SOME ASPECTS OF CHROMIUM(II) REDUCTION OF ORGANIC COMPOUNDS.

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PREFACE

Recent years have witnessed a very great change in the chemist's conception of the phenomena of oxidation and reduction. The terms, once strictly limited to reactions involving 'fixation' of oxygen, not only conferred the status of a privileged element upon oxygen but also failed to accomodate elimination of hydrogen unless it ultimately formed water. Similarly, combination of a metal with sulphur or chlorine, while apparently analogous to combinations with oxygen, was unprovided for within the system.

Not until the advent of electronic theory was it possible to formulate a logical basis of classification by consideration of the electrons involved. Such a treatment leads to the development of definitions, which although very broad and general in nature, have proved to be of the greatest utility. A generally accepted definition of oxidation is a chemical transformation involving loss of electrons and accompanied by the reverse process, reduction. Such a definition covers electron transfer but does not clearly accomodate the incomplete transfer found in typical organic redox reactions involving covalent linkages. A practical approach to the formulation of a definition is to

disregard the mechanism and consider only the initial and final states. Many organic reactions only involve partial loss or gain of electrons in that electrons are moving farther away from or closer to a carbon atom. If such reactions are considered to be oxidations and reductions respectively, nearly all reactions could also be termed oxidation-reductions and the problem of where to draw a line between the two presents itself.

Since all chemical reactions involve changes in electronic structure there is no fundamental distinction between oxidation-reduction and other reactions. Ingold in 1934[1] pointed out that "reduction and oxidation are to be regarded as the prototypes of a more general classification based on the reception and donation of electrons". This is the generalized concept of oxidation-reduction and it includes all chemical reactions.[2]

The instances in which the chromium(II) ion has been used as a reducing agent are not very numerous and the somewhat analogous zinc and acid reduction is much more frequently encountered in the literature. Interest in the reduction of organic compounds by this method which stimulated the present investigation stems from two main sources. The more immediate originates in work done by Anet and Marion[3] on the degradation reactions of annotinine. During the course of this work it was found necessary to consider

the route of chromium(II) chloride reduction. Clarification of the relationships between the various compounds indicated that chromium(II) chloride must, in a manner analogous to the removal of vicinal halogen atoms reduce both vicinal chlorohydrins and haloamines to the appropriate olefins. Consequently it was considered of interest to investigate simpler compounds of this type in order to establish analogies for this behavior.

The second and more fundamental stimulus lies in the very nature of the reaction. Little interest has been shown in the mechanism of the reaction and the instances where it has been used are very few. However of all the common methods of reduction it seems to lend itself most readily to a detailed study of mechanism. In the first place a homogeneous reaction medium is readily obtainable. Secondly the work of Taube[4] had established that since chromium(III), particularly in acid medium, is fairly inert to substitution and the rate of oxidation of chromium(II) is comparatively rapid, any group found in the coordination sphere of chromium(III) did not combine with it after the act of oxidation of chromium(II). Consequently it is possible to follow the fate of a halide ion and hence gain information about the probable mechanism. Finally from an analytical standpoint, the highly colored nature of the various chromium compounds encountered is of great convenience.

The distinctive color of the reagent as well as many of the chromium species found as reaction products provides a ready qualitative estimation of the extent and sometimes even the route of reduction.

The compounds studied were mainly halogen compounds, amongst those benzyl chloride. The subsequent detailed study of the latter compound comprises the greater part of the present investigation.

Acknowledgements.

This work was supported by a grant from the National Research Council of Canada. The author wishes to thank Dr. F. A. L. Anet for his guidance and assistance as research director. Gratitude is also due Laurent Isabelle without whose help and encouragement this thesis would not have been completed.

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ABSTRACT

2-Bromoethanol and 2-bromoethylamine hydrobromide have been shown to behave analogously to annotinine chlorohydrin on reduction with chromium(II) chloride. 2-Bromoethanol yielded 20% ethylene and was shown to undergo considerable hydrolysis under the reaction conditions. 2-Bromoethylamine hydrobromide yielded both ethylene and ethylamine. 2-Chloroethanol was not reduced under the conditions used. Phenacyl acetate yielded 96% acetophenone separated as the 2-4-dinitrophenylhydrazone. A number of compounds have been reduced and the chromium(III) products of reduction identified spectroscopically as well as separated on an ion exchange resin. Phenacyl acetate, 2-nitropropane, α-chloroacetophenone, α-bromoacetophenone and trans 1-2-dibromocyclohexane yielded mainly $Cr(H_2O)_6^{+++}$. Carbon tetrachloride, p-toluenesulfonyl chloride and tetrabromoethane yielded $CrX(H_2O)_5^{++}$. There is therefore an anomaly in the behavior of trans 1-2-dibromocyclohexane and tetrabromoethane.

The chromium(II) perchlorate reduction of benzyl chloride has been shown to involve formation of an intermediate organo-chromium compound of a type previously unknown. This compound has been named benzylpentaaquo-

chromium(III) perchlorate. Countercurrent distribution has been used to demonstrate the presence of only one chromium organic compound and to obtain a pure solution of the perchlorate. Separation was carried out at 5°C. with the solvent system 0.01M. perchloric acid-butanol and gave after seventy transfers a separation of the chromium organic compound (partition coefficient 0.35) from $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$. Solutions of the benzylchromium(III) perchlorate varied from yellow to reddish brown depending on the concentration. The compound has a molar extinction coefficient of 1,830 at 358mμ. and 49 at 540mμ. Decomposition of the complex in the absence of oxygen yielded bibenzyl, in the presence of oxygen, benzaldehyde. Catalytic hydrogenation yielded toluene. Solutions of the complex reacted very quickly with aqueous mercuric chloride with no change in the pH of the solution to give benzylmercuric chloride and $Cr(H_2O)_6^{+++}$ in equimolar amounts. On this basis the compound has been designated as a chromium(III) complex with one benzyl group per chromium atom and two positive charges. The six coordinate positions normal for chromium (III) are completed by five molecules of water and a normal octahedral structure is proposed.

INTRODUCTION

Reduction, in the most general terms has been defined as the giving of electrons to a compound, oxidation as their removal. Chromium(II) reduction sometimes involves a one electron change and gives rise to dimerized organic products[5]. In the present investigation no dimerized products were obtained and hence it can be assumed there is an overall two electron change. A further interesting consideration of such electron transfers is the actual mechanism by which the transfer is effected. Electron transfer reactions occuring in solution can involve participation of the solvent or can be accompanied by transfer of a group from oxidant to reductant. The latter case would then involve attack at some specific atom and subsequent formation of some type of intermediate complex.

In many cases it is difficult to determine the actual mechanism in operation due to the instability of such intermediate complexes. One method of avoiding this difficulty is by the use of ions which are relatively non-labile with respect to substitution[6]. Coordination compounds can be roughly divided into two general groups, normal complexes and penetration complexes[7]. Normal complexes are characterized by a comparatively weak bond of large distance between

the coordinated ligands and the central group. They are readily and reversibly dissociated into their component parts and show no deep-seated electronic changes. The latter is detected by changes in the magnetic susceptibility of the central ion. On the other hand, penetration complexes are characterized by non-facility of equilibrium, unusually short bond distances and deep-seated electronic rearrangements. Dipositive chromium forms normal complexes and it is readily labile to substitution. Chromium(III) on the other hand forms penetration complexes, and the rate of substitution on chromium(III) is slow. This is nicely illustrated by the fact that violet chromium(III) chloride, $Cr(H_2O)_6Cl_3$, which contains $Cr(H_2O)_6^{+++}$ rather than any of the various chloride complexes, can be precipitated by passing hydrogen chloride into a solution containing the aquochromium(III) ion[8].

Taube working in conjunction with a series of co-workers has published a good deal of work on bridging and non-bridging effects in redox reactions of metal[6]. In his work on electron transfer between metal ion centers in solution he has been mainly concerned with changes in the first coordination spheres and the following generalized treatment may be drawn from his observations. Two types of activated complexes can be distinguished which Taube calls "outer-sphere" activated complex and "bridged" activated

complex. In the case of outer-sphere activated complexes the number and identity of groups in the first coordination sphere remains unchanged on electron transfer and changes occur largely in the solvent and ion atmospheres. When reactant and product complex ions are substitution-inert and coordinately saturated they are reasonably assumed to proceed via the outer-sphere activated complex. It is a feature of such systems that little change in the dimensions of the molecule occurs on electron transfer. However whether geometric requirements affect the rate in such processes is not at all certain. Furthermore in the case of ligands which are unfavorable to the formation of a bridged activated complex electron transfer through the intact coordination spheres may still be the easier route to products.

In the bridged activated complex process a common group is shared and therefore there must be important changes in the first coordination sphere of at least one of the partners. The ease of substitution of the compounds involved is an important factor in determining the reaction mechanism and permitting classification. When the oxidizing agent is substitution-inert, the reducing agent is substitution-labile and the product is substitution-inert evidence for a bridged structure can be obtained by simple analysis of the reaction products. In such cases it is possible to assume that any group found in the coordination sphere of the product when it

is formed from the reducing agent must have been present in the activated complex.

In the case of chromium(II) reduction since chromium(III), particularly in acid solution, is fairly inert to substitution while the rate of oxidation of chromium(II) is comparatively rapid it can be shown that any group found combined with chromium(III) did not combine with it after the act of oxidation of chromium(II). Taube[4] showed this experimentally by carrying out the reduction of a substitution-inert complex ion $Co(NH_3)_5Cl^{++}$ with chromium(II) in the presence of free chloride ions containing the radioactive isotope Cl^{36}. The complete transfer of Cl^- from $Co(NH_3)_5Cl^{++}$ to chromium(II) was established spectrophotometrically. The radioactivity of the chloride attached to the chromium(III) after the reaction was ten counts per minute above background; on complete mixing of the chloride ion in the system a counting rate of 2,250 per minute would have been observed. On the basis of this work therefore it was possible to assume that any group found in the coordination sphere of chromium(III) when it is formed from chromium(II) must have been present in the activated complex. This assumption has been used in the present investigation.

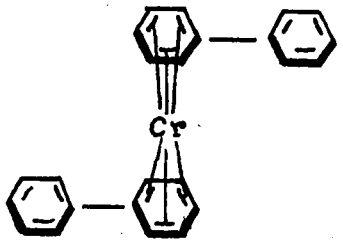
Since one of the most important considerations of the mechanism of chromium(II) reduction is that of the oxidation states of the chromium some examples of the known oxidation states of chromium are of interest. Chromium is now known to exist in seven states, from zero to six inclusive. The varying valency of chromium arises from the possibility of electrons in the shell below the valency electron shell being able to function readily as valency electrons. Belonging to group VIa, it is one of the transitional elements characterized by incomplete inner shells and by little change in properties from one element to the next within the period. It also shows chemical resemblance to its neighbouring elements molybdenum and tungsten. Chromium also bears strong resemblance to iron and aluminium being grouped with them for qualitative analysis.

Chromium(0) has an electron configuration of $1s^2$, $2s^2$, $2p^6$, $3s^2$ $3p^6$ $3d^5$, $4s^1$, an electron having entered the 4s level before completion of the 3d level.

The metal carbonyl, chromium(0) hexacarbonyl was reported in 1926[9] in poor yields from phenylmagnesium bromide and chromium(III) chloride in the presence of carbon monoxide at atmospheric pressure. The preparation was later improved by

using higher pressure[10]. In 1952 Malatesta et al.[11] were successful in preparing and characterizing some very interesting chromium(0) derivatives. These compounds are regarded as analogous to the simple volatile metal carbonyls, having the central atom in the zero oxidation state. The chromium(0) derivatives reported are all hexaaryl isonitriles, eg. $Cr(CNC_6H_5)_6$, and were obtained by addition of the isonitrile to a suspension of chromium(II) acetate in ethanol. These complexes are diamagnetic, very stable towards aqueous alkali but slowly attacked by dilute acids.

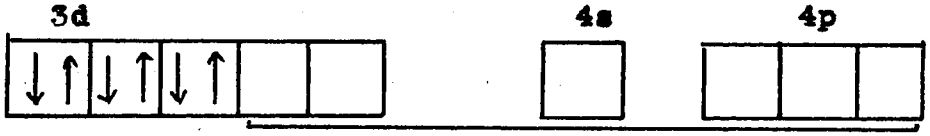
Although it was generally felt that the organometallic compounds of chromium would be too unstable to isolate Hein[12] felt that it would be possible using efficient cooling. From the reaction of phenylmagnesium bromide and chromium(III) chloride in ether at -10°C. he was able to obtain mixtures of penta-, tetra-, and triphenylbromides. From this he was able to obtain a series of chromium organic compounds and salts of these compounds. Zeiss and Tsutsui[13] reported corroboration of the key aspects of this work and showed the chromium triphenyl and tetraphenyl of Hein to be actually chromium(0) compounds, benzene diphenyl chromium(0) and bis-diphenyl chromium(0) respectively. For the structure of these compounds they propose a sandwich type structure in which π electrons from phenyl groups are donated to the metal orbitals.



The salts of these compounds involve chromium(I), e.g. $(C_6H_6)(C_6H_5)_2Cr^+I^-$.

Fischer and Hafner[14] reported preparation of a chromium(O) compound, $(C_6H_6)_2Cr$, which can be considered the parent compound from which Hein's compounds are theoretically derived. They reduced anhydrous $CrCl_3$ by Al, Mg or Zn in the presence of $AlCl_3$ and benzene by heating 15 hours at 150°C. After further reduction with $Na_2S_2O_4$ and purification, a 38-48% yield based on Cr, of $Cr(C_6H_6)_2$ was obtained. Weiss and Fischer[15] consider that since the chromium atoms in this compound are on the centers of symmetry it has a sandwich structure with the C_6H_6 hexagons aligned, not opposed.

Chromium(O) compounds of this type can be considered to have an electronic structure suitable for d^2sp^3 orbital hybridization.



Coordination with dipyridyl is one method of enhancing the stability of unusual valence states. In 1952 Hein and Herzog[16] reported isolation of a unipositive chromium

complex stabilized by coordination with dipyridyl. By reduction of $(Cr(dipy)_3)(ClO_4)_2$ with magnesium in aqueous ammonium perchlorate they were able to obtain 70 to 80% yield of $(Cr(dipy)_3)ClO_4$. The chromium(I) complex is dark blue, sensitive to atmospheric oxidation, insoluble in water but soluble in various polar solvents. The compound is paramagnetic, having a molar susceptibility of 2.0 to 2.1 Bohr magnetons consistent with the presence of one unpaired electron and indicating inner orbital d^2sp^3 binding.

Chromium in the dipositive state is one of the more familiar oxidation states the metal is found in. The chromium(II) salts are powerful reducing agents and unlike the bivalent salts of iron, manganese and tin are capable of reducing water directly[17]. This property presents a complication in the case of reductions which proceed at a very slow rate. Chromium(II) compounds are very sensitive to oxygen, numerous references and patents for the process of removal of oxygen by salts of chromium(II) being found in the literature. However, some chromium(II) complexes which are more stable to oxidation have been prepared using hydrazine as a complexing agent[18], the reducing properties of the latter accounting in part for this stability. Chromium(II) complexes of aa'-dipyridyl, hexamethylenetetramine, o-phenanthroline and 8-hydroxyquinoline have also been reported[19].

The most stable chromium salts are those of chromium(III)[20] and this is the most familiar oxidation state of the metal. Chromium(III) forms coordination compounds in which the coordination number is six. The tendency is to achieve the electronic structure of krypton. There is also a tendency to form a symmetrical structure, an octahedral structure being formed for a coordination number of six. The coordinating groups may be neutral molecules, negative ions, or both. Neutral groups which can coordinate with chromium(III) include H_2O, NH_3, SO_2, NO, NO_2, CO, S, C_2H_5OH, C_6H_6, N_2H_4, NH_4OH, etc. Negative ions which coordinate include F^-, Cl^-, Bi^-, I^-, $(CN)^-$, $(CNS)^-$, $(OH)^-$, $(NO_2)^-$, $(SO_3)^{-2}$, $(SO_4)^{-2}$, $(C_2O_4)^{-2}$, $(CO_3)^{-2}$, $(NO_3)^-$, etc. The number of ions containing chromium(III) is thus very great.

A tetrapositive chromium compound was reported by Klemm and Huss[21]. These workers found that fluorination of $KCl-CrCl_3$ in a 3-1 molar mixture gave in addition to CrF_3 also K_2CrF_6. The latter compound is yellow-green in aqueous solution and the solid compound is decomposed by heat to CrF_5 and a chromium(III) compound. Another chromium(IV) compound, barium tetroxochromate, Ba_2CrO_4 has been reported[22]. This compound can be obtained by pyrolysis of barium hexahydrochromate(III), $Ba(Cr(OH)_6)_2$, and barium hydroxide in an atmosphere of nitrogen, by reduction of barium chromate and barium hydroxide mixture with hydrogen at 400-500°C., or by

pyrolysis in nitrogen of a mixture of barium chromate, chromium oxide and barium hydroxide. The barium tetroxochromate(IV) decomposes slowly in water and disproportionates to chromium(III) and chromium(VI) in dilute hydrochloric acid. Evidence for the tetrapositive state is indicated by a molar susceptibility of 2.82 Bohr magnetons (theoretical 2.83 for an outer orbital complex with two unpaired electrons) and and also an X-ray pattern similar to that of Ba_2TiO_4.

Chromium(V) was reported as early as 1905 by Weinland[23] who isolated the complexes $K_2(CrOCl_5)$ and (pyH)$(CrOCl_4)$. More recently the reaction between barium chromate-(VI) and barium carbonate at 1,000°C. under nitrogen has been reported to yield barium chromate(V), $Ba_3(CrO_4)_2$ [22]. This compound is a green black powder which decomposes slowly in water and disproportionates to chromium(III) and chromium(VI) in dilute acid. The pentavalency of the chromium is substantiated by an X-ray pattern similar to $Ba_3(PO_4)_2$ and a molar susceptibility of 1.17 Bohr magnetons corresponding to the one unpaired electron expected for an outer orbital complex of chromium(V). Strontium, lithium and sodium salts have also been prepared. Chromium(V) compounds of the type $M_5(CrO_4)_3OH$, where M is barium or strontium have also been been reported from the pyrolysis of the metal chromate(VI) and hydroxide under nitrogen[11].

Chromium in the sexavalent state is a very commonly

encountered state of the metal. It occurs in chromium trioxide as well as in the various chromates and dichromates.

As mentioned earlier the instances where chromium(II) reduction of organic compounds is encountered are not too numerous. Reduction of an organic compound by this reagent was first reported by Berthelot[24] in 1866. He observed that in alkaline solution chromium(II) sulfate readily reduces acetylene to ethylene.

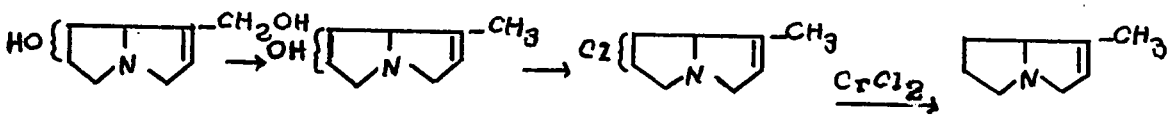
Traube and Passarge[17] further investigated this reduction, showed it to occur also in acid medium and patented rights to its use in the manufacture of ethylene. They also showed maleic and fumaric acids are reduced to succinic acid in both alkaline and acidic media by chromium(II) chloride. Both cinnamic acid and sodium phenylpropiolate yielded hydrocinnamic acid but only in alkaline media. They showed oximes to be reduced to amines in alkaline solution. Ammoniacal chromium(II) chloride solution reduced nitrous oxide to nitrogen quantitatively. Nitrates however were reduced to ammonia in both acid and alkaline solution but quantitatively only in the latter case. Nitrites could not be reduced to ammonia quantitatively. Salts of hydroxylamine were reduced to ammonia in alkaline medium.

In 1926 Conant and Cutter[5] reported on chromium(II) chloride reductions yielding dimolecular products. Their work involved reduction of typical aromatic aldehydes,

αβ-unsaturated aldehydes and some αβ-unsaturated ketones. These compounds underwent dimerization but it is not clear by what mechanism. Chromium(II) chloride in acidic aqueous or alcoholic solution was reported to be without effect at room temperature on representative aliphatic or aromatic saturated ketones, aliphatic aldehydes, αβ-unsaturated acids and esters, alcohols (excepting certain aromatic carbinols) and olefinic hydrocarbons.

Von Braun and Rudolph[25] studying the reduction of non-aromatic imide chlorides having adjacent double bonds, >C:CH.CCl:NR', to Schiff bases >C:CH.CH:NR' found the usual methods unsuitable. An ether solution of chromium(II) acetate containing HCl however effected rapid although not quantitative reduction. Imide chlorides of aromatic acids were also reduced by this method but not saturated aliphatic imide chlorides.

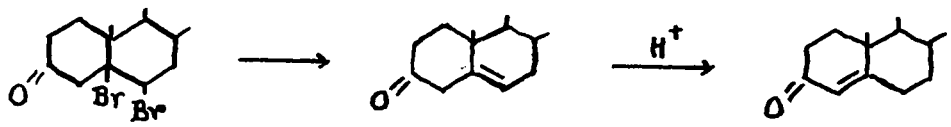
In 1943 Adams and Mahan[26] in a paper proving the position of the double bond in retronecine, reduced chloro-isoheliotridene to the unsaturated base isoheliotridene. Reduction was effected by refluxing the chloro compound three and one half hours under nitrogen with a concentrated hydrochloric acid solution of chromium(II) chloride and the dehalogenated product was isolated in 88% yield.



Retronecine Chloroisoheliotridene

Desoxyretronecine Isoheliotridene

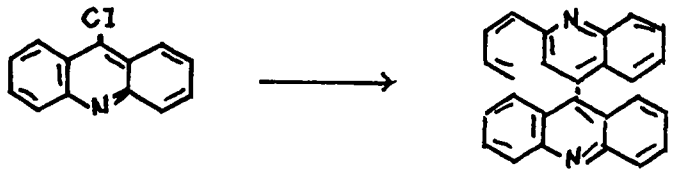
The usual method for the removal of halogen from 5-6-dibromo-3-keto steroids by means of zinc dust and acetic acid often gives poor yields of impure quality. The alternate procedure, treatment with sodium iodide does not give the undesirable by-products but frequently fails to give halogen free products. In 1945 Julian et al.[27] found that chromium(II) chloride solution gave rapid, complete dehalogenation to the Δ4-3-ketosteroids.



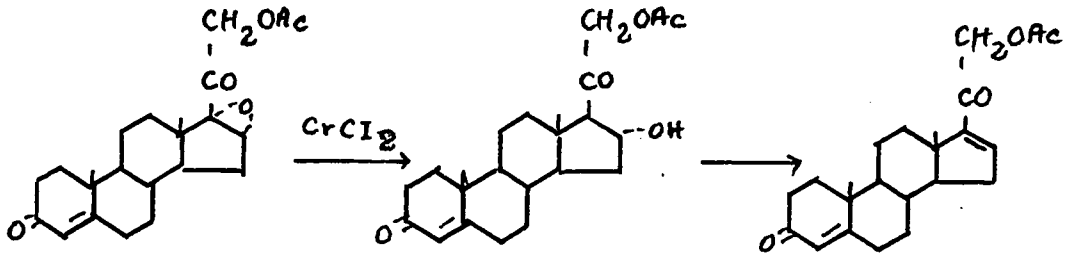
They also showed 5-6-dibromosterols to give Δ^5-sterols and α-bromo ketones the parent ketones.

Royer[28], following the work of Von Braun and considering 9-chloroacridine a vinylogous iminochloride attempted to prepare acridine by chromium(II) sulfate reduction. However this reaction produced diacridyl in almost quantitative yield. The reaction apparently involves dimerization but

at what stage or through what mechanism was not established.

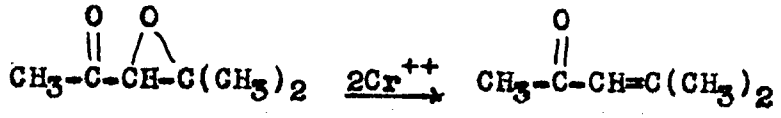


In 1954 Cole and Julian[29] reported the reduction of epoxy ketones by chromium(II) chloride. They found that certain epoxy ketones yielded almost exclusively the 16-α-hydroxy steroids and their dehydration products the αβ-unsaturated ketones.

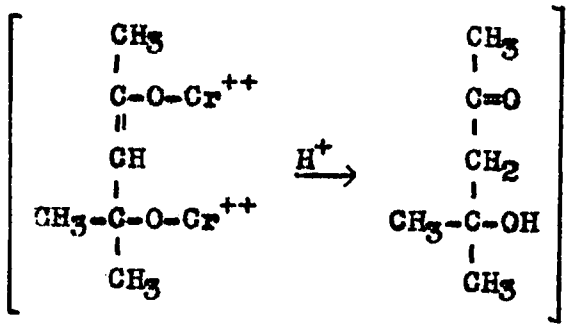


This is in contrast with other methods, for example metal hydride reduction or dehalogenation of the bromohydrins, which yield the physiologically active 17-α-hydroxysteroids. The authors attribute the unusual course of this reduction to the high acidity of the chromium(II) chloride reagent. This is supported by the observation that when chromium(II) acetate is used only a small amount of the unsaturated compound is isolated.

The authors suggest the conversion of 4-methyl-3-4-epoxy-2-pentanone to mesityl oxide is a good illustration of the general nature of this reaction.

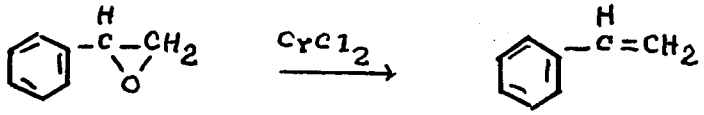


Since two moles of chromium(II) salt are required they consider the possible formation of an intermediate complex which is rapidly cleaved by acids.



The unsaturated ketone could be formed by dehydration of the hydroxy ketone or by loss of a hydrated chromium ion during ketonization. However the above mechanism is purely speculative as there is no available supporting evidence.

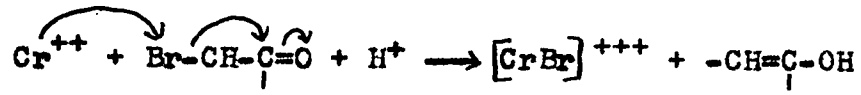
The same authors obtained 80% styrene from styrene oxide with an acetic acid solution of chromium(II) chloride at room temperature.



However ethylene oxide and cyclohexene oxide were not readily reduced by the reagent.

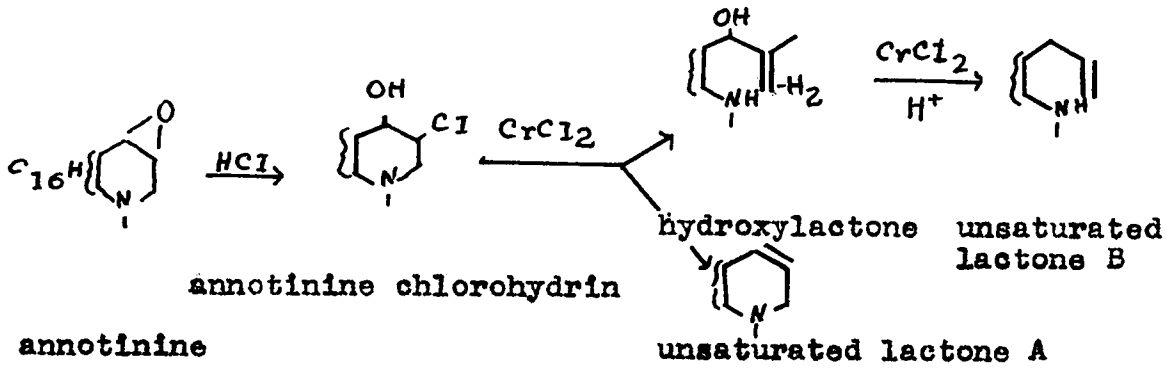
In 1956 Evans and co-workers[30] used chromium(II) acetate in acetic acid to preferentially remove the 2-bromine in 2-4-dibromoketones. For example they hydrogenalized the 2-bromine atom in 2-4-dibromocholestan-3-one. They suggest

the following mechanism:



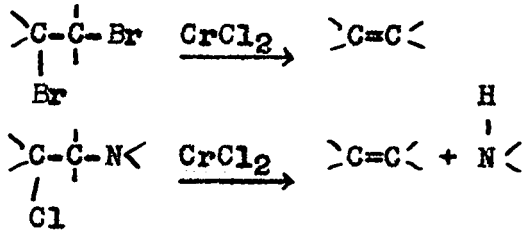
Finally as previously stated, Anet and Marion[3] working on degradation reactions of annotinine obtained evidence that chromium(II) chloride must, in a manner analogous to removal of vicinal halogen atoms reduce both chlorohydrins and amino halogens to olefins.

It had been shown that annotinine reacted with hydrochloric acid to form annotinine chlorohydrin which could be reduced with chromium(II) chloride to a mixture of unsaturated lactone A and hydroxylactone. This hydroxylactone on more drastic treatment with chromium(II) chloride in strongly acidic solution gave unsaturated lactone B. The relationships of these compounds on clarification present the following picture:

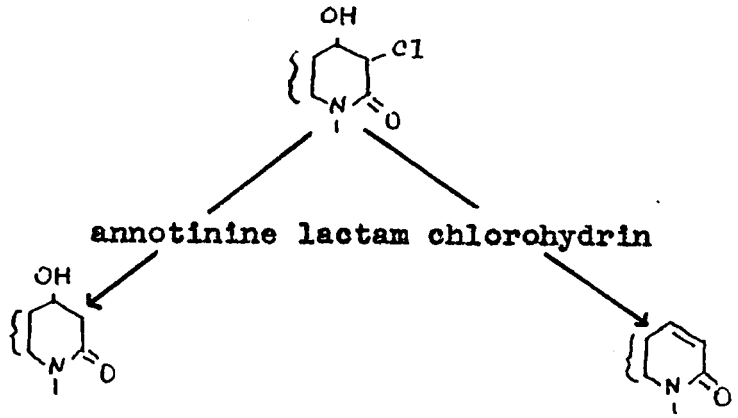


It is interesting to note that hydroxylactone has the same empirical formula as the compound resulting from simple replacement of the chlorine by hydrogen. However the

reaction apparently proceeds in a manner analogous to the removal of vicinal halogen atoms.



It was further observed that annotinine lactam chlorohydrin prepared either by oxidation of annotinine chlorohydrin or by treatment of annotinine lactone with hydrochloric acid, gave two main products on chromium(II) chloride reduction.



A B

It is important to note here that the unsaturated compound B is formed under conditions which do not dehydrate A. That is B is not formed by replacement of the chlorine by hydrogen forming A followed by dehydration. It is apparently formed as in the vicinal dibromides and β-chloroamines by elimination of the OH and Cl groups.

EXPERIMENTAL

Preparation of Aqueous Chromium(II) Chloride Solution.[30a]

A solution of chromium(III) chloride hexahydrate (300g) in concentrated hydrochloric acid (900 ml) was prepared. An apparatus of the type used by Lingane and Pecsok[31] and shown in Fig. 1 was used for the reduction and storage of the reagent. Mossy zinc (300g) was amalgamated with mercury by stirring in an acidic solution of mercuric chloride. The storage bulb was charged with the washed amalgamated zinc and the apparatus thoroughly flushed with nitrogen. All nitrogen used in this work was de-oxygenated by passage through a series of traps containing chromium(II) chloride over amalgamated zinc. The chromium(III) solution was added and after standing overnight the intense blue color characteristic of chromium(II) ion was observed.

A solution of one half this strength was prepared by dilution of the chromium(III) solution with an equal volume of water before reduction.

Reduction of Ethylene Chloride.

A one liter three-necked flask was equipped with a separatory funnel, an inlet for nitrogen and a reflux condenser. The latter was connected to a series of four traps.

The total yield of chromium(II) solution from

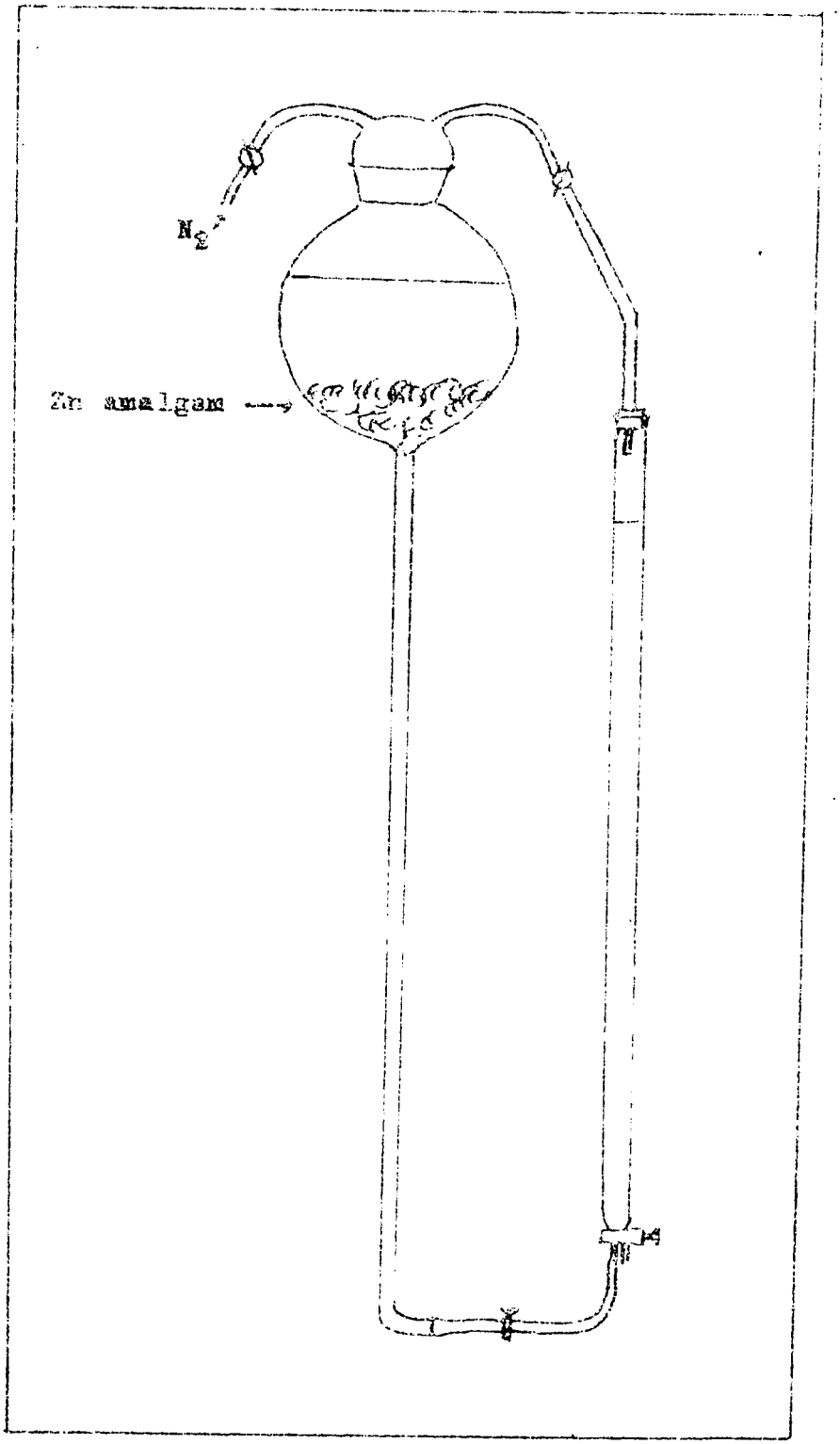


Fig. I. Apparatus for reduction and storage of chromium(II) reagent.

reduction of 300g of chromium(III) chloride in concentrated hydrochloric acid was transferred to the reaction flask under an atmosphere of nitrogen. Ethylene chloride (0.1 mole) was added followed by ethanol (900 ml). The reaction mixture was heated under reflux for four hours using just sufficient nitrogen to facilitate boiling.

The first and second traps contained bromine (0.1 mole and 0.05 mole respectively), the third water and the fourth 2N sodium hydroxide solution. After the four hour reflux the contents of the bromine traps were combined, washed with water and the organic layer drawn off. The latter was washed twice with water, twice with sodium carbonate solution (5%) and dried over calcium chloride. The yield of ethylene bromide was very small (4.3g, 23%).

Experiments were carried out prolonging the time of reflux, decreasing the acidity of the reaction medium and refining the mode of recovery of ethylene with no significant change in yield in any case.

Dilution of the first cut of distillate from the reaction mixture with water produced turbidity indicating the presence of unreacted ethylene chloride.

Reduction of Ethylene Bromide.

The reduction of ethylene bromide was carried out in the same manner. An alcoholic solution of ethylene bromide (0.05 mole) was added to chromium(II) chloride solution

(ca. 0.2 mole of a 50% concentrated HCl solution) under nitrogen.

No reaction was observed after fifteen minutes at room temperature. The reaction mixture was heated under reflux for four hours and evolved ethylene steadily. The ethylene bromide recovered from the traps was washed, dried, and yielded on distillation 6.71g of pure product (n_D^{25} 1.5356) boiling from 131-131.5°C. and representing a 71.4% yield.

Reduction of Ethylene Chlorohydrin.

Ethylene chloride (0.05 mole) was added under nitrogen to chromium(II) chloride solution (ca. 0.2 mole of 50% concentrated HCl solution). The mixture was heated under reflux for three hours after which time there was no apparent evolution of gas nor visible loss of blue color.

The reaction mixture on distillation yielded nothing before 98°C. and the bromine traps on working up yielded no ethylene bromide.

Reduction of Ethylene Bromohydrin.

Ethylene bromohydrin (0.05 mole) was reduced with chromium(II) chloride (0.1 mole) by refluxing under nitrogen for three hours. During the last half hour a slow stream of nitrogen was passed through the system in order to entrain the ethylene produced and conduct it to the all-glass bromide absorption system. The first trap in the system was filled

with water to scrub out any entrained ethanol. The dibromide was separated, washed and taken up in ether. The washings were extracted with ether and the combined dried ether extracts yielded on distillation 2.1g of pure ethylene bromide (22% yield).

Neither increased time of reflux nor further purification of the starting material produced a significant change in the yield of ethylene.

A Schotten-Baumem reaction modified[32] for the detection of small quantities of ethanol in aqueous solution produced no derivative from the water trap and none from the initial distillate of the reaction mixture.

Control on Hydrolysis of Ethylene Bromohydrin.

Ethylene bromohydrin (5g) was heated under reflux for three hours with 50% concentrated hydrochloric acid (30ml). The mixture was salted out with sodium chloride and then extracted five times with small quantities of ether. The combined ether extracts were dried over magnesium sulfate and on evaporation yielded .9g of residual oil, representing an 18% recovery.

Reduction of 2-Bromoethylamine Hydrobromide.

2-Bromoethylamine hydrobromide (0.05 mole) was reduced with chromium(II) chloride (0.1 mole in 50% concentrated HCl) by heating under reflux for three hours in an

atmosphere of nitrogen. The evolved ethylene was worked up as described in previous experiments and yielded 4.6g (49%) of dried distilled dibromide.

A control on the recovery of dibromide by the method used was made. Ethylene bromide (0.3g) was mixed with a few drops of bromine, washed with water and carbonate solution and extracted with ether as usual. The yield of dried distilled bromide was 2.42g representing an 80.6% recovery. Based on this percentage recovery the yield of this reduction could be approximated at 62%.

The residue of the reaction mixture was rendered alkaline with sodium hydroxide and steam distilled into a dilute hydrochloric acid solution. Distillation was continued until the distillate no longer left a residue on evaporation. The acidic solution was evaporated to dryness yielding 3.49g of white solid.

An aqueous solution (100 ml) of a sample of this solid (.1157g) was prepared. Excess silver nitrate was added to 30 ml of this solution for a gravimetric determination of chloride ion present in the sample. A sample weighing .0347g gave .1051g of dried silver chloride. On this basis the percentage of chlorine in the unknown is 74.9. This percentage of chlorine and the fact that addition of alkali to a solution of the sample gave distinct evolution of ammonia indicated the presence of ammonium chloride.

Crystallization from ethanol-ether yielded ethylamine hydrochloride (m.p. 96-98°C.) which did not depress the melting point of known ethylamine hydrochloride and which gave a benzamide melting at 70.0°C. (lit. m.p. 71.0°C.)[33].

A crude separation on the total yield of white solid was carried out by fractional crystallization from ethanol-ether. In this way 1.43g of ammonium chloride, 1.17g of ethylamine hydrochloride and an oily residue which would not crystallize, but probably contained more amine hydrochloride, were obtained. The theoretical yield of ammonium chloride required to correspond to a 60% yield of ethylene would be .03 moles or 1.6g. Similarly the theoretical yield of ethylamine hydrochloride required to correspond to a 40% yield of that compound would be .02 moles or 1.6g.

Reduction of Monochloroacetic Acid.

Monochloroacetic acid (0.1 mole) was dissolved in water (25ml) and added to chromium(II) chloride solution (0.12 mole) under nitrogen. There was no evidence of reaction at room temperature. The mixture was heated gently and resulted in almost immediate loss of blue color. After heating under reflux for three hours the reaction mixture was cooled, brought to a pH of approximately three and steam distilled.

Aliquots of 250ml of the distillate were taken and titrated against standard alkali as long as the distillate

gave a negative test for chloride ion.

A sample of the distillate was neutralized and evaporated to dryness. The residue gave a positive ferric chloride test for acetate and yielded an anilide melting at 110°C. which did not depress the melting point of known acetanilide.

The combined acid content of the distillate indicated a theoretical yield of acetic acid.

Reduction of Phenacyl Acetate.

Phenacyl acetate (.84g) was reduced with excess chromium(II) chloride in the usual manner. The 2-4-dinitrophenylhydrazone was prepared by direct treatment of the reaction mixture and yielded 1.55g of dried derivative (representing a 96.2% yield). This derivative melted at 244.0°C. and did not depress the melting point of the 2-4-dinitrophenylhydrazone of known acetophenone.

Ion Exchange Separation of Chromium(III) Species Produced on Oxidation of Chromium(II) Solution.

A 25ml buret was packed to a height of 15cm with washed, degassed Dowex 50 X 12, 200-400 mesh cation exchange resin. The reaction mixture to be separated was absorbed on the column and in many cases distinct bands were visible.

The column was first eluted with 1M perchloric acid[34] until all the dipositive species had been removed. This was followed by elution with 5M perchloric acid to bring

down the more firmly bound tripositive species.

The column was thoroughly washed with 1M perchloric acid after each separation and reused.

Preparation of 1M Chromium(II) Solution in 1M Perchloric Acid Solution.

Chromic acid (70g) was dissolved in distilled water (200ml) and perchloric acid (396.2g) cautiously added. A solid precipitate formed towards the end of the addition was dissolved by the addition of further water (15ml). Hydrogen peroxide (30% solution) was carefully added with stirring until no further reaction occured. The solution was then made up to a total volume of 700ml with distilled water.

Washed, amalgamated, mossy zinc (60g) was placed in the storage flask and the apparatus thoroughly flushed with nitrogen. The chromium(III) solution was introduced and after standing overnight did not appear completely reduced. A further addition of amalgamated zinc (100g) was made which facilitated the reduction.

From this point on chromium(II) solution in perchloric acid media was used exclusively.

Oxidation of Chromium(II) Solution With Various Organic Compounds.

The oxidation of chromium(II) solution with a variety of organic compounds was studied on a qualitative

scale. This was carried out using .001 moles of halogen and slightly less than .002 moles of chromium(II) solution. The procedure was to prepare a homogeneous solution (10ml) of the halogen in water or water-acetone as required in a large test tube. The chromium(II) solution was added under nitrogen and a stream of nitrogen maintained until oxidation appeared complete. If necessary the tube was cooled in ice. Of the compounds thus treated a few of the ones which appeared interesting were studied further. The spectra in the visible region was run on a sample of the reaction mixture using a DK 2 Beckmann spectrophotometer. A sample of the reaction mixture was also applied to the ion exchange column and the chromium species separated.

α-Chloroacetophenone, α-bromoacetophenone, phenacyl acetate, trans 1-2-dibromocyclohexane dibromide and 2-nitropropane in this way yielded predominantly chromium uncomplexed with halogen, $Cr(H_2O)_6^{+++}$. On the other hand carbon tetrachloride, tetrabromoethane and p-toluenesulfonyl chloride yielded halogen complexed chromium, $CrX(H_2O)_5^{++}$.

Standard reference spectra were prepared from known samples of the uncomplexed and complexed chromium (Fig. II). These were verified with spectra described in the literature by Elving and Zemel[35] who report a molar extinction coefficient of 17.8 for $Cr(H_2O)_5Cl^{++}$ at 605mμ and 13.9 for $Cr(H_2O)_6^{+++}$ at 575mμ. Typical spectra are shown in Fig. III,

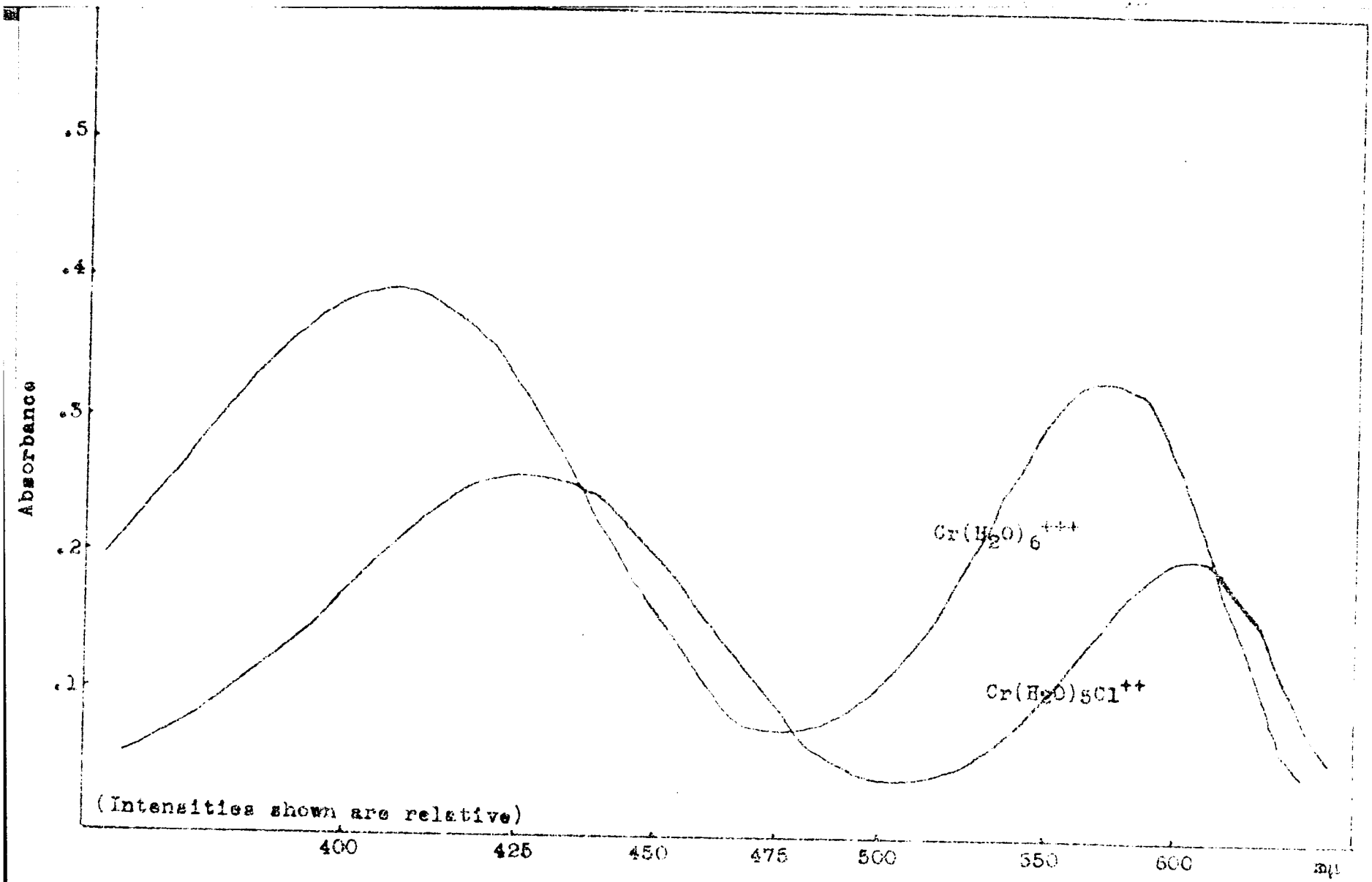


Fig. II. Reference spectra of chromium(III) species.

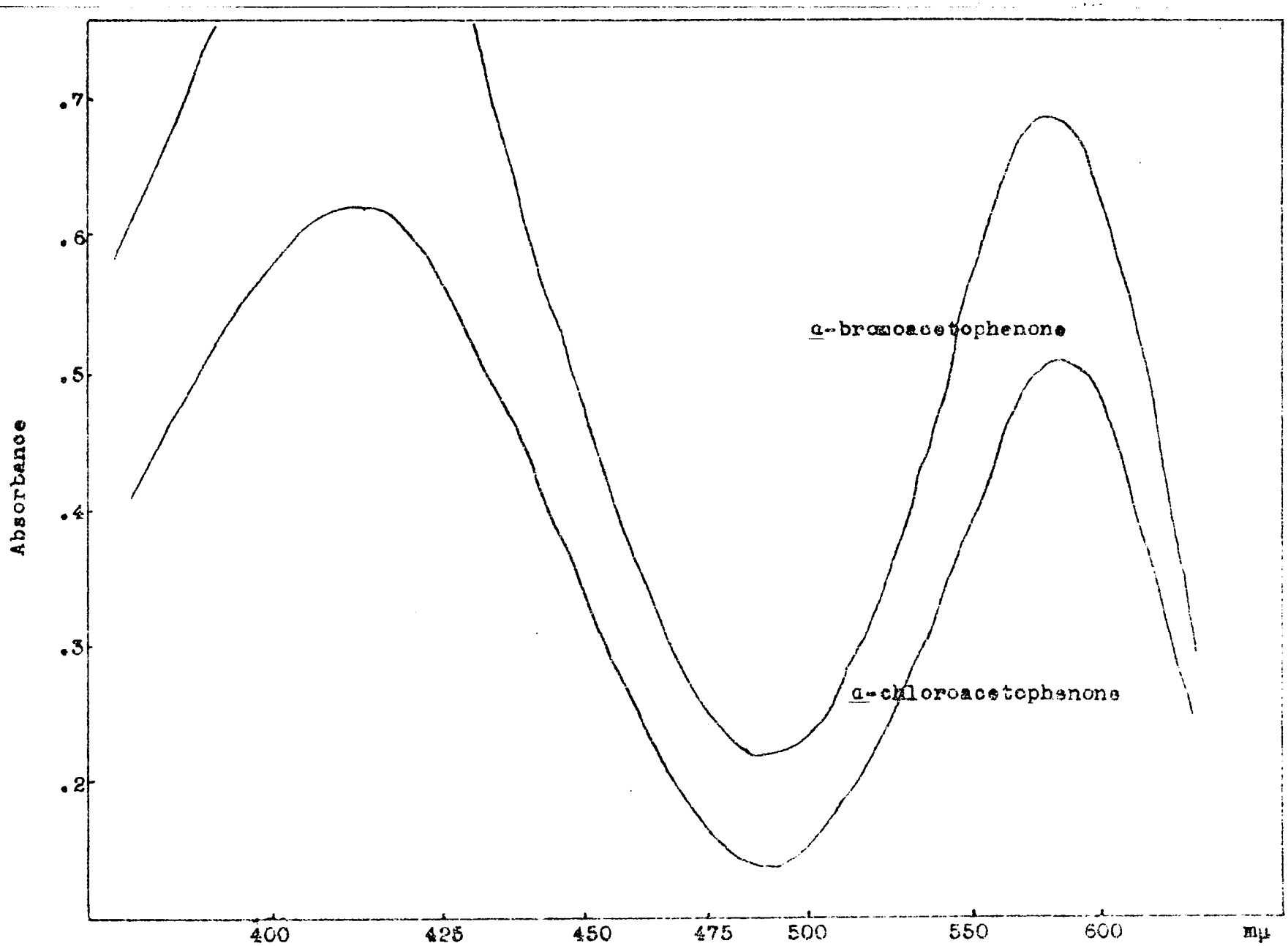


Fig. III. Spectra of chromium(III) species formed in reduction of α-haloacetophenones with chromium(II) perchlorate.

which shows the products of the α-haloacetophenones and Fig. IV which shows the products of trans 1-2-dibromocyclohexane and tetrabromoethane. The absolute concentrations were not known in any case and the intensities shown are therefore only relative. These figures are tracings of the actual spectra obtained.

Effect of Bromide Ion Concentration on Reaction of α-Bromo-acetophenone.

Chromium(II) solution (7.002 moles) was oxidized with α-bromoacetophenone (.001 mole) under nitrogen using acetone solvent (10ml). The reaction was repeated on the same scale adding an aqueous solution of NaBr (.005 moles). The absorption spectra of a sample of each reaction mixture was taken (Fig. V).

Reduction of Benzyl Chloride With Chromium(II) Perchlorate.

Benzyl chloride (0.05 mole, 6.3g) was reduced with 1M aqueous chromium(II) perchlorate (0.11 mole, 110ml) in 1M perchloric acid media by stirring under nitrogen at room temperature for four hours. A homogeneous reaction mixture was obtained by addition of methanol (25ml). Unlike previous reductions which passed directly to either the green or dichloric blue of chromium(III), the reaction mixture became a murky brown color. The reaction mixture was extracted twice with ether. The ether extracts were combined, washed with water and the washings added to the reaction mixture.

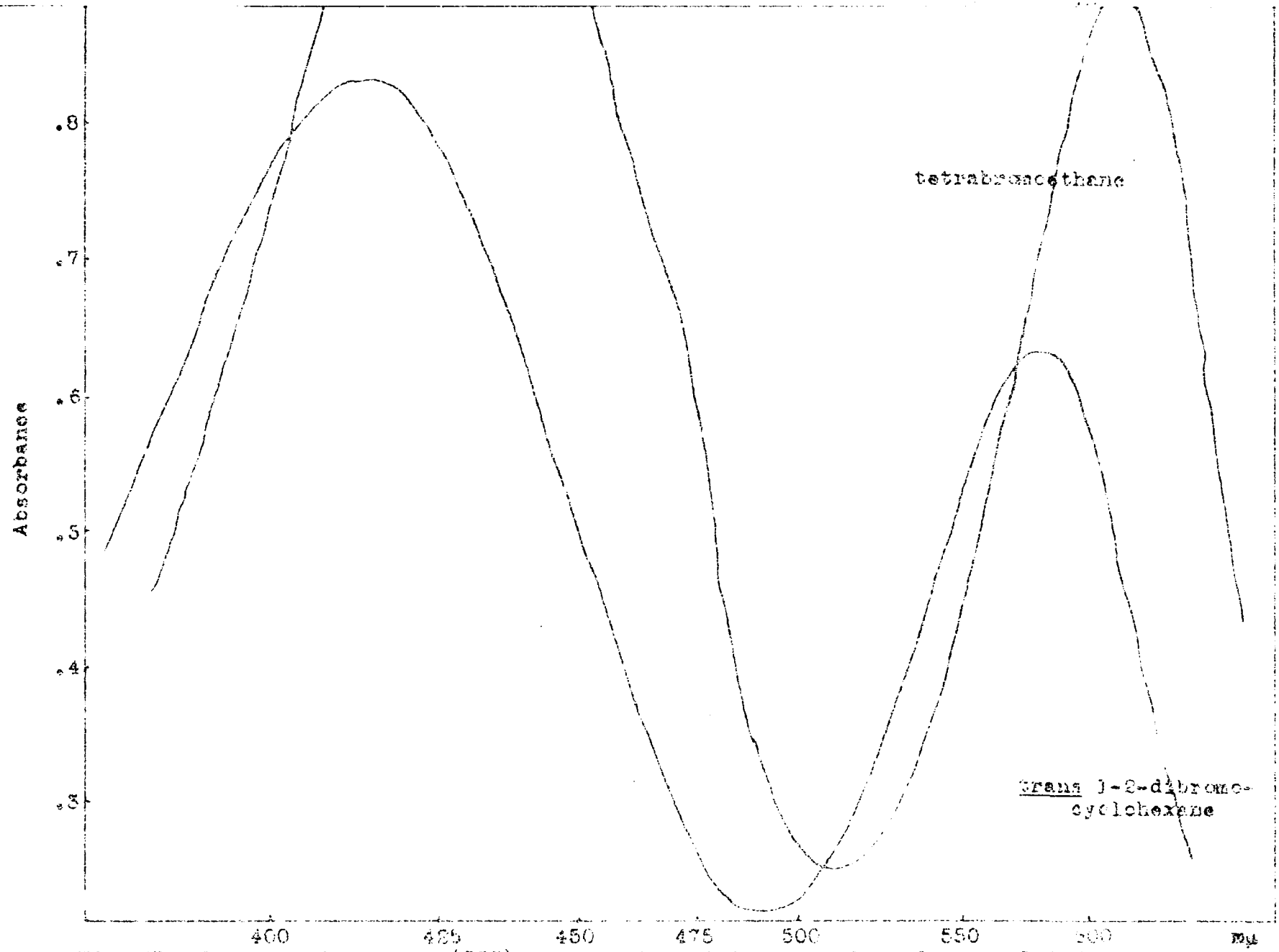


Fig. IV. Spectra of chromium(III) species formed in reduction of trans 1-2-dibromocyclohexane and tetrabromoethane with chromium(II) perchlorate.

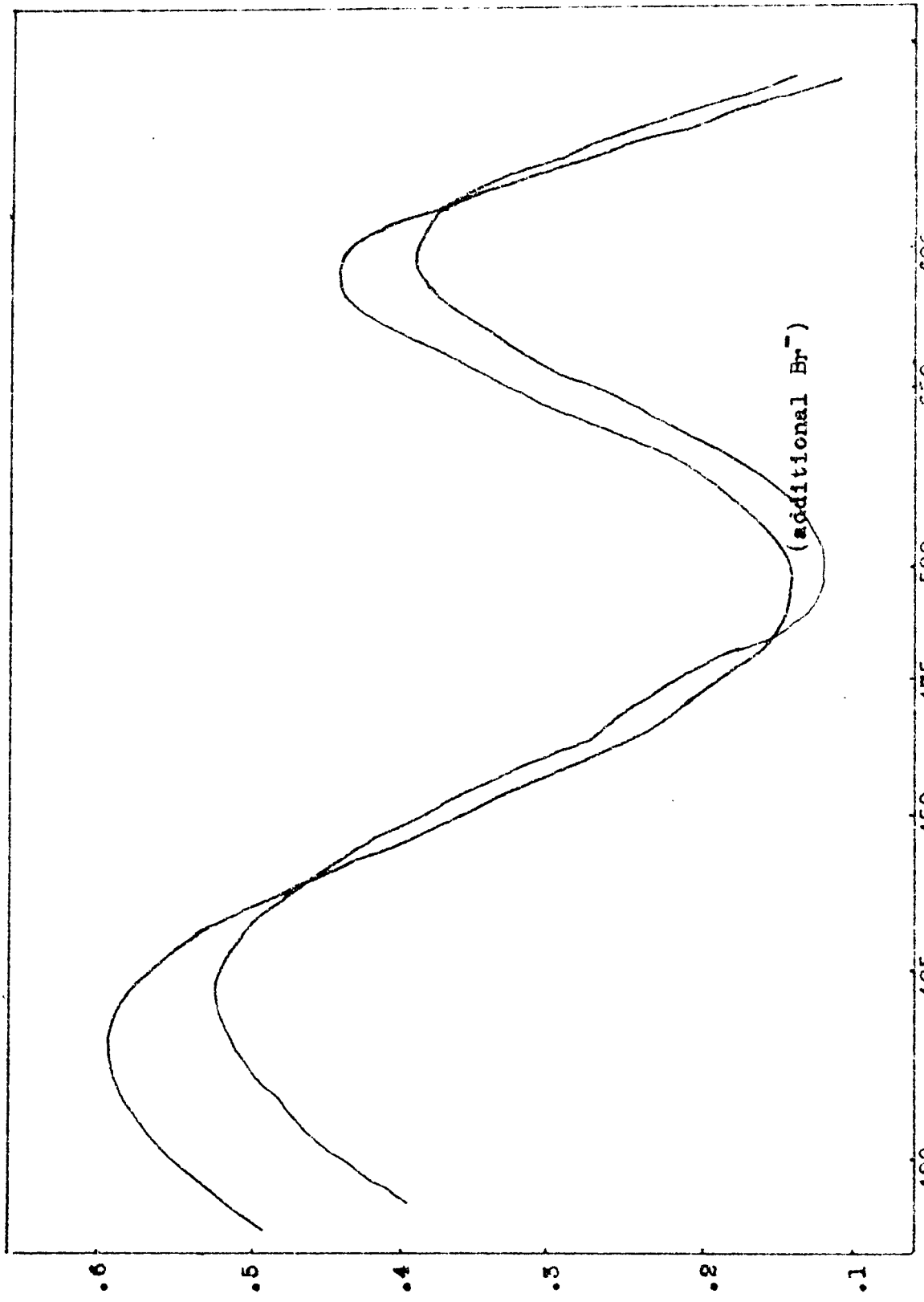


Fig. V. Effect of bromide ion concentration on reduction of α-bromoacetophenone with chromium(II) perchlorate.

The ether extract was dried over magnesium sulfate, the solvent distilled off and a few drops of high boiling residue obtained. An ultra violet spectrum on the ether distillate showed at the very most only a trace of toluene.

The reaction mixture was steam distilled. The first fraction after ether, was taken up in ether, dried and distilled yielding toluene (0.5ml, b.p. 110°C.). The second fraction yielded pure crystalline bibenzyl (0.7g, m.p. 52°C.) which did not depress the melting point of known bibenzyl.

The reduction was repeated on the same scale and yielded on the first extraction with ether both toluene (0.8g) and bibenzyl (0.5g). Steam distillation of the reaction mixture yielded further bibenzyl (0.5g). The reaction mixture was rendered alkaline with sodium hydroxide solution and yielded nothing on steam distillation.

Numerous runs of this reaction were made, with slight variations in technique in some cases, and yielded no significantly different results. In no case did immediate extraction yield a reasonable percentage recovery of products. The brown color was observed to be transitory, the reaction mixture eventually becoming mainly the dichloric blue with some green chromium(III). Further standing or heating produced successive small amounts of products. Standing in air small amounts of benzaldehyde were obtained.

Preparation of Butanol Extracts of Benzylchromium(III) Perchlorate.

Benzyl chloride was reduced with chromium(II) perchlorate as described above. The reaction mixture was stirred until a sample did not precipitate metallic silver from silver nitrate solution. The reaction mixture was extracted four times with small portions of pre-cooled ether, each ether extract being washed with water and the washings added to the aqueous phase. The latter was pumped to remove ether and extracted three times with small portions of pre-cooled butanol. During the extractions the mixture was kept as cool as possible by the addition of chipped ice. The combined butanol extracts were washed with small portions of a 1M perchloric acid, 1M sodium perchlorate solution until all the chromium decomposition products appeared to have been removed. The butanol extract was a deep amber with distinctly reddish tones. An aqueous solution of the complex was obtained by adding ether to the butanol extract.

Decomposition of Aqueous Solution of Benzylchromium(III) Perchlorate.

An aqueous solution of benzylchromium(III) perchlorate was obtained from the butanol extract and allowed to decompose in an open dish at room temperature. After complete decomposition benzaldehyde odour was easily detected and the sample formed a 2-4-dinitrophenylhydrazone melting at 236°C.

(lit. m.p. 237°C.)[36].

Decomposition of Aqueous Solution of Benzylchromium(III) Perchlorate.

An aqueous solution of benzylchromium(III) perchlorate was obtained from the butanol extract, flushed well with nitrogen and then warmed uner nitrogen. After complete decomposition the solution was cooled and crystalline bibenzyl separated out. The sample did not yield 2-4-dinitrophenylhydrazone.

The decomposition was repeated with the addition of acrylonitrile (.5ml). There was a precipitate of polymerized acrylonitrile quickly formed.

Decomposition of Aqueous Solution of Benzylchromium(III) Perchlorate by Sodium Bisulfite.

Addition of sodium bisulfite immediately decomposed an aqueous solution of benzylchromium(III) perchlorate. The spectra of a butanol extract of the decomposition mixture was run and found to have a very intense band at 270-280mμ with a bump at 271mμ. Washing with alkalie removed the compound causing this absorption.

The spectra of p-toluene sulfonic acid was checked and did not correspond. p-Toluene sulfinic acid was prepared[37] and the spectra found to be very similar but slightly shifted.

Decomposition of Benzylchromium(III) Perchlorate by Acetate Ion.

An aqueous solution of benzylchromium(III) perchlo-

rate was immediately decomposed on the addition of either sodium or potassium acetate.

Decomposition of Benzylchromium(III) Perchlorate by Mercuric Chloride.

An aqueous solution of benzylchromium(III) perchlorate was immediately decomposed by the addition of mercuric chloride solution yielding a white precipitate and dichloric blue chromium. The white precipitate was filtered off and crystallized from ethanol yielding shining plates (m.p. 104.5°C.). Benzylmercuric chloride was prepared[38] (m.p. 104.0°C.) and a mixed melting point with the unknown showed no depression.

The change in pH on decomposition of the benzylchromium(III) perchlorate with mercuric chloride was checked. A small beaker containing aqueous solution of complex was equipped with a magnetic stirrer and the electrodes of the pH meter immersed in the solution. The pH was observed, the solution decomposed by addition of mercuric chloride solution, and the final pH of the decomposed solution noted.

Initial pH (relative) = 4.50

Final pH = 4.55

Attempted Ion Exchange Separation of Benzylchromium(III) Perchlorate.

A 25ml buret was packed to a height of 8 cm. with washed, degassed Dowex 50 X 12, 200-400 mesh cation exchange resin. Aqueous solution of benzylchromium(III) perchlorate

(5ml) was applied to the column and absorbed in a band at the top. This band was not eluted with:

1. 30ml .1M $HClO_4$
2. 30ml 1M $HClO_4$
3. 50ml 5M $HClO_4$

It is quite likely that the cross linkage of this resin was too high for the size of the molecule as Dr. F. A. L. Anet was later successful in achieving separation using Dowex 50 X 4 resin[39].

Paper Electrophoresis of Benzylchromium(III) Perchlorate.

A spot of aqueous solution of benzylchromium(III) perchlorate applied to filter paper was observed to absorb ultraviolet light after decomposing thereon.

The paper used in the run was sprayed with .1M $NaClO_4$-$HClO_4$ buffer and the same placed in the cells. A tray of ice was placed over the paper to keep the temperature as cool as possible. A potential of 400 volts was applied to the paper on which three spots were applied.

1. $Cr(H_2O)_6^{+++}$
2. $CrCl(H_2O)_5^{++}$
3. Aqueous solution of complex.

After two hours the $Cr(H_2O)_6^{+++}$ was generally spread to about two thirds the length of the paper, the $CrCl(H_2O)_5^{++}$ to about one third the way and no sign of the benzylchromium(III) perchlorate was visible.

The path of the benzylchromium(III) perchlorate on the paper was cut into three sections, extracted with methanol and the ultra violet spectra recorded. All three samples showed a similar, intense ultra violet absorption. The buffer was checked and showed no absorption. However a control run on another portion of the paper out of the path of any applied spots and gave an identical ultra violet spectrum. Therefore it was concluded to be some decomposition product of the paper itself.

Catalytic Hydrogenation of Solution of Benzylchromium(III) Perchlorate.

Benzyl chloride (.02 mole, 2.2g) was reduced with aqueous chromium(II) perchlorate solution (.022 mole, 22ml) by stirring under nitrogen at room temperature, for three hours. The reaction mixture was extracted four times with small portions of pre-cooled ether. Each ether extract was washed with water and the washings added to the aqueous phase. The latter was pumped to remove ether and then extracted twice with pre-cooled aqueous butanol. The butanol extract was washed four times with a 1M perchloric acid, sodium perchlorate buffer. The last two washings were completely yellow. The butanol was immediately hydrogenated adding chipped ice and 100mg of palladium charcoal catalyst and carrying out the hydrogenation in an ice bath. The hydrogenation was set up and equilibrium obtained before addition of

catalyst. The volume of hydrogen absorbed, the temperature and the barometric pressure were recorded. When there was no longer any further absorption of hydrogen the mixture was filtered through celite, the celite carefully washed with water and butanol and the two phases separated. The butanol phase was washed with water until all blue color was removed. It was then dried over sodium sulfate, suitably diluted with methanol to a known accurate volume and the ultra violet absorption spectrum recorded. In each case a spectrum indicating pure toluene was obtained (Fig. VI.). The intensity at 268.5mμ was recorded. The molar extinction coefficient of toluene standard on our instrument was previously established to be 236 at this wave length. Using the formula[40], E molar = $\frac{\text{Intensity}}{\text{Molarity}}$, the total number of moles present in the butanol phase was established.

The aqueous phase was made one normal with respect to sodium hydroxide and treated with 30% hydrogen peroxide. The resultant chromate solution was refluxed to destroy the excess hydrogen peroxide, filtered with celite and quantitatively made up to a known suitable volume. The intensity at 372mμ was recorded. Using a molar extinction coefficient of 4,860, established on standard chromate solution, the total number of moles present in the aqueous phase was calculated. In all operations standard procedures of quantitative analysis were observed. Wherever possible control experiments were made

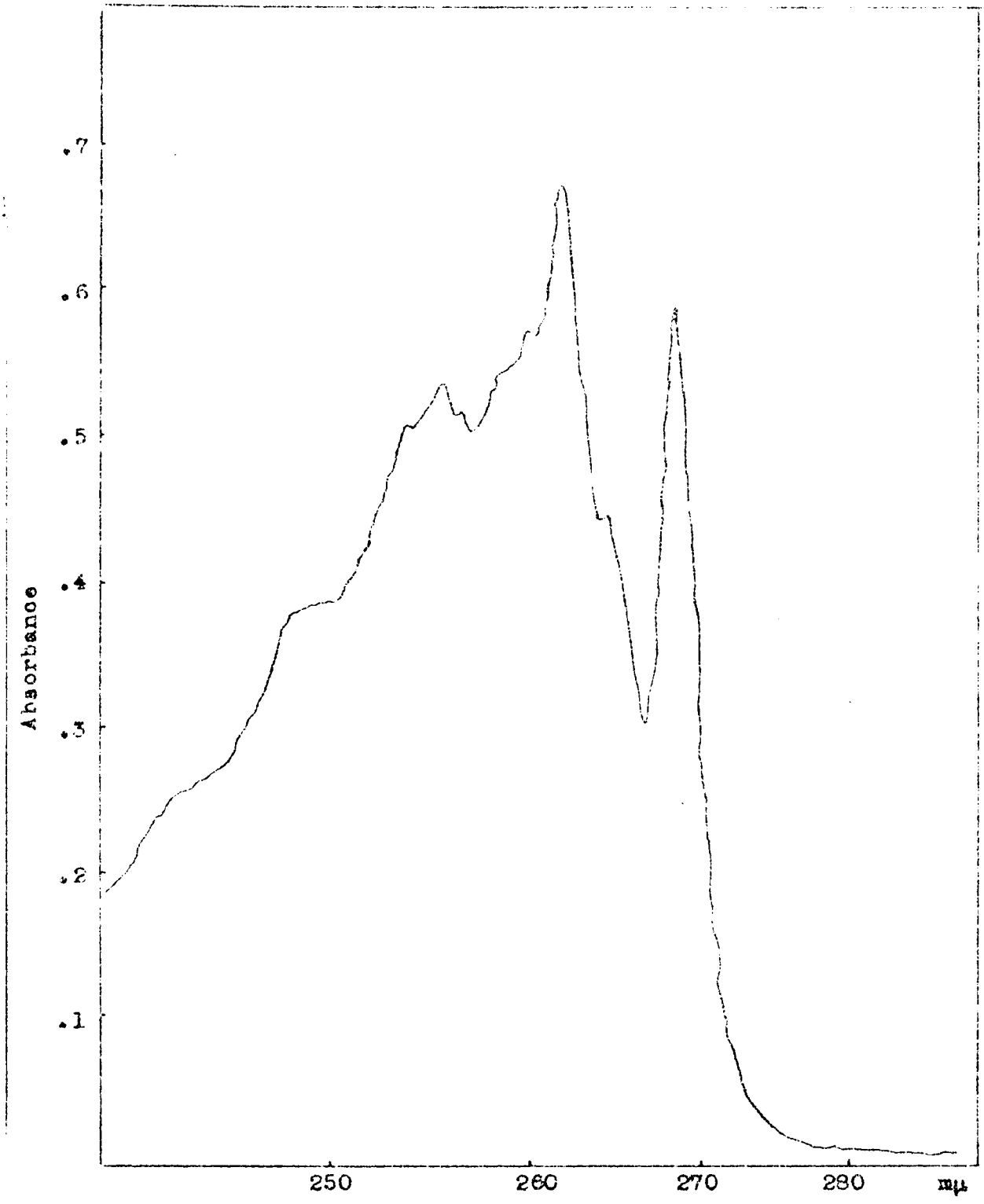


Fig. VI. Ultra violet spectrum of toluene from catalytic hydrogenation of benzylpentaaquochromium(III) perchlorate.

to check the validity of the procedure used. The extinction coefficients established were in good agreement with those reported in the literature[41]. Most significant irregularity observed was the presence of considerable amount of unsaturated impurity in the butanol being used. The difficulty was later offset by using previously hydrogenated butanol.

Numerous hydrogenations using this procedure were made but no consistent ratio between chromium and organic component could be obtained. Table I shows some representative values obtained.

TABLE I.

Catalytic hydrogenation of benzylchromium(III) perchlorate.

Toluene	Chromate ion	Hydrogen
.00094 moles	.00017 moles	.00058 moles
.00053	.00051	.00066
.00078	.00040	.00071
.0019	.0016	.00083
.0028	.0025	.00081
.0015	.00068	.0012*
.0034	.0016	.0019*
.00013	.00056	

*hydrogenated butanol used.

Hydrogenation of Butanol Solvent.

Reagent grade butanol (100ml) was equilibrated with the $NaClO_4$-$HClO_4$ washing solution, palladium on charcoal catalyst (100mg) was added and hydrogenation carried out as usual. After forty five minutes 10ml of hydrogen had been absorbed (T = 16.0°C., P = 767.3 mm).

Distilled water (100ml) and catalyst (100mg) were similarly treated and absorbed 2.8ml of hydrogen.

The ultraviolet spectrum was run placing hydrogenated butanol in the reference cell and regular butanol in the sample cell. The spectrum showed end absorption typical of unsaturated compounds.

Preparation of Standard Chromate Solution and Calculation of the Molar Extinction Coefficient.

Pure potassium dichromate was carefully weighed, and an alkaline solution prepared. The intensity at 372mμ was measured. The molar extinction coefficient of three samples was calculated and the average molar extinction coefficient established.

TABLE II.

Molar extinction coefficient of chromic ion at 372mμ.

	Sample A	Sample B	Sample C
wt of $K_2Cr_2O_7$	.087g	.083	.073
dilution	1/50	1/50	1/50
intensity	.58	.56	.48
E molar	4,870	4,870	4,840

Average E molar = 4,860

Preparation of Toluene Standard and Calculation of the Molar Extinction Coefficient.

Pure toluene was weighed into a volumetric flask, diluted with methanol and the intensity at 268.5 mμ measured. The molar extinction coefficient was calculated and the

average molar extinction coefficient established.

TABLE III.

Molar extinction coefficient of toluene at 268.5mμ.

	Sample A	Sample B	Sample C
wt of toluene	.44g	.49	.51
intensity	.46	.51	.52
E molar	239	235	234

Average E molar = 236

Countercurrent Distribution of Benzylchromium(III) Perchlorate.

Several preliminary countercurrent distributions were made which helped to achieve satisfactory conditions for the separation. Since many of these experiments were made before the necessity of an inert atmosphere was appreciated considrable difficulty with decomposition was encountered. However they did serve to establish the most satisfactory solvent system.

Benzylchromium(III) perchlorate was prepared in the usual manner from chromium(II) perchlorate (20ml) using no solvent and allowing to stir four hours at room temperature. The solvent system used was butanol -.01M perchloric acid and all solvent used was flushed with nitrogen. The cooled reaction mixture was flushed with nitrogen and sufficient butanol and .01M perchloric acid added to yield 80ml of each phase. Tubes 0 and 1 were filled with 40ml of each phase and 70 transfers made under an atmosphere of nitrogen. The

temperature was kept between 3 to 5°C. throughout the separation.

The apparent maximum was observed to be at tube 18.

Aqueous phase (10ml) from tubes 15 to 22 inclusive was removed and added directly to mercuric perchlorate solution. The samples were filtered, water (5ml) added to clear the turbidity caused by the butanol and their absorption at 575mμ measured on the Beckmann DK 2 spectrophotometer. Butanol solvent was used in the reference cell. The values obtained are shown in Table IV.

TABLE IV.

Experimental distribution curve.

Tube	x	Intensity
15	3	.318
16	2	.370
17	1	.420
18	0	.434
19	1	.424
20	2	.370
21	3	.268
22	4	.142

The partition coefficient was calculated to be .35 and a theoretical curve developed. (See section C of the Discussion.)

Molar Extinction of Benzylchromium(III) Perchlorate.

The benzylchromium(III) perchlorate was observed to have a low intensity maximum at 540mμ and a high intensity maximum at 358mμ. (Fig. VII). Samples (10ml) from each of tubes 19 and 24 of the countercurrent distribution were removed and added to 5ml of water. A portion (10ml) of the

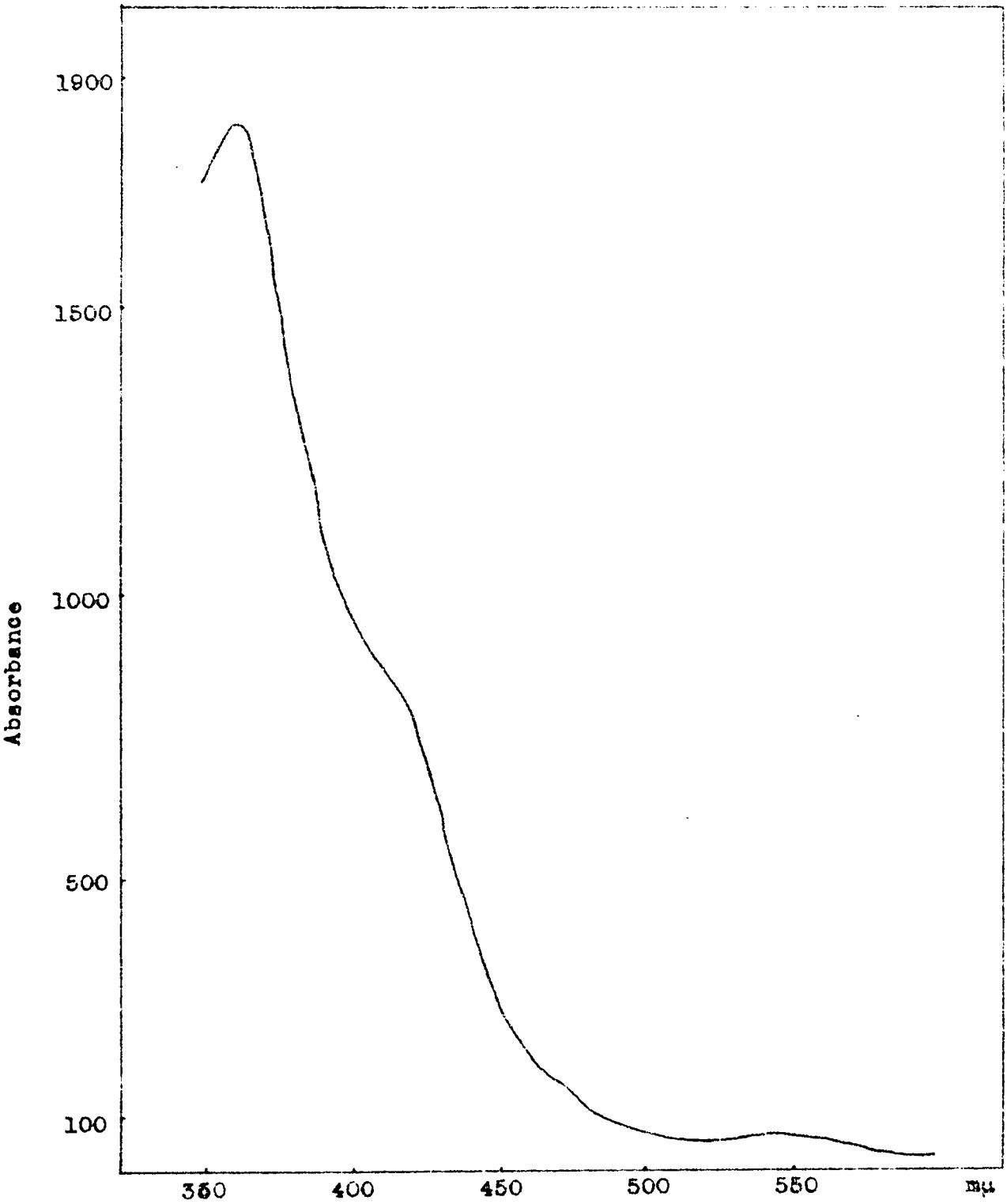


Fig. VII. Spectrum of benzylpentaaquochromium(III) perchlorate.

sample from tube 19 was allowed to decompose, converted to chromate and the molarity calculated as previsouly described.

$$I_{370m\mu} = .76$$

no. moles = .000047

$$I_{540m\mu} = .23$$

$$M = .000047 \times 100 = .0047$$

$$E_{540m\mu} = \frac{.23}{.0047} = 49$$

Similarly using tube 24:

$$I_{370m\mu} = .72$$

no. moles = .0000045

$$I_{358m\mu} = .83$$

$$M = .0000045 \times 100 = .00045$$

$$E_{358m\mu} = \frac{.83}{.00045} = 1830$$

Chromiumbenzyl Ratio by Mercuric Chloride Decomposition.

Aqueous phase (20ml) was removed from tubes 18 and 21 and added immediately to mercuric chloride solution. These solutions were filtered through sintered glass filters which had been previously dried and weighed. The precipitate was dried to constant weight in the filter. The filtrate was made up to a volume of 35ml and the absorption at 575mμ in 5 cm cells was recorded using water in the reference cell. The molar extinction coefficient of uncomplexed chromium(III) at 575mμ is reported in the literature to be 13.9[35]. Therefore the following calculations are possible:

Tube 18: weight HgCl = .0710g = .00022 moles

$I_{575m\mu} = .50$

$M = \frac{.50}{13.9 \times 5} = .0075$

no. moles $Cr(H_2O)_6^{+++} = \frac{.0075}{1000} \times 35 = .00026$

Cr:$PhCH_2$-:: 1 : .85

Tube 21: weight $PhCH_2$-HgCl = .0440g = .00014 moles

$I_{575m\mu} = .31$

$M = \frac{.31}{13.9 \times 5} = .0045$

no. moles $Cr(H_2O)_6^{+++} = \frac{.0045}{1000} \times 35 = .00016$

Cr:$PhCH_2$-:: 1 : .88

DISCUSSION OF RESULTS

A. Chromium(II) Chloride Reduction of 2-Bromoethanol and 2-Bromoethylamine.

In an attempt to demonstrate that the reduction of 2-chloroalcohols and 2-chloroamines proceeds analogously to the reduction of vicinal dihalides, which produce alkenes, the reduction of various simple compounds of suitable structure was undertaken. First of all, for the purpose of establishing a satisfactory experimental technique, the reduction of ethylene chloride was attempted. The chloro compound was refluxed with a hydrochloric acid solution of chromium(II) chloride under an atmosphere of nitrogen and the evolved ethylene worked up as the dibromide. A negligible yield of ethylene was obtained and unreacted ethylene chloride found in the reaction mixture. Failure of the compound to undergo reduction was also indicated by the intense blue color, characteristic of the chromium(II) ion, which persisted. Neither increased time of reaction nor increased acidity of the reaction mixture produced any significant improvement. The chloro compound is apparently not sufficiently reactive to be reduced under the conditions used.

Ethylene bromide treated in a similar manner produced a 71% yield of ethylene isolated as the dibromide.

2-Chloroethanol was not reduced under the conditions used. Presumably this is due to the fact that, as in the case of the ethylene chloride, the compound is not sufficiently reactive.

2-Bromoethanol was reduced slowly under the same conditions and yielded 20% ethylene. However since under the reaction conditions there is extensive hydrolysis there may be no other reduction products formed. Indeed no ethanol was found to be produced.

2-Bromoethylamine hydrobromide was reduced to a mixture of ethylene, ethylamine and ammonia. On the basis of a rough separation by fractional crystallization of the chloride salts the ammonia was estimated to comprise approximately 60% of the mixture and the ethylamine 40%.

Consequently in the case of the bromohydrin no "normal" reduction product, that is a product formed by simple replacement of the halogen by hydrogen, was observed. In the case of β-halogenated amine both the "normal" reduction product and the unsaturated product were found. Thus the simple β-halogenated alcohol and amine studied have been shown to react analogously to vicinal dihalides and in the same manner as observed in annotinine chlorohydrin although in the latter case the chloro compound appears to be more reactive.

B. Oxidation of Chromium(II) Perchlorate With Some Organic Compounds.

The investigation of the reaction was then directed towards the species of chromium produced by the reduction of various organic compounds. Chromium(II) ion in a perchloric acid media was employed because that anion does not tend to complex with chromium[42]. The reagent was oxidized with an excess of the organic compound using sufficient suitable solvent to yield a homogeneous reaction mixture. The reactions were carried out under an atmosphere of nitrogen and the spectrum of a sample of the resultant mixture was taken. The reaction mixture was then separated on an ion exchange column. It had been established that the $Cr(H_2O)_6^{+++}$, bearing a triple positive charge is more firmly bound to the resin than the $CrX^{++}(H_2O)_5$[34]. Hence, while the latter is readily eluted with one molar perchloric acid, the former is removed only with five molar acid although not quantitatively. The highly colored nature of the two species allowed for ready determination of the state of the chromium produced. This was checked by comparison of the spectra in the visible region with reference spectra. (Fig. II). As previously stated (page 4) it is possible to assume that any group found in the coordination sphere of chromium(III) when it is formed from chromium(II) must have been present in the activated complex. Therefore any reaction resulting in the

production of chromium coordinated with halide must proceed by attack at the halide atom. If attack does not take place at the halogen the chromium will not be coordinated with halogen.

Some of the compounds studied and the variety of chromium species identified in the reaction mixture are listed in Table V.

TABLE V.

Chromium(III) ions produced in oxidation of chromium(II) by organic compounds.

Organic compound	Chromium species
carbon tetrachloride	mainly $CrCl^{++}(H_2O)_5$
phenacyl acetate	$Cr^{+++}(H_2O)_6$
2-nitropropane	$Cr^{+++}(H_2O)_6$
p-tolenesulfonylchloride	$CrCl^{++}(H_2O)_5$
α-chloroacetophenone	mainly $Cr^{+++}(H_2O)_6$
α-bromoacetophenone	mainly $Cr^{+++}(H_2O)_6$
trans 1-2-dibromocyclohexane	mainly $Cr^{+++}(H_2O)_5$
tetrabromoethane	$CrBr^{++}(H_2O)_5$
benzyl chloride	see section C

The first four compounds present no difficulty proceeding as would be expected. In the present investigation the α-haloacetophenones were found to yield mainly chromium uncomplexed with halogen. The fact that the product was mostly uncomplexed chromium rather than exclusively that product was investigated. When the spectra of the reaction

mixture of these compounds was examined there was a slight bathochromic shift in the peak corresponding to $Cr(H_2O)_6^{+++}$, that is towards the peak observed for $CrX(H_2O)_5^{++}$. (Fig. III). Similarly when the reaction mixtures were separated on an ion exchange resin a small amount of green eluent with one molar perchloric acid was observed. This corresponds to chromium(III) complexed with one halogen and bearing a double positive charge. It must be noted however that the amount was very small and did not by any means approach a value of one half the total chromium(III) produced.

One possible explanation is that due to the presence of halogen ions in solution a small amount of chromium(II) complexed with halogen could occur from random proximity of the halogen ions. Thus when oxidation occurs these ions would be included in the coordination sphere of the chromium(III) formed. The validity of this theory was tested by carrying out the reduction of α-bromoacetophenone with added bromide ion. The effect of added bromide ion should be to increase the availability of these ions and increase the incidence of chromium(III) complexed with bromine. This was indeed the case. (Fig. V). The spectrum of the reaction mixture containing added bromide ion showed increased bathochromic shift from the spectrum of pure uncomplexed chromium(III). Thus the random occurence of halide ions is probably responsible for the formation of some

of the halogen complexed chromium.

It seems logical to expect that reduction of trans 1-2-dibromocyclohexane and tetrabromoethane to the corresponding olefins are analogous reactions and would proceed by similar mechanisms. However experimental investigation showed the trans 1-2-dibromocyclohexane reaction mixture to contain almost exclusively uncomplexed chromium $Cr(H_2O)_6^{+++}$ while the tetrabromoethane yielded only chromium complexed with halogen $CrBr(H_2O)_5^{++}$. (Fig. IV). This was immediately observable from the color of the reaction mixture and was verified by examination of the spectra of the mixtures as well as separation on the ion exchange column. There does not seem to be any simple explanation for this phenomenon.

The reduction of benzyl chloride gave quite irregular results and the subsequent detailed investigation forms the next section of this work.

C. Chromium(II) Perchlorate Reduction of Benzyl Chloride.

As mentioned in the previous section reduction of benzyl chloride gave anomalous results. It was expected that the reduction would produce either the blue-violet $Cr(H_2O)_6^{+++}$ or green $CrCl(H_2O)_5^{++}$. However in this case the reaction mixture passed through an intermediate dark brown stage before yielding mainly uncomplexed chromium(III). Immediate extraction of the reaction mixture yielded only traces of the expected product toluene. On standing crystals of bibenzyl

separated from the reaction mixture and benzaldehyde was formed on standing in air. Repeated extractions yielded successive small amounts of product but never could immediate extraction be shown to give a reasonable yield of product. Heat appeared to hasten the decomposition of the intermediate.

Suspecting the presence of some type of chromium organic intermediate , the reaction mixture was extracted with butanol yielding a deep amber extract with reddish tones and a blue aqueous solution. The extract could be induced into aqueous solution by the addition of ether to the butanol phase. Repeated washing of the butanol phase with water removed first the blue phase and finally yielded a yellow solution of the complex.

An aqueous solution of the intermediate when decomposed in air yielded benzaldehyde. When the decomposition was carried out under nitrogen the product was bibenzyl. In both cases the inorganic product was predominantly uncomplexed chromium.

These preliminary observations indicated the presence of a chromium organic intermediate the organic moiety being a benzyl group. Furthermore since the final chromium did not appear complexed with chlorine the complex could involve a chromium carbon bond.

Since all attempts at isolating the compound or a

crystalline salt proved fruitless it was necessary to work with the complex as an aqueous solution of its perchlorate salt.

The preparation of a pure solution presented considerable difficulty. Initially it was thought that the most serious factor contributing to decomposition was temperature, however later work showed the true difficulty lay in the sensitivity of the complex to oxygen. Consequently most of the early experiments which were not carried out in an inert atmosphere were considerably complicated by decomposition. Typical of this was an unsuccessful attempt at paper electrophoresis. The unsuccessful attempts at separation on an ion exchange column also suffered from this difficulty. In this case however failure was due mainly to the use of a too highly cross-linked resin which did not allow for passage of a molecule as large as the complex. This is indeed supported by the fact that a successful separation has since been achieved by Dr. F. A. L. Anet using a resin with less cross-linkage.

Preparation of a pure solution was achieved by counter current distribution with the solvent system 0.01M perchloric acid-butanol after 70 transfers in a cool room (3 to 5°C.). The separation was carried out under an atmosphere of nitrogen. Calculation of the partition coefficient can then be made as follows[43];

$$N = \frac{nKr}{Kr + 1} \qquad \text{Equation I}$$

In this equation N is the apparent maximum, n is the number of transfers, K is the partition coefficient and r is the ratio of volumes of upper and lower phases, in our case 1.

Therefore: $18 = \frac{70K}{K + 1}$

$$K = .35$$

Then if y is the fraction of complex in a given tube, which is n tubes removed from the maximum, calculation of a theoretical distribution curve is possible.

$$y = \frac{1}{\sqrt{2\pi n \frac{Kr}{(Kr + 1)^2}}} e^{-\frac{x^2}{\left[2n \frac{Kr}{(Kr + 1)^2}\right]}}$$

$$\text{or } y = Ae^{-\frac{x^2}{c}} \qquad \text{Equation II}$$

$$A = \frac{1}{\sqrt{2 \times \frac{22}{7} \times 70 \times \frac{.35}{(1.35)^2}}}$$

$$= .109$$

$$\text{and } c = 2 \times 70 \times \frac{.35}{(1.35)^2}$$

$$= 26.88$$

Therefore using Equation II the points for a theoretical distribution curve can be determined (Table V).

TABLE V.

Theoretical distribution curve.

x, position of tube	y, fraction in tube
0	.109
1	.105
2	.094
3	.077
4	.060
5	.043

Figure VIII shows a plot of both the experimental and the theoretical distribution curves which correspond within experimental error. The fact that the actual curve is lower than the theoretical curve beyond the maximum is consistent with a small amount of decomposition in the leading tubes due to traces of unremoved oxygen in the solvent.

The pure complex obtained from counter current distribution was observed to have a low intensity maximum at 540mμ and a high intensity maximum at 358mμ (Fig. VII). From the intensity I at these wave lengths and the molarity M the extinction coefficient E can be calculated[40].

$$E = \frac{I}{M}$$

$$\text{Therefore } E_{540m\mu} = \frac{.23}{.0047} \approx 50$$

$$E_{358m\mu} = \frac{.83}{.00045} \approx 1800$$

Work was then directed towards establishing the ratio between the chromium and organic group, presumably the

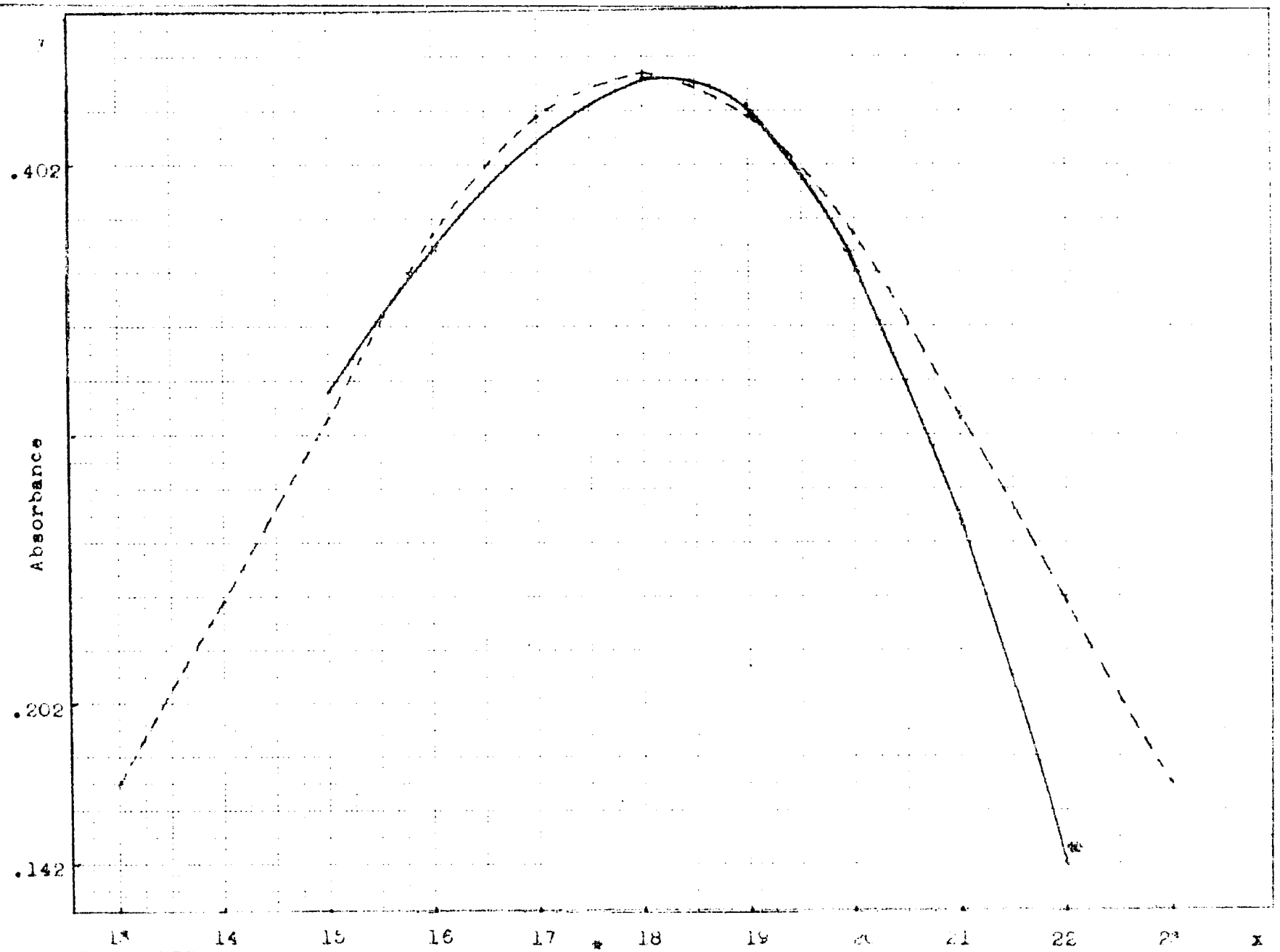


Fig. VIII. Theoretical and experimental distribution curves for counter current distribution of benzylpentaaquochromium(III) perchlorate.

benzyl group. Numerous attempts to achieve this by catalytic hydrogenation of the complex and spectrophotometric analysis of the toluene and chromium produced proved fruitless. The hydrogenation did indeed yield pure toluene but no consistent ratio could be obtained. Various controls on the technique, the activity of the catalyst, the purity of reagents yielded no improvement. It is interesting to note here that although the solvent used was reagent grade butanol it was shown to contain very appreciable amounts of unsaturated impurity which was absorbing hydrogen during the hydrogenation. In order to offset this hydrogenated butanol was used in later experiments. The most likely explanation for the failure to obtain a ratio by this method is the combined operation of a variety of factors, perhaps the most important of which would be the decomposition which occurs in the time required to carry out the operation.

However a simple approach to the ratio was found and proved reproduceable and reliable. The solution of complex had been observed to undergo decomposition by various compounds - sodium bisulfate, acetate ion and finally mercuric chloride. In the latter case uncomplexed chromium(III) and a white precipitate were immediately formed. The precipitate was shown to be benzylmercuric chloride. The rapidity of the reaction was particularly suited to our need to avoid decomposition. The reaction also appeared to be quantitative .

Repeated analysis by this method on the purest solution of complex available yielded consistently a ratio of approximately one to one.

It is interesting to note that Herwig and Zeiss[44] in reporting the preparation of triphenylchromium(III) since completion of this investigation, also used mercuric chloride decomposition analytically. They found that triphenylchromium(III) was rapidly cleaved by mercuric chloride yielding quantitatively three moles of pure phenylmercuric chloride for each chromium present.

In order to establish the valence state of the chromium in the complex the change in pH on mercuric chloride decomposition was observed. There was no significant change in pH accompanying the decomposition. Since the initial pH of 4.5 represents a hydrogen ion concentration of .00003 moles per liter while the complex was present in a concentration of .01 moles per liter, it is evident that formation or loss of an equivalent of hydrogen ion would be experimentally observable.

If the chromium in the complex is in the chromium(II) form the production of chromium(III) would involve the loss of an electron. Including water in the reaction one could represent this as follows:

$$H_2O \longrightarrow OH^- + 1/2H_2 - e$$

$$H_2O + e \longrightarrow OH^- + 1/2H_2$$

Therefore the overall effect would be an equivalent loss in pH. Moreover the fact that no mercurous chloride was formed makes the presence of chromium(II) improbable.

Similarly it can be shown that the presence of chromium(IV) would produce a gain in pH.

$$H_2O \longrightarrow 2H^+ + 1/2O_2 + 2e$$

$$1/2H_2O - e \longrightarrow H^+ + 1/4O_2$$

Since the complex decomposed in nitrogen to bibenzyl, in air to benzaldehyde and formed toluene on catalytic hydrogenation it can be assumed that the organic moiety is a benzyl group. The mercuric chloride decomposition to form benzyl mercuric chloride can be considered analogous to the mercuric chloride decomposition of a Grignard reagent. Following the analogy it is reasonable to conclude that the complex is an organo-metallic compound in which a benzyl anion is complexed to chromium. As previously stated chromium(III) has a coordination number of six. Since there was no chlorine in the coordination sphere of the chromium in the complex, and the only other group present, perchlorate anion, does not tend to complex with chromium(III) the five remaining coordinate positions must be occupied by water molecules. Consequently the complex can be designated with reasonable certainty as benzylpentaaquochromium(III), $PhCH_2\text{-}Cr(H_2O)_5^{++}$. In the present investigation the ion was identified as a solution of its perchlorate salt.

The various reactions discussed can then be represented as follows:

$$PhCH_2Cl + 2Cr^{++} + 10H_2O \longrightarrow PhCH_2 - Cr(H_2O)_5^{++} + CrCl(H_2O)_5^{++}$$

$$PhCH_2 - Cr(H_2O)_5^{++} + HgCl_2 \longrightarrow PhCH_2 - HgCl + Cr(H_2O)_6^{+++} + Cl^-$$

$$PhCH_2 - Cr(H_2O)_5^{++} + 1/2H_2 \xrightarrow{Pd} PhCH_3 + Cr(H_2O)_6^{+++}$$

$$PhCH_2 - Cr(H_2O)_5^{++} \longrightarrow 2PhCH_2\bullet + Cr(H_2O)_n^{++}$$

$$2PhCH_2\bullet \longrightarrow PhCH_2CH_2Ph$$

$$2PhCH_2 - Cr(H_2O)_5^{++} + 2O_2 \longrightarrow 2PhCHO + 2Cr(H_2O)_n^{++} + H_2O$$

The stability of the benzylpentaaquochromium(III) perchlorate is no doubt due to the inertness of chromium(III) complexes to substitution discussed earlier in this work (page 11). The compound can be considered as analogous to the chloride complex, $Cr(H_2O)_5CL^{++}$, of chromium(III) although unlike that complex it has a tendency to dissociate homolytically to give benzyl radicals and chromous ions. This is evidenced by the formation of bibenzyl and the fact that a solution of the benzylchromium(III) perchlorate polymerized acrylonitrile when warmed under nitrogen. This difference is not surprising when one considers the strongly electronegative nature of chlorine. The most reasonable structure for the compound is the normal octahedral complex structure which compounds of coordination number six normally form[20]. Another, less likely structure that could be considered is a complex of the tropylium ion and chromium(I), involving a sandwich structure of the type discussed earlier for dibenzene-Cr(I) with one ring involved per chromium atom. This is quite

unlikely in view of the evidence presented. Furthermore such a structure has been excluded by later work by Dr. F. A. L. Anet[39] who showed that o-methyl, o-methyl and p-methyl-benzyl halides gave different compounds on reduction with chromium(II) perchlorate. If a tropylium ion structure was involved all the carbon atoms would be equivalent and these compounds should yield the same organo-metallic compound.

Dr. Anet further showed that chromium(II) chloride reduction in hydrochloric acid gave toluene rather than the organo-metallic compound. In this case the initially formed complex, $Cr(H_2O)_4Cl{\cdot}CH_2Ph^+$ has chloride ion as well as water molecules in the coordination sphere. Taube[45] has shown that such a chlorine atom favors reduction by bridging with the reducing agent. The resultant chromium(II), no longer substitution-inert, gives benzyl anions which react with the solvent to form toluene. Therefore isolation of the benzyl-pentaaquochromium(III) perchlorate in the chromium(II) perchlorate reduction is dependent on two factors. First the benzylpentaaquochromium(III) perchlorate is reduced by chromium(II) extremely slowly and secondly dipositive complexes of chromium(III) are substitution-inert.

Further work on this subject[46] has shown that the chromium(II) perchlorate reduction of chloroform yields an analogous organo-chromium compound dichloromethylpentaaquo-chromium(III) perchlorate.

CLAIMS TO ORIGINAL RESEARCH

1. The same type of reduction has been observed in the simple compounds 2-bromoethanol and 2-bromoethylamine as occurs in annotinine chlorohydrin[47].

2. Chromium(II) has been oxidized with a variety of organic compounds and the chromium(III) products of reaction identified.

3. The reaction of benzyl chloride with chromium(II) perchlorate has been studied in detail. One product has been shown to be an organo-chromium compound of a type previously unknown. A structure has been proposed for this compound and considerable evidence in favor of it reported[39].

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