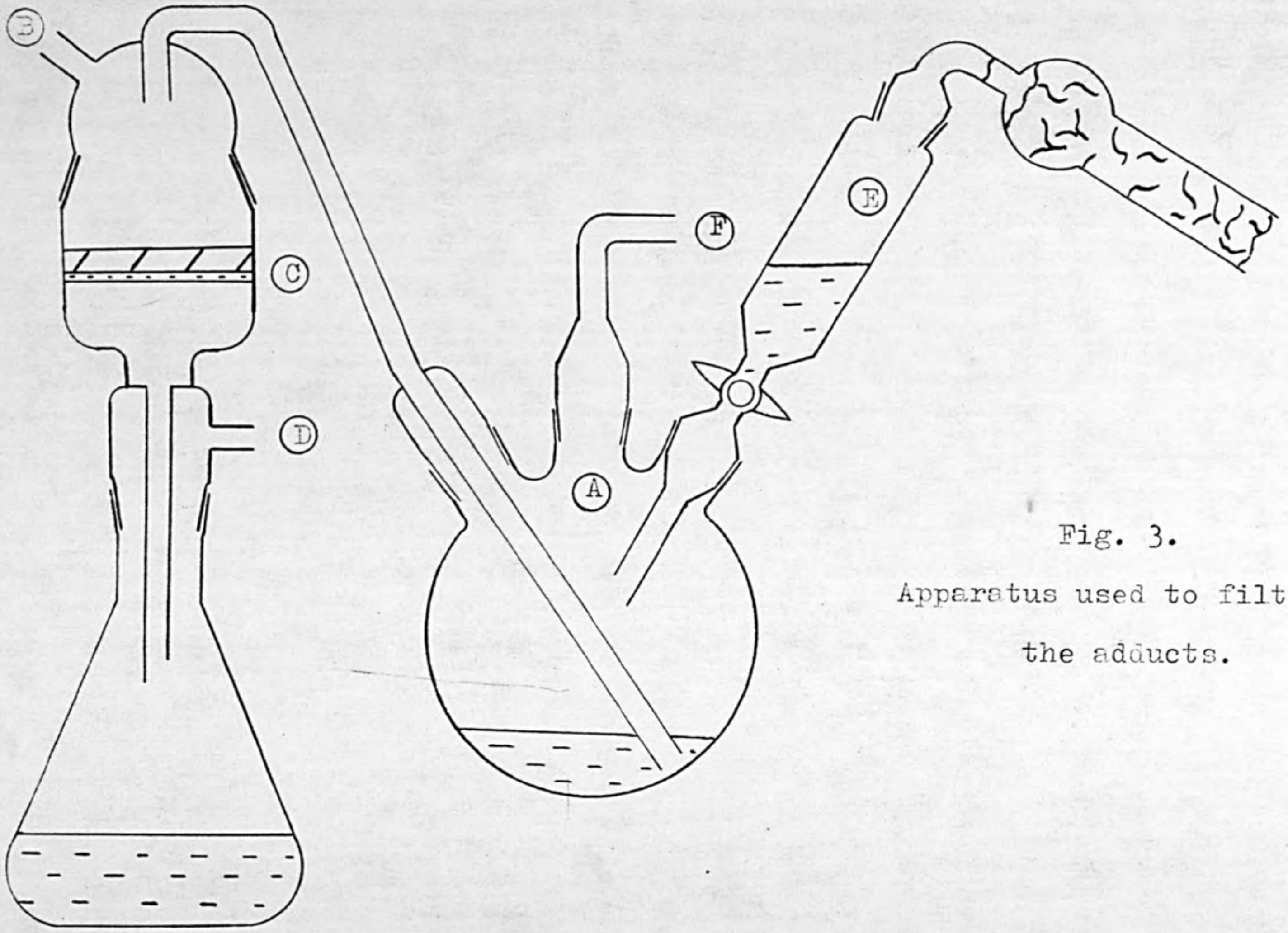


Fig. 3.

Apparatus used to filter the adducts.

Transferences of the adducts or complexes were carried out in a dry box. As already mentioned the adducts are extremely hygroscopic so that the adducts were filtered using the apparatus in fig. 3, so that no moisture could infiltrate into the system.

The reaction solution was drawn over from the reaction flask A, by applying a vacuum at B, through the filter pad C. The solution was then filtered by applying the vacuum at D. Fresh solvent was introduced into A by the dropping funnel E, and then pulled over onto the adduct on C by applying the vacuum at B. The solvent was then pulled through the adduct by applying the vacuum at D. This washing was continued until the filtrate was clear. The adduct was then pumped dry by high vacuum.

Section c, Oxidations with chromyl chloride

I. Reaction of chromyl chloride with benzyl chloride

(21 preparations)

a). To a solution of 20 ml; 0.17 mole, of $C_6H_5CH_2Cl$ in 100 ml of CCl_4 was added a solution of 5 ml; 0·06 mole of CrO_2Cl_2 in 100 ml of CCl_4. The solution was filtered after five days, the supernatent liquid was red. Yield of adduct; 16·88g, 0·06 mole, 99% theoretical.

b). To a solution of 20 ml; 0·174 mole of $C_6H_5CH_2Cl$ in 100 ml of CCl_4 was added a solution of 7·7g; 0·05 mole of CrO_2Cl_2 in 10 ml of CCl_4. The yield of adduct obtained after 7 days was 14·5g; 0·05 mole, quantitative.

c). To a solution of 5 ml, 0·043 mole of $C_6H_5CH_2Cl$ in 25 ml of CCl_4 maintained at 60° was added 1 ml; 0·012 mole of CrO_2Cl_2 in 3 ml of CCl_4. Throughout the experiment the temperature of the reaction solution was maintained at 60°. The yield of adduct obtained after 5 days was 2·86g; 0·01 mole, 83% theoretical.

d). To a solution of 9 ml; 0·11 mole of CrO_2Cl_2 in 100 ml of CCl_4 was added a solution of 10 ml; 0·09 mole of $C_6H_5CH_2Cl$ in 20 ml of CCl_4. Yield of adduct after 5 days was 20·94g; 0·075 mole, 85 5% theoretical.

e). To a solution of 5 ml;0·043 mole of $C_6H_5CH_2Cl$ in 25 ml of CCl_4 maintained at 55° throughout the preparation a solution of 0·8 ml; 0·01 mole of CrO_2Cl_2 was added. Yield of adduct after 9 hours, 2·79g; 0 01 mole quantitative.

f). To a solution of 3 ml; 0·026 mole of $C_6H_5CH_2Cl$ in 50 ml of CS_2 was added 1 ml; 0·012 mole of CrO_2Cl_2. Throughout the solution was maintained at 45°. Yield of adduct after 2 days, 3·64g; 0·013 mole, quantitative.

g). To a solution of 11 ml; 0·096 mole of $C_6H_5CH_2Cl$ in 43 ml of CS_2 was added 1 ml; 0·012 mole of CrO_2Cl_2. Throughout the reaction the solution was maintained at 45°. The yield of adduct obtained after 2 days was 3·74g; 0·013 mole, quantitative.

h). To 11·5g; 0·74 mole of CrO_2Cl_2 was added over 5 hr., 2 ml; 0·017 mole of $C_6H_5CH_2Cl$. No solvent was used in the preparation. Yield of adduct after 24 hr., 3·8g 0·014 mole, 80% theoretical.

II Reaction of chromyl chloride with benzyl bromide

(2 preparations)

To a solution of 25 ml of $C_6H_5CH_2Br$; 0·21 mole in 125 ml of CS_2 was added over 15 mins. a solution of 8 ml CrO_2Cl_2; 0·1 mole in 25 ml of CS_2. Yield of adduct 20·4g; 0·063 mole, after 24 days, 63% theoretical. The filtrate was coloured which was shown to be due to bromine.

III Reaction of chromyl chloride with benzyl alcohol

A solution of 1 ml; 0·01 mole of $C_6H_5CH_2OH$ in 25 ml of CS_2 was added dropwise over 5½ hours to a solution of 1·5 ml; 0·019 mole of CrO_2Cl_2 in 75 ml of CS_2. After the addition the solution was instantly filtered, the filtrate was deep red. The yield of adduct 1·9g; 0·007 mole, 72% theoretical.

IV Reaction of chromyl chloride with toluene

(4 preparations)

To a solution of 4·63 ml; 0·0435 mole of $C_6H_5CH_3$ in 100 ml of CCl_4 was added 2 ml; 0·025 mole of CrO_2Cl_2 in 20 ml CCl_4. Yield of adduct after 80 days, 4·9g; 0·024 mole, quantitative.

V Reaction of chromyl chloride with o-nitrotoluene

(4 preparations)

To a solution of 40 ml; 0·34 mole of o-$NO_2C_6H_4CH_3$ in 100 ml of CS_2 was added a solution of 4 ml CrO_2Cl_2; 0·04 mole, in 20 ml CS_2. Yield of adduct after 24 days, 11·1g; 0·05 mole, quantitative. The solution was slightly red.

VI Reaction of chromyl chloride with m-nitrotoluene.

No solvent used. To 25 ml; 0·21 mole of m-NO_2-$C_6H_5CH_3$ was added 1 ml; 0·012 mole of CrO_2Cl_2. No adduct had precipitated after 5 days. On addition of excess CS_2 an adduct was obtained. Yield of adduct 3·0g

VII Reaction of chromyl chloride with p-nitrobenzyl chloride

To a solution of 10·5g; 0·061 mole of p-NO_2-$C_6H_4CH_2Cl$ in 80 ml of CS_2 was added a solution of 2 ml of CrO_2Cl_2; 0·025 mole in 10 ml of CS_2. Yield of adduct after 23 days, 3·66g; 0·011 mole, 45% theoretical. The filtrate was deep red.

VIII Reaction of chromyl chloride with dioxane.

To a solution of 25 ml; 0·29 mole of $C_4H_8O_2$ in 150 ml of CCl_4 was added a solution of 10 ml; 0·123 mole of CrO_2Cl_2 in 15 ml of CCl_4 over 45 mins. Yield of adduct after 3 days, 31·0g; 0·128 mole, quantitative.

Section d. Preparation and reactions involving chromyl acetate

The method of Krauss (61) was used, 5g; 0·05 mole of CrO_3 were added to 200 ml of CCl_4. To this mixture was then added 2 ml; 0·02 mole of acetic anhydride and the mixture mechanically shaken for 3 hr., during which time the solution became deep red. The chromyl acetate was not isolated but used 'in situ' for the following qualitative experiments.

I Reaction of chromyl acetate with benzyl chloride.

Approx. 5 ml of the chromyl acetate solution was added to 3·5 ml of benzyl chloride in 10 ml of CCl_4. The solution became warm and was cooled in an ice bath. A dark brown precipitate was immediately evident. The precipitate was isolated and hydrolysed and the resulting solution extracted with ether. No benzaldehyde could be detected by means of G.L.C. The filtrate was similarly examined and again a negative result for benzaldehyde was obtained. However the presence of benzoic acid in the filtrate was confirmed.

II Reaction of chromyl acetate with benzaldehyde

To approx. 5 ml of the chromyl acetate solution was added a small quantity of benzaldehyde. Precipitation occured immediately. This dark brown precipitate was isolated and found to have a similar I.R. spectrum to the precipitate formed in the first experiment. Only benzoic acid could be isolated from the filtrate.

Section e. Kinetics

The kinetics were followed by directly determinating the quantity of adduct produced at suitable time intervals, by the following method.

A solution of the hydrocarbon ($4{\cdot}35.10^{-2}$ mole) except for xylenes ($2{\cdot}175.10^{-2}$) was made up to 200 ml in a suitable solvent, usually carbon disulphide. The solution was brought to the required temperature 25° or 40° by standing in a thermostate. When equilibrium had been reached, 2 ml of chromyl chloride ($2{\cdot}467.10^{-2}$ mole) purified as described on page 142, was added directly from a pipette. Standard aliquot portions, 14·9 or 14·5 ml of the reaction solution were then rapidly pipetted into tared flasks using the specially constructed pipette fig. 4. The flasks, which were fitted with ground glass tops were stoppered, placed into water tight black polythene containers which were then immersed in the thermostate. At suitable intervals a flask was removed and placed into a I.S.L. centrifuge. After centrifution the reaction solution was decanted off of the adduct, which was then twice washed with clean solvent. The adduct was then pumped dry, in the flask, under vacuum. The flask and adduct were then weighed, and the weight of the adduct calculated. The runs were performed in duplicate. Therate constants and errors were determined by using the least squares method. The fastest reaction required 6 hrs, whereas the slowest reaction benzal chloride at 25° was followed for over 700 hrs.

In the case of the toluenes the following expression was used to determine the rate constants k.

$$k = \frac{2.2\cdot 303}{t(2A - B)} \log_{10} \frac{B(2A - x)}{2A(B - x)}$$

where: t, time in secs.

A, initial concentration of hydrocarbon, mole/1.

B, initial concentration of chromy chloride, mole/1.

x, quantity of chromyl chloride reacted in mole/1.

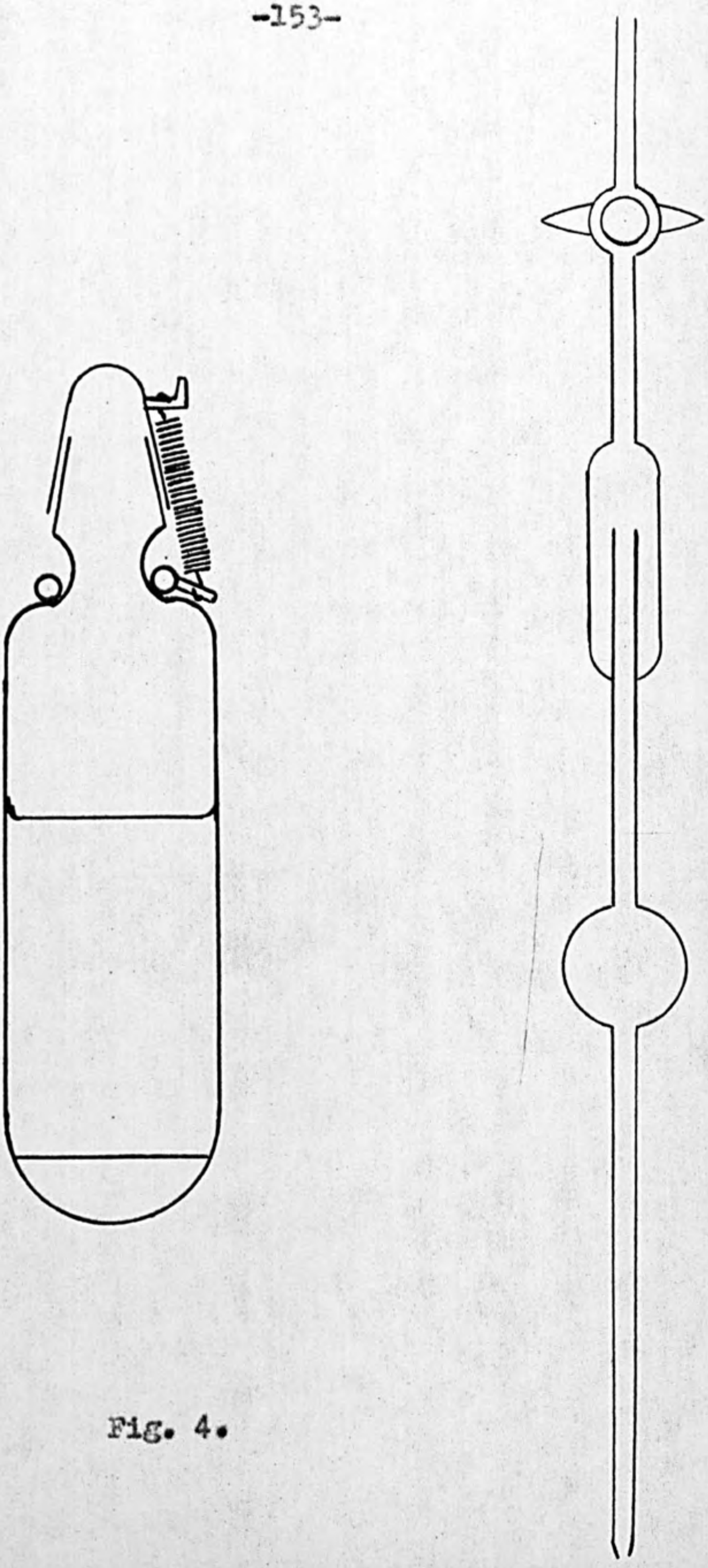


Fig. 4.

The expression in the case of the benzyl chloride:

$$k = \frac{2{\cdot}303}{t(A - B)} \log_{10} \frac{B(A - x)}{A(B - x)}$$

The symbols having the same meanings as in the first expression.

The values of enthalpy ΔH^*, entropy ΔS^* and Gibb's free energy ΔG^* for the activated state were calculated from standard thermodynamic expressions (35):

$$\Delta H^* = 2{\cdot}303R \frac{T_1 T_2}{(T_2 - T_1)} \log_{10}\left(\frac{k_2}{k_1} - \frac{T_2}{T_1}\right)$$

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T_1}$$

$$\Delta G^* = 2{\cdot}303 RT_1 \log_{10} \frac{Nhk_1}{RT_1}$$

where; k_1 and k_2 are the rate constants at 25° and 40° respectively.

T_1 and T_2 are the two temperatures 298°K and 313°K. The other symbols are the common thermodynamic constants.

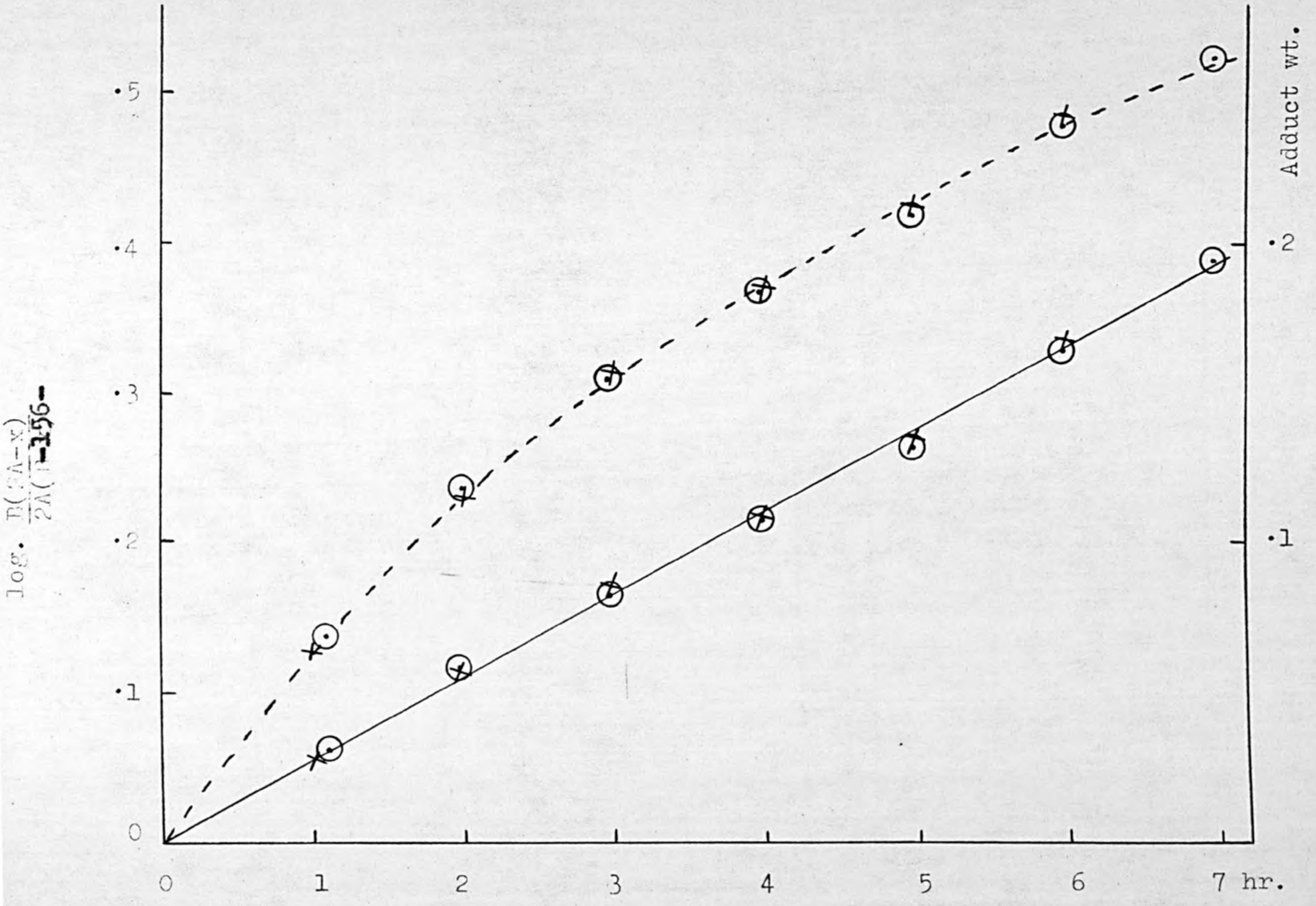
Section f. Kinetic results

The following examples are representative of the kinetic runs:

p-chlorotoluene at 40°, run R is shown as X and run V as ⊙ in the fig. 5.

Table 2, run R.

Time(hr)	Adduct obtained (g)	$\log_{10} \frac{B(2A - x)}{2A(B - x)}$
1	•064	•057
2	•116	•115
3	•157	•171
4	•186	•219
5	•213	•270
6	•242	•337
Table 3, run V.		
1½	•069	•062
2	•118	•118
3	•155	•168
4	•184	•215
5	•209	•262
6	•239	•329
7	•261	•389


log. B(2A−x) / 2A(
0
·1
·2
·3
·4
·5
Adduct wt.
·1
·2
0
1
2
3
4
5
6
7 hr.

p-nitrobenzyl chloride at 40°

Run CF is shown as ⊙ and run CL as X in fig. 6.

Time (hr)	Adduct obtained (g)	$\log_{10} \frac{B(A - x)}{A(B - x)}$
Table 4, run CF.		
22	·065	·022
44	·114	·042
89	·198	·084
162	·292	·149
187	·311	·167
211	·336	·190
235	·348	·203
Table 5, run CL.		
23	·067	·023
66	·158	·063
118	·234	·106
163	·300	·156
234	·344	·199
265	·383	·246

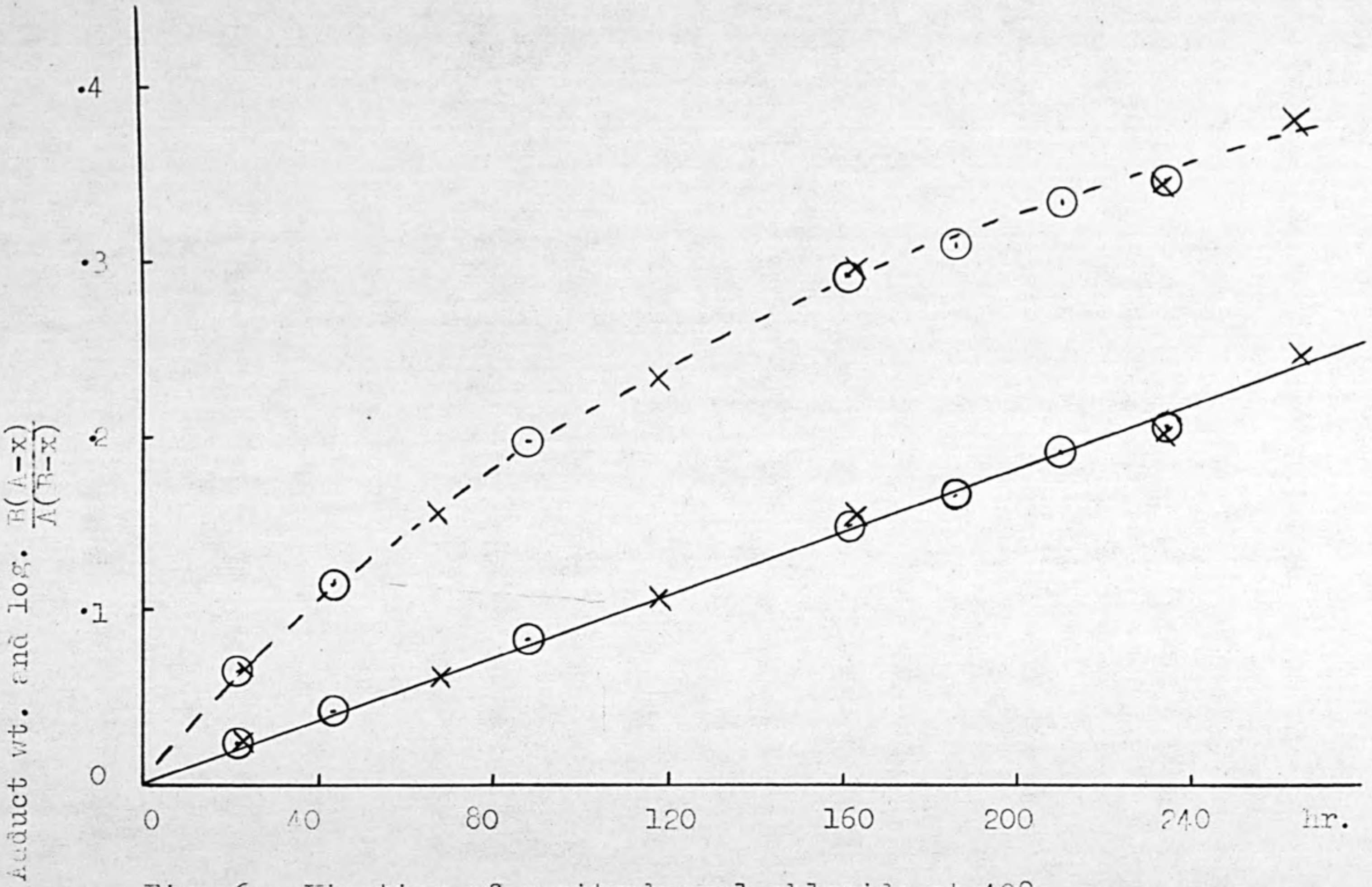


Fig. 6. Kinetics of p-nitrobenzyl chloride at 40°.

Table 6 Rate constants for toluenes.

Hydrocarbon	Temp. °c	Solvent	Rate, l.mole^{-1}.sec^{-1}.
Toluene	25	CS_2	$1\cdot35 \pm 0\cdot04.10^{-4}$
Toluene	25	CS_2	$1\cdot28 \pm 0\cdot03.10^{-4}$
p-$(CH_3)_3$C-	25	CS_2	$4\cdot53 \pm 0\cdot13.10^{-4}$
p-$(CH_3)_3$C-	25	CS_2	$4\cdot42 \pm 0\cdot12.10^{-4}$
p-CH_3-	25	CS_2	$5\cdot10 \pm 0\cdot27.10^{-4}$
p-CH_3-	25	CS_2	$5\cdot38 \pm 0\cdot17.10^{-4}$
m-CH_3-	25	CS_2	$2\cdot21 \pm 0\cdot06.10^{-4}$
m-CH_3-	25	CS_2	$2\cdot38 \pm 0\cdot07.10^{-4}$
p-Cl-	25	CS_2	$5\cdot28 \pm 0\cdot25.10^{-5}$
p-Cl-	25	CS_2	$5\cdot26 \pm 0\cdot21.10^{-5}$
p-br-	25	CS_2	$4\cdot76 \pm 0\cdot07.10^{-5}$
p-br-	25	CS_2	$4\cdot95 \pm 0\cdot09.10^{-5}$
p-I-	25	CS_2	$6\cdot35.10^{-5} \pm 0\cdot16$
p-I-	25	CS_2	$6\cdot51 \pm 0\cdot21.10^{-5}$
m-Cl-	25	CS_2	$1\cdot53 \pm 0\cdot03.10^{-5}$
m-Cl-	25	CS_2	$1\cdot50 \pm 0\cdot05.10^{-5}$
m-br-	25	CS_2	$1\cdot49 \pm 0.02.10^{-5}$
m-br-	25	CS_2	$1\cdot47 \pm 0\cdot02.10^{-5}$

Table 6 Rate constants for toluenes continued.

Hydrocarbon	Temp. °c	Solvent	Rate, l.mole^{-1}.sec^{-1}.
m-I-	25	CS_2	$1{\cdot}70 \pm 0{\cdot}02.10^{-5}$
m-I-	25	CS_2	$1{\cdot}73 \pm 0{\cdot}02.10^{-5}$
m-NO_2-	25	CS_2	$1{\cdot}99 \pm 0.06.10^{-6}$
m-NO_2-	25	CS_2	$1{\cdot}94 \pm 0{\cdot}10.10^{-6}$
p-NO_2-	25	CS_2	$2{\cdot}55 \pm 0{\cdot}05.10^{-6}$
p-NO_2-	25	CS_2	$2{\cdot}49 \pm 0{\cdot}02.10^{-6}$
o-NO_2-	25	CS_2	$1{\cdot}12 \pm 0{\cdot}07.10^{-6}$
o-Cl-	25	CS_2	$1{\cdot}63 \pm 0{\cdot}04.10^{-5}$
Toluene	40	CS_2	$4{\cdot}76 \pm 0.15.10^{-4}$
Toluene	40	CS_2	$4{\cdot}58 \pm 0{\cdot}10.10^{-4}$
p-$(CH_3)_3C$-	40	CS_2	$1{\cdot}44 \pm 0{\cdot}03.10^{-3}$
p-$(CH_3)_3C$-	40	CS_2	$1{\cdot}48 \pm 0{\cdot}03.10^{-3}$
p-CH_3-	40	CS_2	$1{\cdot}61 \pm 0{\cdot}04.10^{-3}$
p-CH_3-	40	CS_2	$1{\cdot}57 \pm 0{\cdot}03.10^{-3}$
m-CH_3-	40	CS_2	$6.47 \pm 0{\cdot}08.10^{-4}$
m-CH_3-	40	CS_2	$6{\cdot}60 \pm 0{\cdot}06.10^{-4}$

Table 6, Rate constants for toluenes continued.

Hydrocarbon	Temp. °c	Solvent	Rate, l. $mole^{-1}$. sec^{-1}.
p-Cl-	40	CS_2	2·26 ± 0·05.10^{-4}
p-Cl-	40	CS_2	2·22 ± 0·03.10^{-4}
p-br-	40	CS_2	1·84 ± 0·04.10^{-4}
p-br-	40	CS_2	1·84 ± 0·06.10^{-4}
p-I-	40	CS_2	2·06 ± 0·02.10^{-4}
p-I-	40	CS_2	2·04 ± 0·04.10^{-4}
m-Cl-	40	CS_2	7·22 ± 0·02.10^{-5}
m-Cl-	40	CS_2	7·23 ± 0·02.10^{-5}
m-br-	40	CS_2	6·14 ± 0·09.10^{-5}
m-br-	40	CS_2	6·48 ± 0·11.10^{-5}
m-I-	40	CS_2	7·26 ± 0·12.10^{-5}
m-I-	40	CS_2	7·40 ± 0·13.10^{-5}
m-NO_2-	40	CS_2	9·06 ± 0·32.10^{-6}
m-NO_2-	40	CS_2	9·46 ± 0·34.10^{-6}
p-NO_2-	40	CS_2	1·20 ± 0·04.10^{-5}
p-NO_2-	40	CS	1.22 + 0.04.10^{-5}

Table 6. Rate constants for toluenes continued.

Hydrocarbon	Temp. °c	Solvent	Rate, l. mole^{-1}. sec^{-1}.
o-NO_2-	40	CS_2	5·42 ± 0·09.10^{-6}
o-Cl-	40	CS_2	6·82 ± 0·08.10^{-5}
Toluene	40	CCl_4	4·38 ± 0·09.10^{-4}
p-NO_2-	40	CCl_4	1·27 ± 0·02.10^{-5}
Toluene (solvent corrected for)	40	C_6H_6	7·13 ± 0·32.10^{-4}

Table 7. Variation of toluene with initial concentration

CrO_2Cl_2 mole/l.	Toluene mole/l.	Temp. °c	Solvent	Rate, l. mole^{-1}. sec^{-1}.
0·2467	0·2175	40	CS_2	3·33 ± 0 14.10^{-4}
0·1234	0·435	40	CS_2	4·00 ± 0·13.10^{-4}
0·1234	0·2175	40	CS_2	4·67 ± 0·12.10^{-4}

Table 8. Rate constants for benzyl chlorides.

Hydrocarbon	Temp.$^{\circ}$c	Solvent	Rate,l.mole^{-1}.sec^{-1}.
$PhCH_2Cl$	25	CS_2	2·31 ± 0·18.10^{-5}
$PhCH_2Cl$	25	CS_2	2·59 ± 0·18.10^{-5}
p-Cl-	25	CS_2	1·50 ± 0·01.10^{-5}
p-Cl-	25	CS_2	1·46 ± 0·01.10^{-5}
m-Cl-	25	CS_2	4·64 ± 0·05.10^{-6}
m-Cl-	25	CS_2	4·23 ± 0·11.10^{-6}
o-Cl-	25	CS_2	3·01 ± 0·10.10^{-6}
p-NO_2-	25	CS_2	1·47 ± 0·03.10^{-6}
p-NO_2-	25	CS_2	1·41 ± 0·04.10^{-6}
m-NO_2-	25	CS_2	1·13 ± 0·07.10^{-6}
m-NO_2-	25	CS_2	1·13 ± 0·03.10^{-6}
o-NO_2-	25	CS_2	6·37 ± 0·01.10^{-7}
$PhCH_2Cl$	40	CS_2	9·60 ± 0·14.10^{-5}
$PhCH_2Cl$	40	CS_2	9·52 ± 0·13.10^{-5}
m-Cl-	40	CS_2	1·60 ± 0·05.10^{-5}
m-Cl-	40	CS_2	1·56 ± 0·09.10^{-5}

Table 7. Rate constants of benzyl chlorides continued.

Hydrocarbon	Temp. °c	Solvent	Rate, l.mole^{-1}.sec^{-1}
p-NO_2-	40	CS_2	$5{\cdot}46 \pm 0.18.10^{-6}$
p-NO_2-	40	CS_2	$5{\cdot}86 \pm 0{\cdot}09.10^{-6}$
m-NO_2-	40	CS_2	$4{\cdot}37 \pm 0{\cdot}09.10^{-6}$
m-NO_2-	40	CS_2	$4{\cdot}45 \pm 0{\cdot}14.10^{-6}$
o-NO_2-	40	CS_2	$3{\cdot}25 \pm 0{\cdot}01.10^{-6}$
o-Cl-	40	CS_2	$1{\cdot}04 \pm 0{\cdot}05.10^{-5}$

Table 9. Other rate constants.

$PhCH_2Br$	25	CS_2	$8{\cdot}53 \pm 0{\cdot}29.10^{-6}$
$PhCHCl_2$	40	CS_2	$5{\cdot}01 \pm 0.01.10^{-6}$
$PhCHCl_2$	25	CS_2	$1{\cdot}72 \pm 0{\cdot}03.10^{-6}$
$PhCH_2Cl$ (excess CrO_2Cl_2)	25	CS_2	$2{\cdot}45 \pm 0{\cdot}08.10^{-5}$

Table 10, Physical constants for toluenes.

Hydrocarbon	ΔH^* k.cal	ΔS^*_{298} cal/deg	ΔG^*_{298} k.cal.
Toluene	15·1	25·6	22·7
p-$(CH_3)_3C$-	14·0	26·8	22·0
p-CH_3-	13·1	29·5	21·9
m-CH_3-	12·3	33·8	22·4
p-Cl-	17·3	20·1	23·3
m-Cl-	18·7	17·8	24·0
p-I-	13·7	31·6	23·2
m-I-	17·4	22·1	24·0
p-br-	15·9	25·1	23·3
m-br-	17·3	22·6	24·1
p-NO_2-	18·8	21·0	25·1
m-NO_2-	18·5	22·7	25·2
o-NO_2-	20·2	18·1	25·6
o-Cl-	18·3	19·0	24·0

Table 10. Physical constants for toluenes, continued

$$\frac{\partial \Delta H^{*}}{\partial \sigma^{+}} = 6{\cdot}0 \pm 0{\cdot}9 \text{ k.cal.}$$

$$\left(\frac{\partial \Delta G^{*}}{\partial \sigma^{+}}\right)_{298} = 3{\cdot}15 \pm 0{\cdot}12 \text{ k.cal}$$

$$\left(\frac{\partial \Delta G^{*}}{\partial \sigma^{+}}\right)_{313} = 3{\cdot}01 \pm 0{\cdot}12 \text{ k.cal.}$$

$$\frac{\partial \Delta S^{*}}{\partial \sigma^{+}} = 9{\cdot}3 \pm 3{\cdot}2 \text{ cal/deg.}$$

Table 11. Physical constants for benzyl chlorides.

Hydrocarbon	ΔH^* k.cal	ΔS^* cal/deg	ΔG^*_{298} k.cal.
$PhCH_2Cl$	17·4	21·1	23·7
p-Cl-	16·4	25·4	24·0
m-Cl-	16·3	28·3	24·7
o-Cl-	15·9	30·4	25·0
p-NO_2-	17·5	26·5	25·4
m-NO_2-	17·5	27·0	25·6
o-NO_2-	20·7	17·3	25·9

$$\left(\frac{\partial \Delta G^*}{\partial \sigma^+}\right)_{298} = 2{\cdot}39 \text{ k.cal.} \qquad \frac{\partial \Delta S^*}{\partial \sigma^+} = 5{\cdot}52 \text{ cal/deg.}$$

$$\frac{\partial \Delta H^*}{\partial \sigma^+} = 1{\cdot}36 \text{ k.cal.}$$

Table 12. Hammett reaction values.

Toluene:

$^{+}$ at 25° = $-2{\cdot}31 \pm 0{\cdot}10$

$^{+}$ at 40° = $-2{\cdot}20 \pm 0{\cdot}08$

at 40° = $-2{\cdot}28 \pm 0{\cdot}08$

Benzyl chlorides:

$^{+}$ at 25° = $-1{\cdot}71 \pm 0{\cdot}16$

$^{+}$ at 40° = $-1{\cdot}68 \pm 0{\cdot}16$

Section g, analysis

Carbon and hydrogen were determined simultaneously by using a Baird and Tatlock semi-micro combustion apparatus as described by Belcher and Ingram (5,54,55).

Total chlorine was determined using a Baird and Tatlock semi-micro combustion apparatus (6,56). The accuracy claimed for both the combustion techniques is 0·3%. The instruments were periodically checked using micro-analytical standard samples of sucrose and p-chlorobenzoic acid.

Ionic chlorine was determined as silver chloride by the standard gravimetric procedure (105).

Chromium was determined by precipitating the chromium as chromium hydroxide with ammonium hydroxide from a solution buffered with ammonium chloride (105). The chromium hydroxide was subsequently pyrolysed to chromium trioxide and weighed. If there was any possibility of the chromium containing residual oxidizing power, sodium metabisulphite was added to the solution before addition of the alkali.

The aldehyde contents of the adducts and complexes were determined as their 2.4.dinitrophenylhydrazones. Following the recommendation of Iddles and co-workers (52,53) the 2.4.dinitrophenyl hydrazine was prepared in 2N hydrochloric acid. As a precaution the adducts were hydrolysed with ferrous sulphate, as any reducible chromium would preferentially react with the ferrous sulphate and not with the liberated aldehyde.

During the course of the investigation two gas chromatographic fractometers were used, namely a Perkin Elmer fractometer and a Wilkins 600 fractometer the latter fitted with a disc integrater.

Section h. infra red and other physical techniques

Infra red spectra were obtained using either an Unicam S.P.200 recording spectrometer or a Grubb Parsons spectromaster. Good spectra were obtained for the adducts. The spectra obtained from the S.P.200 were calibrated using reference peaks in a polystyrene spectrum. The spectra were obtained as cells, using suitable solvents such as carbon tetrachloride or carbon disulphide, or as mulls, using nujol or hexachloro 2.4.butadiene as the supporting phases, depending on the range under investigation.

A number of adducts were subjected to differential thermal analysis. The initial results were obtained on an experimental apparatus (39), and subsequently run on a Perkin Elmer D.S.C. 1B differential scanning calorimeter.

An X-ray spectrum of a benzyl chloride adduct was obtained which showed that the compound was X-ray amorphous.

Section i, determination of oxidising power

Two methods were used to obtain information pertaining to the oxidation state of the adduct chromium. In the first the magnetic susceptibilities of the adducts were determined using a 'Gouy' balance. The tube was filled under vacuum to exclude any possibility of hydrolsis. The apparatus was standardized using the complex; $Hg(Co(SCN)_4)$ whose volume suceptibility was known. The results of the determinations were expressed in Bohr magnetons ( ). The following table was used to indicate the values associated with the possible states of chromium (75)

Table 13.

	No.of unshared electrons	μcal	μobs
Cr^{VI}	0	0	0
Cr^{V}	1	1·73	1·7–1·8
Cr^{IV}	2	2·83	2·8–3·1
Cr^{III}	3	3·87	3·85–3·9

The second method involved redox titrations which although incapable of differentiating between the actual oxidation states of the chromium, was never the less found to be extremely useful and gave the average oxidation state. The method involved dissolving a known quantity of adduct in an acidic solution of potassium iodate and titrating the liberated iodine with standard sodium thiosulphate, using starch indicator. The method was checked by determinations with ferrous to ferric and stannous to stannic systems.

Section j. Infra red spectra of the adducts.

Spectra obtained as described in section h.

The following abbreviations are used:

s, strong   sh, shoulder   w, weak   m, medium.

Table 14. Toluene adducts.

Toluene	p-CH_3-	m-CH_3-
3300 s	3300 s	3300 s
1618 s	1631 w	1618 s
1594 s	1613 w	1587 s
1572 s	1592 s	1577 sh
1455 s	1560 s	1515 w
1387 m	1541 w	1460 s
1377 w	1464 s	1377 m
1321 m	1418 w	1326 w
1229 m	1379 m	1311 w
1174 m	1318 w	1299 w
1023 w	1238 m	1258 m
845 m	1175 s	1170 sh
755 m	1024 m	1161 m
676 w	980 w	1022 w
	955 w	980 sh
	860 m	784 w
	813 m	750 w
	769 m	676 m

Table 14. Infra red spectra of toluene adducts continued.

p-$(CH_3)_3C$-	m-I-	p-I-
3300 s	3300 s	3300 s
1618 sh	1616 s	1618 sh
1594 s	1610 s	1610 s
1554 s	1577 s	1577 s
1462 s	1555 sh	1550 s
1417 m	1553 s	1465 sh
1376 s	1511 w	1460 s
1323 w	1458 s	1405 m
1239 m	1422 w	1377 m
1182 m	1376 s	1316 w
1123 m	1297 w	1227 m
1023 m	1218 s	1175 m
996 w	1175 w	1053 m
980 w	1058 w	1007 m
955 w	1021 m	845 m
862 w	954 w	816 m
837 w	787 w	692 w
712 m	713 w	
	680 w	

Table 14.

Infra red spectra of toluenes continued.

m-Cl-	p-Cl-	o-Cl-
3300 s	3300 s	3300 s
1629 sh	1623 sh	1617 sh
1620 s	1618 s	1610 s
1610 sh	1613 sh	1584 s
1590 s	1587 s	1558 w
1565 s	1559 s	1529 w
1462 s	1488 m	1464 sh
1435 sh	1462 s	1457 s
1377 m	1411 m	1443 s
1294 w	1384 m	1376 m
1214 m	1305 w	1304 w
1166 w	1225 m	1279 s
1074 w	1089 m	1218 m
995 w	1022 s	1165 w
954 w	1012 w	1056 w
790 w	853 w	977 w
741 m	827 w	874 w
701 m	717 w	762 m
666 m		728 m
		648 w

Table 14. Infra red spectra of toluene adducts continued.

m-NO$_2$-	p-NO$_2$-	o-NO$_2$-
3300 s	3300 s	3300 s
1637 sh	1650 sh	1597 m
1629 s	1639 sh	1527 s
1608 s	1629 s	1486 w
1577 m	1597 s	1458 m
1531 s	1524 s	1416 s
1458 s	1460 m	1376 m
1376 m	1416 w	1348 m
1353 s	1376 w	1309 w
129 w	1326 w	1080 w
1217 m	1302 w	978 w
1167 w	1217 m	957 w
1104 w	1173 w	868 w
1093 m	1012 w	842 w
995 w	955 w	790 w
968 w	828 m	778 w
947 m	740 m	732 m
911 w		703 w
826 m		

Table 14. Infra red spectra of toluene adducts continued.

p-br-	m-br-
3300 s	3300 s
1616 s	1616 s
1581 s	1585 s
1559 sh	1558 s
1554 s	1456 s
1484 w	1429 w
1458 s	1376 s
1407 m	1292 w
1377 m	1220 s
1304 w	1211 s
1225 m	1164 w
1174 m	1066 w
1067 m	1021 m
1010 m	992 m
977 w	898 m
955 w	956 m
849 m	786 m
817 w	721 m
703 w	686 m
	669 m

Table 15. Infra red spectra of benzyl chlorides adducts.

m-Cl-	p-Cl-	o-Cl-
3300 s	3300 s	3300 s
1623 sh	1626 sh	1618 sh
1616 s	1616 s	1610 s
1608 sh	1585 s	1580 s
1587 s	1558 s	1560 sh
1562 s	1488 w	1534 m
1517 m	1457 m	1462 m
1464 m	1412 s	1445 s
1433 m	1379 m	1408 m
1376 w	1304 w	1385 sh
1292 w	1292 sh	1377 m
1212 s	1225 s	1305 w
1166 w	1171 s	1279 s
1073 w	1089 s	1218 m
995 w	1012 m	1166 w
954 w	852 m	1056 m
883 m	825 m	976 m
789 m	768 w	955 m
741 m	717 m	872 w
700 m		761 m
666 m		727 m
		649 w

Table 15. Infra red spectra of benzyl chloride adducts cont.

m-NO_2-	p-NO_2-	o-NO_2-
3300 s	3300 s	3300 s
1634 sh	1653 sh	1595 m
1629 s	1637 sh	1527 s
1608 s	1629 s	1486 w
1576 m	1597 s	1460 m
1531 s	1527 s	1418 s
1453 s	1453 m	1374 m
1376 w	1416 m	1346 m
1353 s	1376 w	1309 w
1297 w	1344 s	1269 w
1219 s	1325 w	1079 w
1217 s	1300 w	975 w
1168 w	1217 m	956 w
1104 sh	1174 w	867 w
1093 m	1110 w	859 w
976 w	1012 w	838 w
950 w	975 w	789 w
913 w	955 w	779 w
826 w	853 m	738 m
812 w	826 s	701 w
732 m	743 m	650 m
	729 w	

Table 15. Infra red spectra of benzyl chloride adducts cont.

Benzyl chloride
3300 s
1684 w
1618 s
1594 s
1572 s
1455 s
1388 m
1377 w
1321 m
1227 s
1174 m
1023 w
990 w
845 m
755 m
678 w

Table 16. Infra red spectra of other adducts.

Benzyl bromide	Benzyl alcohol
3300 s	3300 s
1681 w	1681 w
1619 s	1621 s
1616 s	1614 s
1594 s	1595 s
1572 s	1572 s
1453 s	1455 s
1377 w	1389 m
1322 w	1377 w
1229 m	1321 m
1174 m	1229 m
1022 w	1174 m
1000 w	1022 w
845 m	1000 w
755 m	975 w
678 w	845 m
	754 m
	680 w

Section k. Co-ordination complexes.

All the chromic chloride complexes were prepared in a similar manner, using the chromic chloride as obtained from the dehydration of the hexa-aqua chromic chloride. The chromic chloride was always transfered in a dry box and extensive precautions taken to preclude moisture at every stage of the preparations. The chromic chloride, and the aldehyde together with a small quantity of thionyl chloride; to maintain anhydrous conditions, were gently warmed in a 'pear' flask immersed in an oil bath. The mixture was heated until the chromic chloride had completely dissolved. The oil bath was not allowed to rise more than 15° above the melting point of the aldehydes in the case of the nitro-aldehydes, higher temperatures approx. 100° were required for the chloro-aldehydes. The hot solution was filtered as shown in fig. 7. By applying a vacuum at A the hot solution was filtered through the pad C and subsequently allowed to cool in flask B. On cooling the complex crystallised and was removed by filtration and purified by washing with carbon disulphide containing thionyl chloride, as the nitro-aldehydes are solids at room temperature the complexes formed from them had to be leached out from the

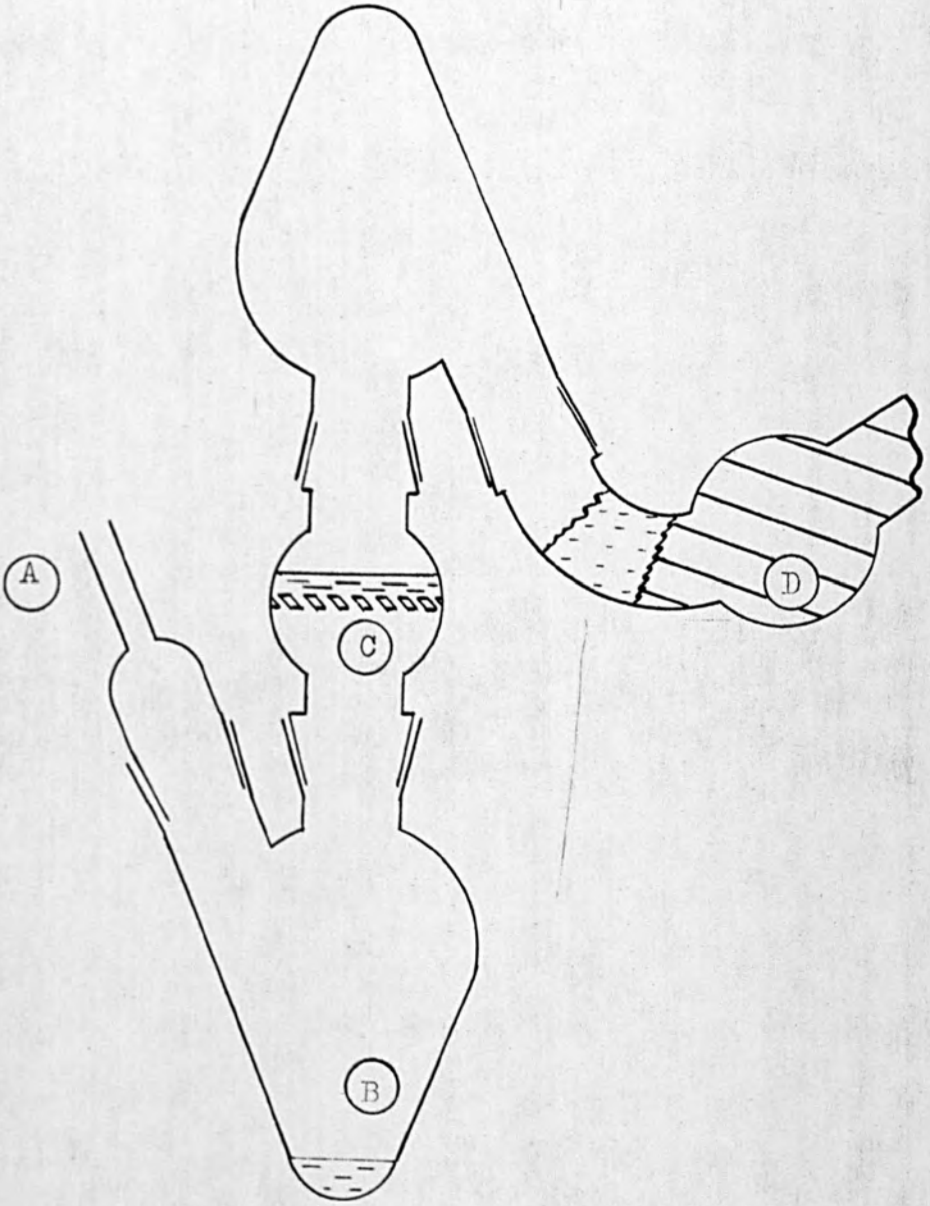


Fig. 7. Filtration apparatus used in the preparation of chromic chloride complexes.

excess aldehyde, by solvent extraction of the aldehyde. The metabenzaldehyde complexes were unique among the series as they appeared to form directly without an intermediate simple dissolution-crystallization process.

Recrystallization of the complexes was attempted from chloro- and nitrobenzene, however although the complexes dissolved, with the exception of the metabenzaldehyde complexes they were recovered in a different form. Complexes of a 3:1 composition were changed into 2:1 complexes.

Because the chromic chloride obtained from dehydration was always deficient in chromium and chlorine, and these deficiencies must manifest themselves in the chromic chloride complexes, which could not be recrystallized. Other methods (44,104) which result in purer chromic chloride were investigated. These methods invariable include a stage in which the chromic chloride is sublimed in an atmosphere of chlorine or hydrogen chloride.

However the sample of sublimed chromic chloride obtained (see section a), had changed its properties. It was now pink, but more important was unaffected by the co-ordinating compounds. It could also be left open to the atmosphere without appreciable depreciation. It is known that (78) there are two forms of chromic chloride, and presumably the form; which forms co-ordination complexes readily, is changed into the second form on sublimation. Therefore it was concluded that, only the chromic chloride formed by the dehydration method was applicable to complex formation, and the defidencies inherent in the complexes must be accepted.

Preparation of a complex.

The following preparation is typical of the method used.

1·54g; 0·01 mole of chromic chloride and 7·90g; 0.05 mole of p-nitrobenzaldehyde, m.p. $106 \cdot 5^{\circ}$ were mixed with 1 ml of thionyl chloride. The mixture was maintained between $110-120^{\circ}$ for three hours. The hot solution was filtered as already described, and allowed to cool. The excess aldehyde was leached out, yielding 5·50g; 0·009 mole, 93% theoretical, of a pink complex.

Section l. Analysis of co-ordination complexes.

The analysis was carried out as described in section g.

Table 17. $CrCl_3.(C_6H_5CHO)_3$

Element	Found	Theory
C	53·1	52·9
H	3·95	3·78
Cr	10·3	10·9
Cl	22·0	22·4

Table 18. $CrCl_3.(C_6H_5CHO)_2$

C	45·5	45·4
H	3·26	3·24
Cr	14·1	14·0
Cl	28·4	28·8

$CrCl_3.(C_6H_5CHO)_3$ - rust.

$CrCl_3.(C_6H_5CHO)_2$ - pink.

Analysis of co-ordination complexes continued.

Table 19. $CrCl_3.(o\text{-}NO_2C_6H_5CHO)_3$

Element	Found	Theory
C	41·4	41·3
H	2·68	2·45
Cr	8·6	8·5
Cl	14·4	17·4

Table 20. $CrCl_3(o\text{-}NO_2C_6H_5CHO)_2$

C	35·3	36·5
H	2·20	2·17
Cr	12·4	11·3
Cl	23·2	23·2

$CrCl_3(o\text{-}NO_2C_6H_5CHO)_3$ - pink.

$CrCl_3(o\text{-}NO_2C_6H_5CHO)_2$ - purple.

Analysis of co-ordination complexes continued.

Table 21. $CrCl_3 .(p-NO_2C_6H_4CHO)_3$

Element	Found	Theory
C	41·3	41·3
H	2·41	2·45
Cr	8·4	8·5
Cl	16·8	17·4

Table 22. $CrCl_3(p-NO_2C_6H_4CHO)_2$

C	37·3	36·5
H	2·41	2·17
Cr	8·9	11·3
Cl	23·0	23·2

$CrCl_3(p-NO_2C_6H_4CHO)_3$ - pink.

$CrCl_3(p-NO_2C_6H_4CHO)_2$ - purple.

Analysis of co-ordination complexes continued.

Table 23. $CrCl_3(m\text{-}NO_2C_6H_4CHO)_2$

Element	Found	Theory
C	36•2	36•5
H	2•15	2•17
Cr	11•5	11•3
Cl	23•0	23•2

$CrCl_3(m\text{-}NO_2C_6H_4CHO)_2$ - mauve.

Analysis of co-ordination complexes continued.

Table 24. $CrCl_3(o\text{-}ClC_6H_4CHO)_3$

Element	Found	Theory
C	41•2	43•5
H	2•5	2•6
Cr	11•2	9•0
Cl (ionisable)	18•1	18•4

Table 25. $CrCl_3(o\text{-}ClC_6H_4CHO)_2$

C	38•1	38•3
H	2•48	2•3
Cr	11•5	11•8
Cl (ionisable)	21•8	24•2

$CrCl_3(o\text{-}ClC_6H_4CHO)_3$ -- grey green.
$CrCl_3(o\text{-}ClC_6H_4CHO)_2$ - lilac.

Analysis of co-ordination complexes continued.

Table 26. $CrCl_3(p\text{-}ClC_6H_4CHO)_3$

Element	Found	Theory
C	42·0	43·5
H	2·7	2·6
Cr	8·5	9·0
Cl (ionisable)	17·9	18·4

Table 27. $CrCl_3(p\text{-}ClC_6H_4CHO)_2$

C	36·8	38·3
H	2·2	2·3
Cr	12·4	11·8
Cl (ionisable)	23·4	24·2

$CrCl_3(p\text{-}ClC_6H_4CHO)_3$ - green.

$CrCl_3(p\text{-}ClC_6H_4CHO)_2$ - purple.

Analysis of co-ordination complexes continued.

Table 28. $CrCl_3(m\text{-}ClC_6H_4CHO)_2$

Element	Theory	Found
C	38·3	37·3
H	2 3	2 3
Cr	11·8	12·5
Cl (ionisable)	24·2	24·7

$CrCl_3(m\text{-}ClC_6H_4CHO)_2$ - blue.

Section m. Infra red spectra of co-ordination complexes.

Spectra obtained as in section h.

Table 29.

o-NO_2-	m-NO_2-	p-NO_2-
1689 w	1637 s	1658 s
1631 s	1610 s	1642 sh
1560 w	1577 m	1596 s
1520 m	1527 s	1522 s
1443 s	1458 s	1458 s
1383 m	1377 m	1412 w
1340 m	1348 s	1376 m
1279 m	1299 w	1342 s
1203 s	1279 w	1321 w
1140 w	1215 m	1292 w
969 w	1168 w	1211 m
889 w	1078 w	1168 w
859 w	913 w	1109 w
855 w	827 m	1018 w
838 w	736 m	1006 w
789 w	723 m	850 m
742 w	690 w	826 s
701 w	667 w	739 m
		709 sh
		702 m

Table 29. Infra red spectra of co-ordination complexes cont.

p-Cl-	m-Cl-	o-Cl-
1642 s	1621 s	1681 w
1634 s	1613 sh	1623 s
1590 s	1590 s	1618 sh
1567 s	1567 s	1582 s
1486 m	1466 m	1560 s
1460 s	1437 w	1543 w
1408 m	1381 m	1462 m
1381 m	1372 m	1458 sh
1304 m	1294 m	1448 sh
1222 s	1232 w	1433 m
1166 m	1215 s	1383 m
1088 s	1167 w	1300 w
1007 m	1096 w	1274 s
852 s	1080 w	1214 m
834 m	913 w	1157 w
826 m	897 w	1152 w
761 w	883 w	1050 m
712 m	804 s	1034 w
	743 m	840 m
	703 m	769 s
	669 m	720 m

Table 29. Infra red spectra of co-ordination complexes cont.

$(C_6H_5CHO)_3CrCl_3$
1635 m
1619 s
1614 s
1595 s
1575 s
1455 s
1388 m
1323 m
1227 s
1203 w
1176 s
1020 w
1002 w
943 w
845 m
756 m
684 w

Section n. Stannic chloride co-ordination complex.

The white crystalline complex between stannic chloride and benzaldehyde was prepared by the standard procedure of Pfeifer. To a solution of benzaldehyde in chloroform or benzene was added a quantity of stannic chloride. The addition was performed in a dry box. The complex which formed immediately, was filtered, washed and pumped dry.

Table 30. Infra red spectrum of $SnCl_4.(C_6H_5CHO)_2$
This spectrum was obtained as described in section **h.**

1695 w	1319 m
1618 s	1229 s
1605 s	1172 m
1592 s	990 w
1577 s	846 m
1453 s	749 m
1395 s	677 w
1376 w	

Table 31. For comparison the infra red spectrum of benzaldehyde was obtained.

1701	s
1597	m
1584	m
1456	m
1392	m
1311	m
1203	s
1168	m
828	s
745	s

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KINETICS OF OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE

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Abstract—The kinetics of oxidation of substituted toluenes with chromyl chloride in carbon disulphide solution has been studied. The value obtained for the Hammett reaction constant, ρ, is $-2{\cdot}20 \pm 0{\cdot}08$. This is consistent with the theory that reaction involves a cyclic transition state.

IT HAS been known[1] that chromyl chloride reacts with toluene to yield a brown, amorphous solid the composition of which corresponds to $PhCH_3{\cdot}2CrO_2Cl_2$ and which hydrolyses to benzaldehyde. Recently,[2] we have presented evidence directly related to the structure of the adduct. However, although kinetic studies[3] have shown that reaction is first order with respect to each of the reactants, whilst isotopic tracer studies[4,5] have shown that carbon–hydrogen bond cleavage occurs in the rate determining step, the mode of cleavage of the carbon–hydrogen bond has not been clarified. The mechanism of the related oxidation of diphenylmethane has been discussed by Nenitzescu[6] and Wiberg,[7] the former favouring a carbonium ion mechanism and the latter a free radical mechanism. We have studied the effects of substituents on the rates of reaction of a series of substituted toluenes with chromyl chloride in order to obtain evidence relating to the rate determining step.

Our results show that nuclear substituted toluenes exhibit good second-order kinetics on the assumption that Eqs. (1) and (2) apply.

$$XC_6H_4CH_3 + CrO_2Cl_2 \xrightarrow{\text{slow}} XC_6H_4CH_3/CrO_2Cl_2 \tag{1}$$

$$XC_6H_4CH_3/CrO_2Cl_2 + CrO_2Cl_2 \xrightarrow{\text{fast}} XC_6H_4CH_3/2CrO_2Cl_2 \tag{2}$$

Thus, second-order rate constants were obtained by calculating the slope of the line of $\ln B(2A - x)/2A(B - x)$ against time, where:

A = initial concentration of the toluene
B = initial concentration of chromyl chloride
$(B - x)$ = concentration of chromyl chloride at time t.

The "least squares" rate constants thus obtained are given in Table 1.

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closer to our value of −2·20 than is the value for bromination, the difference is probably still too large to be explained solely in terms of difference in electronegativities.

Before free radical formation is ruled out altogether it is necessary to consider the possibility of pre-transition state complex formation since this could lead to a significant increase in the value of ρ.[15] Indeed, Wheeler has suggested that π complex formation may occur before hydrogen abstraction.[16] If this were the case it would be reasonable to expect large solvent effects in changing from aliphatic to aromatic solvents. We have detected no significant difference in reaction rate for oxidation of toluene in carbon disulphide, carbon tetrachloride and benzene. The relevant rate constants are shown in Table 1. The observed changes in rate are appreciably less than those noted by Stairs for a series of halogenated alkanes.[17]

It seems probable, therefore, that the reaction of toluene with chromyl chloride involves a cyclic transition state of the type considered by Wilberg,[18] and believed by him to offer a possible explanation both for oxidations by chromic acid and by chromyl chloride. The value obtained for ρ is then explicable in that a bond is being formed between benzylic carbon and oxygen whilst the carbon–hydrogen bond is being broken, as shown in Fig. 1.

Apart from its non-linearity, this transition state may be compared with that for the bimolecular solvolysis of benzyl halides. Thus, hydride ion abstraction may be regarded as replacing halide ion expulsion whilst, in each case, a bond is being formed from carbon to oxygen. The value of ρ^+ for solvolysis of benzyl halides in 48% aqueous ethanol is reported as −2·18.[15] Whilst it is recognised that significantly different solvents are employed in the two reactions, the similarity in ρ values is noteworthy.

We therefore conclude that the kinetics of oxidation of substituted toluenes are best explained on the assumption that the reaction involves a cyclic transition state.

Whilst writing this paper we have become aware of a recent publication in which a transition state identical to the one we favour is postulated for the chromyl chloride oxidation of phenylmethanes.[19] However, the writers draw their conclusions from a consideration of non kinetic evidence. Nenitzescu *et al.*[19] have drawn analogy with heterolytic mechanisms, as we have. However, there is no obvious reason why unpaired electron shifts should not occur in the proposed cyclic transition state since the degree of charge separation would be similar. Our earlier work[2] has shown that the toluene adduct consists of benzaldehyde co-ordinated with chromium compounds in oxidation states intermediate between III and VI. Thus a second C—H bond has been broken at the adduct stage. It is unlikely that this second step involves hydride ion abstraction since the carbon is now bonded to a strongly electronegative group. It seems much more plausible that the organic group attached to chromium is an incipient alkoxy radical which readily loses a hydrogen atom to a second molecule of chromyl chloride. Further, no attempt has been made to explain why, if chromyl

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The rate constant for the reaction of benzyl chloride, which forms only a 1:1 adduct,[1] was calculated on the assumption that the equivalent of Eq. (1) only applies. Again, good second-order kinetics were observed.

Our value of the rate constant for the oxidation of toluene in carbon tetrachloride is 22% lower than that of Stairs and Burns.[3] However, this discrepancy is easily accounted for since Stairs and Burns used residual oxidizing power as their criterion for extent of reaction. We have found that residual oxidizing power is variable and usually less than theoretical.[2] Thus, rate constants based on this property would be expected to be high.

In agreement with the oxidation of substituted diphenylmethanes by chromic acid[8] electron withdrawing substituents are seen to slow the reaction whereas electron releasing substituents have the opposite effect. The "least squares" value of the Hammett reaction constant, ρ, evaluated from the kinetic data is $-2{\cdot}28 \pm 0{\cdot}08(0)$. The corresponding value for ρ^+ is $-2{\cdot}20 \pm 0{\cdot}07(9)$. The values of σ and σ^+ employed in the calculations were those given by Brown and Okamoto.[9] The available data do not permit a choice to be made between ρ and ρ^+ values. Unfortunately, methoxy substituted toluenes could not be included since the methoxy group facilitates attack on the aromatic nucleus.[10]

The value obtained for ρ indicates that carbonium ions cannot be produced in the rate determining step, for, if they were, a value between -3 and -5 would be expected.[8]

Conversely, values of ρ^+ for hydrogen atom abstractions from the side chain of substituted toluenes normally lie between $-0{\cdot}75$ and $-1{\cdot}5$.[11] Wilberg has likened oxidation by chromic acid to hydrogen atom abstraction by bromine atoms since the two reactions exhibit similar selectivities.[7] Further, Wiberg and Evans[8] obtained the value $-1{\cdot}17$ for chromic acid oxidation of diphenylmethanes and compared this with the value $-1{\cdot}12$ calculated from the results for the analogous oxidation of toluenes.[12] The value reported for the bromination of substituted toluenes is $-1{\cdot}05$.[13]

In bromination, however, radical stabilization appears to be of greater importance than the electronegativity of the bromine atom since hydrogen attached to carbon directly bonded to halogen is more readily substituted than if the halogen substituent were absent.[13] In contrast, it is well known[1] that benzyl chloride is less readily oxidized than toluene by chromyl chloride. We find that the ratio of the rate constants is approximately 1:5 (Table 1). Thus, in the case of oxidations by chromyl chloride the electronegativity of the attacking species appears to be dominant. It is probably better, therefore, to compare chromyl chloride oxidations with hydrogen atom abstraction by trichloromethyl radicals. Evidence[14] indicates that the methyl group of α-bromo-*p*-xylene is more readily attacked by trichloromethyl radicals than the bromomethyl group. The value of ρ^+ reported for abstraction of benzylic hydrogen atoms by trichloromethyl radicals is $-1{\cdot}46$.[14] However, although this is appreciably

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chloride is the powerful electrophile suggested by Nenitzescu and co-workers, the aromatic ring is so unreactive.

Thus, although it seems essentially proven that a cyclic transition state is involved in the rate determining step it is certainly not clear whether the role of chromyl chloride is one of an electrophile or a free radical.

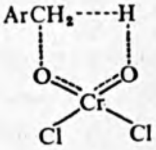

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TABLE 1. SECOND ORDER RATE CONSTANTS FOR THE OXIDATION OF SUBSTITUTED TOLUENES WITH CHROMYL CHLORIDE

Hydrocarbon	Concentration (mole/litre)	Solvent	Rate constant (l/mole sec)
Toluene	0·2175	CS_2	4·67 ± 0·13 × 10^{-4}
p-Me$_3$C—	0·2175	CS_2	1·46 ± 0·03 × 10^{-3}
p-Cl—	0·2175	CS_2	2·24 ± 0·04 × 10^{-4}
m-Cl—	0·2175	CS_2	7·23 ± 0·02 × 10^{-5}
p-Br—	0·2175	CS_2	1·84 ± 0·05 × 10^{-4}
p-I—	0·2175	CS_2	2·05 ± 0·03 × 10^{-4}
p-NO$_2$—	0·2175	CS_2	1·21 ± 0·04 × 10^{-5}
m-NO$_2$—	0·2175	CS_2	9·20 ± 0·33 × 10^{-6}
p-Me—	0·1088	CS_2	1·59 ± 0·04 × 10^{-3}
m-Me—	0·1088	CS_2	6·54 ± 0·07 × 10^{-4}
Toluene	0·2175	CCl_4	4·38 ± 0·09 × 10^{-4}
p-NO$_2$—	0·2175	CCl_4	1·27 ± 0·02 × 10^{-5}
Toluene	0·2175	C_6H_6	7·13 ± 0·32 × 10^{-4}
Benzyl Chloride	0·2175	CS_2	9·56 ± 0·13 × 10^{-5}

All reactions conducted at 40° with a chromyl chloride conc. of 0·1234 mole/litre. All rate constants are the average of two runs.

EXPERIMENTAL

Materials. All materials were commercially available. Solvents were dried over $CaCl_2$ and distilled, the fractions with the literature b.ps being collected. The substituted toluenes were appropriately dried and used without further purification. The CrO_2Cl_2 was subjected to two room temp vac. distillations immediately before use.

Kinetic measurements. Kinetic runs were followed by determining the rate of production of adduct. Samples (15 ml) of reaction mixture, appropriately thermostatted, were pipetted into tared centrifuge tubes fitted with ground glass caps. The filled tubes were inserted into waterproof polythene bags and totally immersed in the thermostat. At appropriate intervals tubes were withdrawn, centrifuged and the solvent decanted. The adduct samples were twice washed with fresh solvent before vac. drying and weighing *in situ*.

has essentially the same infrared spectrum as that of the adducts (see Table). Further, we have crystallised anhydrous chromic chloride from benzaldehyde solution to yield a crystalline solid with a composition corresponding to $(PhCHO)_3CrCl_3$ (Found: C, 53·1; H, 4·4; Cl, 21·3; Cr, 10·9(5). $C_{21}H_{18}O_3Cl_3Cr$ requires: C, 52·9; H, 3·8; Cl, 22·3; Cr, 10·9%). The infrared spectrum of this complex, as shown in the Table, corresponds with that of the adducts.

We conclude therefore that the Etard adducts of toluene, benzyl chloride and benzyl alcohol are composed of benzaldehyde co-ordinated with reduced chromyl chloride. This conclusion in no way conflicts with previously published results and it is reasonable to assume that Etard-type structures are intermediate in the formation of the amorphous co-ordination complexes.

Further work is in progress and results suggest that similar conclusions are applicable to related adducts.

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