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A STUDY OF THE REDUCTION OF ORGANIC HALOGEN COMPOUNDS BY CHROMIUM(II) PERCHLORATE

BY

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A thesis submitted in partial fulfilment
of the requirements of the degree of
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PREFACE

This present work is a continuation of that of M.E. Isabelle.

Chromous ion has not been used very extensively as a reducing agent in organic chemistry. Chromium(II) was found, in the former work, to reduce organic halogen compounds to yield either simple organic products, or organochromium ions.

The present investigation includes a study of the reduction of α-haloketones, halogenated methanes, and vicinal halides.

Acknowledgement

This work was supported by a grant from the National Research Council of Canada.

The author wishes to express her sincere gratitude to Dr. F.A.L. Anet for his guidance as research director.

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ABSTRACT

Phenacyl chloride was found to react with chromium(II) perchlorate, in the presence of methanol, to give both acetophenone and ω-methoxyacetophenone. In the presence of a large excess of methanol, the yield of ω-methoxyacetophenone increased, and that of acetophenone decreased. If, on the other hand, the acid concentration of the methanolic solution was high, acetophenone was formed in over 80% yield, with trace amounts of ω-methoxyacetophenone. In acetone, ethanol and t-butanol, reduction of phenacyl chloride gave mainly acetophenone.

Chloroacetone was also found to yield ω-methoxyacetone, when allowed to react with chromous ion in a large excess of methanol.

The catalysed solvolysis of α-haloketones, by chromium(II) perchlorate in methanolic solution, appears to have no known precedent.

The reduction of methylene iodide with chromous ion did not take place in aqueous solution, but when methanol was used as solvent, iodomethylpentaaquochromium(III) perchlorate was formed. In the reduction of methylene bromide, bromomethylpentaaquochromium(III) perchlorate was obtained.

Reduction of bromoform in methanol gave dibromomethylpentaaquochromium(III) perchlorate. It was found that

when the halomethane contained both bromine and chlorine, attack took place preferentially at the bromine atom. In the reduction of bromodichloromethane, dichloromethylpentaaquochromium(III) perchlorate was formed, and the reduction of dibromochloromethane yielded bromochloromethylpentaaquochromium(III) perchlorate.

The reduction of chloroform in 50% t-butanol-water was found to follow second order kinetics.

Styrene dibromide on reduction was found to yield styrene as the sole organic product and $Cr(H_2O)_5Br^{++}$ as the only inorganic product.

The reduction of meso- and racemic 2,3-dibromobutane was found to be non-stereospecific, mixtures of cis and trans 2-butene being obtained when either isomer was reduced.

The non-stereospecificity of this reduction suggests the possible presence of a radical intermediate, most probably a bromine atom, since such radicals are known to cause isomerization. This postulate is supported by the fact that cis-2-butene undergoes isomerization when present during the reduction of 1,2-dibromocyclohexane by chromous ion.

The reduction of meso-2,3-dibromobutane in 50% t-butanol-water and 75% t-butanol-water, and of racemic 2,3-dibromobutane in 50% t-butanol-water was found to follow

second order kinetics. The reduction of 1,2-dibromo-2-methylpropane in 50% t-butanol-water was also found to be second order.

INTRODUCTION

The concept of oxidation-reduction reactions as consisting of the gain or loss of oxygen, has been superceded by modern theories, which define reduction as the reception of electrons, and oxidation as the donation of electrons[1]. This generalized concept of oxidation-reduction reactions for two-electron transfer processes, becomes identical with the Lewis concept of acid-base reactions, in which the acid acts as an electron pair acceptor, and the base as an electron pair donor.

Simple electron transfers are known to take place in gaseous systems, and evidence for a similar type of reaction in solution has been obtained. Such systems as $MnO_4^{=}$ - MnO_4^{-} and $Fe(CN)_6^{\equiv}$ - $Fe(CN)_6^{\equiv}$, show kinetic behavior indicating a simple electron transfer mechanism, since the overall rate of reaction is much greater than can be accounted for by any possible mechanism based upon dissociation and atom transfer[1]. In the oxidation of ferrous ion by ferric ion in aqueous media, calculations of the reaction rate and activation energy for the reaction, are consistent with the theoretical values, expected of an electron transfer occuring by the process of quantum mechanical tunneling[2]. It has also been shown, by Taube[3], that in the reaction of chromous ion with the complex ion $IrCl_6^{=}$,

the products formed are $IrCl_6^{\equiv}$ and $Cr(H_2O)_6^{+++}$. This reaction represents an example of simple electron transfer unaccompanied by atom transfer.

Electron transfer processes may involve the transfer of a single electron, or may consist in the simultaneous transfer of two electrons. The hypothesis of simultaneous two-electron transfer was discarded by Michaelis[4], who postulated "the principle of compulsary univalent oxidation". This hypothesis held that if an oxidation-reduction reaction involved the overall transfer of two electrons, then the reaction took place by a stepwise process, one electron being transferred at a time. In recent years, this hypothesis has been shown to be unacceptable for many reaction mechanisms, and is no longer considered to be universally valid.

Simultaneous two-electron transfer processes, coupled with atom or group transfer, have been used to explain several mechanisms in organic chemistry. In certain reactions, carbonium ions have been shown to abstract a hydride ion from other reactant molecules in the system[5].

Hydride ion transfer reactions are known to take place with facility in certain processes. In the Cannizzaro reaction[6], in which an aldehyde is transformed into an equimolar mixture of its corresponding alcohol and acid by alkali, the rate controlling step is thought to consist of the donation of a hydride ion to the carbonyl carbon atom of

the aldehyde molecule. It is postulated that α-hydrogens on all alkoxide ions may be easily removed as hydride ions, due to the tendency of the negatively charged oxygen atom to form a double bond with carbon.

Mechanisms, such as the Meerwein-Pondorf-Verley reduction[7], in which aluminum alkoxides catalyse the establishment of equilibrium between a primary alcohol and its aldehyde, and a secondary alcohol and its ketone, are also postulated to go via hydride ion transfer. Such reagents as lithium aluminum hydride and sodium borohydride have received extensive use in organic chemistry as reducing agents, and it is thought that the mechanism of the reduction consists in the donation of hydride ion by the reducing agent.

Examples of simple, simultaneous, two-electron transfer processes, unaccompanied by atom or group transfer, are less well substantiated, but a two-electron transfer mechanism has been put forward to explain the reduction of thallium(III) to thallium(I) by certain reagents. Halpern[8] has found that in the reaction of Tl^{+++} with Hg_2^{++} to yield Tl^{+} and $2Hg^{++}$, no Tl^{++} ion is formed, and he has therefore postulated that the reduction occurs by the direct transfer of two electrons from the Tl^{+++} ion. The oxidation of chromium(II) by thallium(III)[9] has also been postulated to go by a two-electron transfer mechanism[7], and yields as product, along with thallium(I), a dinuclear chromium species.

Many examples of electron transfer, coupled with atom or group transfer, between inorganic ions, have been investigated. A great deal of the work in this latter field has been done by Taube and co-workers, who have studied the mechanisms of several oxidation-reduction reactions in solution.

The processes under consideration involve the transfer of an electron from one metal ion to another, in solution. For these reactions, two varieties of activated complexes are distinguishable. The "outer sphere" activated complex, after electron transfer, maintains intact the number and identity of the groups of its first coordination sphere. The "bridged" activated complex is distinguished by the fact that a common group is shared by the metal ions, resulting in a change in the first coordination sphere for at least one of the ions, on complex formation.

One property of the ions in the reacting systems, which permits their classification as to type, consists in the ease with which they can be made to undergo substitution. Complexes, for which the rate of substitution is rapid, are known as "labile", while those for which the rate is slow, are "inert"[10].

Reactions which employ a substitution-inert oxidizing agent and a substitution-labile reducing agent, and which, after reaction, give rise to a substitution-inert

oxidized product, lend themselves readily to mechanistic studies. In many reactions studied, chromium(II) has been used a reducing agent, because it exhibits the desired properties.

Chromium(II) is substitution labile, whereas chromium(III), on the other hand, is substitution inert. So inert is chromium(III) to substitution, that the hexaaquo-chromium(III) ion has in fact been precipitated from solution as its trichloride salt, by the passage of hydrogen chloride into a solution containing the ion[11]. Even under extremely vigorous conditions, in the presence of 12M HCl, a period of four hours is required to produce an equilibrium mixture of the chromium chloride complexes[12]. It is thought, in this case, that the extraordinarily high hydrogen ion activity, may cause a loosening of the layer of water dipoles oriented about the chromium(III) complex ion, thus permitting the formation of outer sphere complexes, with other ions in solution. However, under normal conditions in dilute acid, the entry of a chloride ion into the coordination shell of the hexaaquochromium(III) ion, is extremely slow. Conversely, the dissociation of the $Cr(H_2O)_5Cl^{++}$ complex ion, reaches equilibrium only after several weeks, and although the $Cr(H_2O)_5Br^{++}$ complex, reacts more quickly than the chloride complex, the dissociation process is still quite slow. The remarkable substitution inertness and lability of chromium(III)

and chromium(II) respectively, can be demonstrated further. It has been shown that the replacement of water in $Cr(H_2O)_6^{+++}$ by solvent water, takes place at 25°, with a half-time of the order of thirty hours. The similar exchange for $Cr(H_2O)_6^{++}$ is so rapid that it has not been measured, and $t_{1/2}$ is likely to be of the order of 10^{-5} seconds[13].

Much of the work done has employed Cr^{++}aq. as reducing agent and Co^{+++} complexes as oxidizing agents, because of the unique properties of Cr^{++}aq. under ordinary conditions, and through its use, much evidence has been ammassed in favor of the "bridged" activated complex mechanism of electron transfer.

The reaction of Cr^{++}aq. with $Co(NH_3)_5Cl^{++}$ as oxidizing agent, has been shown to take place with quantitative transfer of Cl^- to the reducing agent, and it has also been shown that transfer takes place without there being any exchange with chloride ion in solution[3]. This observation suggests that the activated complex for electron transfer has a configuration in which Cl is simultaneously bonded to Cr and Co. In fact, any group which has unpaired electrons for interaction with Cr^{++}, has been found to provide a more accessible path for electron transfer than does a group which lacks unpaired electrons, such as NH_3.

Because of the inertness of chromium(III) to substitution under the conditions of the experiment, 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)[3]. Therefore, it may be concluded that the group was attached in the activated complex. The above reaction was found to be first order in Cr^{++}aq. and first order in Co(III) complex.

It has also been found that the complex $Cr(NH_3)_5X^{++}$ dissociates in acid solution, to yield $(NH_3)_5Cr(OH_2)^{++}$ and X^- as products. However, when Cr^{++} is present, the products include $Cr(H_2O)_5X^{++}$ and NH_4^+, where X^- is a halide ion.[19] Because of their structural simplicity, halide ions have been widely used in the mechanistic studies of electron transfer.

It is of interest to note that in the reaction in which there is spontaneous dissociation, it is the Cr-X bond which is severed, whereas in the presence of Cr^{++}aq., this bond is maintained, and the Cr-NH_3 bond, broken.[19] This reaction was also found to be first order in oxidant and first order in reductant, with electron transfer via the halide bridge, accompanied by the transfer of the halide group from chromium(III) to chromium(II).[19]

Similarly, when the chromium(III) ion is clothed by water molecules rather than by ammonia, and when the halide ion is Cl^-, the electron exchange was found to be rapid but measureable[14]. Using radioactive $(Cr^{51})^{++}$ as reductant, the growth of specific activity in the $Cr(H_2O)_5Cl^{++}$ was measured, and found to increase during the course of the reaction.[14]

This leads to the conclusion[15] that in electron-transfer reactions of chromium(II) and chromium(III) complexes, since the inert chromium(III) species is preserved, reaction must occur by means of a transition state in which the complexing anion acts as a bridging group between the chromium(II) and the chromium(III) atoms.

$$\left[\begin{matrix} \vee \\ -Cr \\ \wedge \end{matrix} \text{----Cl----} \begin{matrix} \vee \\ Cr \\ \wedge \end{matrix} \overset{+4}{-} \right]^{\ddagger}$$

Although the role of the anion is not completely understood, its incorporation into the transition state would cause the lowering of the otherwise high positive charge on the transition state, and would, therefore, increase the stability.

Reactions, testing the ability of other ligands to act as bridging groups in the activated complex, have also been carried out. Most experiments performed had made use of halogens as bridging groups, and no observations had been made as to whether molecules of the solvent water, or the OH^- ion, could also function analogously[16].

Studies employing $Co(NH_3)_5(OH_2)^{+++}$ as oxidant and $Cr^{++}aq.$ as reductant[11], showed that transfer of oxygen to reductant, was quantitative. Through the use of O^{18} enriched oxidizing agents, in normal solvent water, it was observed that one, and only one, oxygen was transferred, and no evidence for a double oxygen bridge could be obtained. The reaction

media, employed in these experiments, were maintained sufficiently acidic to assure that at least fifty percent of the reaction would go via the aquo path. Since, however, quantitative oxygen transfer was observed, it was concluded that by the aquo path, as well as by the hydroxo path (in $Co(NH_3)_5(OH)^{++}$), electron transfer is accompanied by oxygen transfer, and a "bridged" activated complex is postulated for both.

It is also of interest to note that these experiments tend to disprove the postulate that a seven-coordinated aquochromic ion is formed as an intermediate in the reactions studied. Such an intermediate might arise, for example, if the water molecule from the cobalt(III) complex were presented to the face of the octahedron about Cr^{++}. If such an intermediate had been formed, it would lead to a loss of one seventh of the labelled water to the solvent, and this was not found. These observations are in support of the postulate that the bridging group occupies one of the normal coordination positions about the chromium.

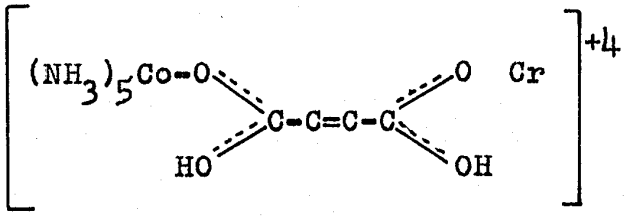
Experiments performed using high concentrations of chloride and bromide ion, showed that these ions also function as non-bridging ligands, although they do so inefficiently. Whether oxygen transfer takes place by a path involving a halide ion is not known, and will be very difficult to ascertain. The participation of chloride ion in the reduction

of $Co(NH_3)_6^{++}$ by Cr^{++}, has been demonstrated, and this reaction does not involve a "bridged" activated complex[17]. It is possible that the reaction, between $Co(NH_3)_5(OH_2)^{+++}$ and $CrCl^+$, takes place by an analogous mechanism, with the chloride ion participating by bringing the electron from Cr^{++} to the exterior of the first coordination shell.

Work, employing carboxylic acids as ligands, has also been done, leading to several interesting results[13].

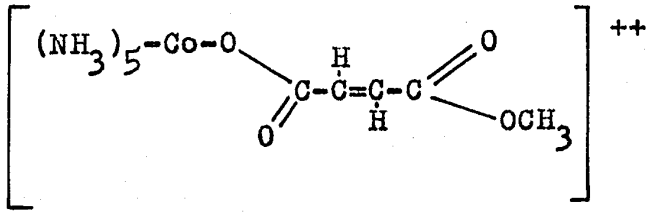
When fumaric acid was used as ligand, the rate of reduction was found to be much higher than for succinic acid, or for several monocarboxylic acids. It was therefore postulated that for succinic acid, as for acetic, butyric and crotonic acid, that attack by Cr^{++} occurred at the carboxyl group adjacent to cobalt(III). To explain the higher rate for fumaric acid, it was thought that attack by Cr^{++} took place at the end remote from the cobalt(III). This mechanism would be possible, because fumarate offers a conjugated system of double bonds for electron transfer. The higher rate would result, because Cr^{++} would not be required to approach as closely to the cobalt(III) centre as when succinate was the bridging group. It was also found that the rate of electron transfer was strongly accelerated by acid. The function of the additional proton might be to improve the conjugation between the cobalt(III) and chromium(II) centres. By associating with the carbonyl oxygen adjacent to

cobalt(III), it could bring about the necessary redistribution of electrons, as indicated in the formation of the activated complex.



Evidence, for the attack of Cr^{++} at the remote end of the ligand[18] for certain bridging groups, has been obtained, using the pentamminocobaltic complex of the monomethyl ester of fumaric acid as oxidizing agent.

For the sake of convenience the complex ion



is designated by $RFCH_3^{++}$.

If the postulated remote attack of $Cr^{++}aq.$ on the complex ion were to take place, it would leave both $Cr^{++}aq.$ and CH_3 attached to the carboxyl group remote from cobalt(III). Ester hydrolysis would consequently be expected to take place, because of the instability of the resulting structure. Titration experiments up to pH 4.5 with standard alkali, performed immediately after one equivalent of $Cr^{++}aq.$ was

allowed to react with one equivalent of $RFCH_3^{++}$, showed that one equivalent of acid had been produced for each equivalent of reacted complex. When such reaction mixtures were distilled at 4°, some two to seven percent of the total methanol was detected in the distillate.

Blank experiments using Cr^{+++} in place of Cr^{++} gave no methanol. Free methanol, added to an acidic solution of the metal ions, was recovered on distillation. When excess pyrophosphate was added to the reaction mixture, followed by extraction with ether for several hours, sixty to seventy percent of the fumaric acid was recovered, identical with results using RF^{++} in place of $RFCH_3^{++}$, and only minute amounts of methanol were detected. On the other hand, if complexing with pyrophosphate was allowed to go to completion, by refluxing the mixture, methanol could be recovered quantitatively on distillation.

In order to explain these results, it has been postulated that ester hydrolysis accompanies electron transfer, to account for the appearance of acid and the extractability of fumaric acid, and that the methanol is left coordinated to chromium(III), to explain the absence of quantitative amounts of methanol from the distillate.

Blank experiments, using RF^{++} as oxidant in methanolic solvent, showed that no methanol became associated with Cr^{++}

when it reacted with the complex, and therefore, in the case of the half ester complex, direct transfer of methanol to Cr^{++} occurred when Cr^{++} attacked the ester end of the ligand.

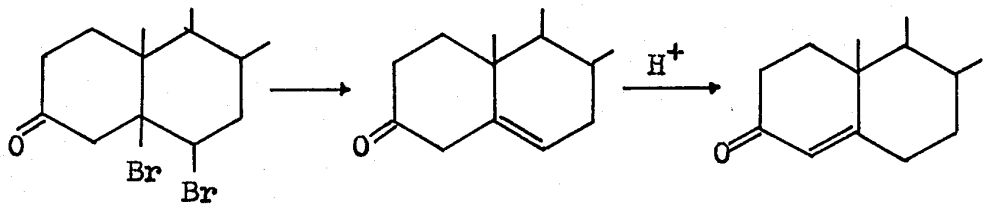
The above series of chemical reactions has produced much evidence for the existence of the postulated "bridged" activated complex, where Cr^{++} acts as the reducing agent, and complexes of chromium(III) and cobalt(III) have been used as oxidizing agents[3,14,15,19]. These reactions have been shown to proceed through activated complexes in which there is interpenetration of coordination spheres.

Fewer examples have been found as evidence for the existence of an "outer sphere" activated complex, but lately, a new avenue has been opened, which will permit investigation along this line. Recently, a complex of chromium(II) has been used[20], which reacts by means of an activated complex, in which there is no interpenetration, as in the "bridged" activated complex. The complex of chromium(II) consists of three dipyridine groups, designated by (dip), associated with the chromous ion. The unique property of this complex is that it reacts retaining its coordination sphere intact. Using $Cr(dip)_3^{++}$ as reducing agent, cobalt(III) complexes react through an "outer sphere" activated complex. The reaction of $Co(NH_3)_6^{+++}$ proceeds so rapidly that its rate has not yet been measured, and is in marked contrast with the slow rate when Cr^{++}aq. is employed

as reducing agent. Rate comparison studies by Taube and co-workers for the same series of cobalt(III) complexes, being reduced by both mechanisms, are now in progress.

Although chromous ion is one of the most powerful soluble reducing agents known, its application as a reducing agent for organic compounds has not been very extensive, and its rival, the somewhat analogous zinc and acid reagent, has been more widely used. Yet, in some cases, chromous ion has been used in preference to zinc as a reducing agent.

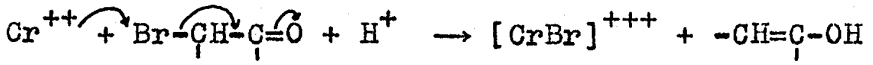
Zinc dust and acetic acid reagent has been generally used to remove halogen from 5,6-dibromo-3-keto steroids, but the yields are poor, and the products impure. Julian et al.[21] showed that when chromium(II) chloride was employed as reductant, rapid and complete dehalogenation occurred to give the Δ4,-3-keto steroids



Similarly, 5,6-dibromoketosterols were reduced to give Δ^5-sterols, and α-bromoketones to give the parent ketones.

Evans[22] employed chromous acetate in acetic acid to preferentially remove the 2-bromine in 2,4-dibromoketones,

and suggested the following possible mechanism for the reaction, although without sufficient evidence.



Although the existence of organochromium compounds has been known for many years, it has not been until recently that simple σ-bonded organochromium compounds have been obtained. All previously known organochromium compounds have been shown to exist as π-complexed sandwich-type structures[23], rather than as simple bonded atoms.

The preparation of the first simple σ-bonded organochromium compound was reported by Anet and Leblanc[24], who obtained in solution, an ion in which chromium is bonded to the benzyl group. This simple organochromium ion has the structure $Cr(H_2O)_5CH_2Ph^{++}$. Although salts containing the ion could not be isolated crystalline, a pure solution of its perchlorate, in dilute perchloric acid, could be obtained, and was found to be fairly stable, with a half-life of 1.5 days at room temperature, in the absence of oxygen.

The complex was prepared by the reduction of benzyl chloride, bromide or iodide, with aqueous chromium(II) perchlorate in 1M perchloric acid, either heterogeneously, or homogeneously in the presence of alcohol. The complex was separated from the other inorganic species by extraction

into butanol, through countercurrent distribution.

The complex ion varied from yellow to brownish-red in color, depending upon its concentration. Decomposition of the complex, in the absence of air, gave bibenzyl, and in the presence of oxygen, gave benzaldehyde. Hydrogenation in the presence of palladium catalyst gave toluene.

In order to ascertain the structure of the complex, it was treated with mercuric chloride, with which it reacted very quickly, without change in pH, to give benzylmercuric chloride, and $Cr(H_2O)_6^{+++}$, in equivalent amounts. It was therefore concluded that the structure of the complex must contain one benzyl group per chromium atom, and must bear two positive charges.

The structure of the compound was postulated as being analogous to the chloride complex of chromium(III), $Cr(H_2O)_5Cl^{++}$, possessing the normal octahedral structure of chromium(III). This would account for the marked stability of the complex, since chromium(III) complexes are known to be substitution-inert[10].

It was found that reduction of benzyl chloride by chromium(II) chloride, in hydrochloric acid, yielded toluene rather than an organometallic compound. The initial chromium complex formed in the reduction would be $Cr(H_2O)_4Cl{\cdot}CH_2Ph^+$, containing a chloride ion in its

coordination sphere, and such chloride complexes are known to undergo reduction[14], by bridging with the reducing agent. The chromium(II) complex formed after reduction, would no longer be substitution-inert, and would dissociate into benzyl anions, which in turn would react with the solvent, to give toluene.

The isolation of the benzylchromium complex in the chromous perchlorate reduction, is due to the fact that it was reduced extremely slowly by chromium(II), as well as to the fact that the dipositive complexes of chromium(III) are substitution-inert.

Although benzyl halides reacted readily to produce organochromium compounds, the simple alkyl halides were found to be resistant to reduction under the experimental conditions. Methyl chloride and methylene chloride were found not to react with chromous ion, whereas chloroform reduced in a few minutes and carbon tetrachloride in a few seconds[25].

The carbon tetrachloride complex decomposed quickly, but the chloroform complex, which proved to be more stable, was obtained as a pure red solution by chromatography on Dowex 50-X4 resin, using 1M perchloric acid as eluent. Decomposition of the complex and analysis of the resulting fragments gave a ratio of Cr:C:Cl very close to 1:1:2. The ease of elution of the complex from Dowex

resin[26], with 1M perchloric acid, indicated it to have two positive charges. The complex ion, therefore, could be shown to have the structure $Cr(H_2O)_5CHCl_2^{++}$, analogous in structure to $Cr(H_2O)_5CH_2Ph^{++}$, being an octahedral complex of chromium(III).

The reaction, which yielded an equivalent amount of organochromium compound and of $Cr(H_2O)_5Cl^{++}$ complex, proceeded as follows:

$$CHCl_3 + 2Cr^{++} + 10H_2O \longrightarrow Cr(H_2O)_5Cl^{++} + Cr(H_2O)_5CHCl_2^{++}$$

If the first step of the reduction of chloroform proceeded with transfer of a chlorine atom from carbon to chromium, then dichloromethyl radicals would be formed.

$$CHCl_3 + Cr^{++} + 5H_2O \longrightarrow Cr(H_2O)_5Cl^{++} + \cdot CHCl_2$$

These radicals could dimerize or react further with chromous ion to produce an organochromium complex.

$$\cdot CHCl_2 + Cr^{++} + 5H_2O \longrightarrow Cr(H_2O)_5CHCl_2^{++}$$

If this reaction were fast, no dimerization would take place.

This mechanism accounts for the observed facts, that no free chloride ion was produced, and that equivalent amounts of $Cr(H_2O)_5Cl^{++}$ and $Cr(H_2O)_5CHCl_2^{++}$ were formed. It is also in accord with the fact that carbon tetrachloride was reduced most easily and methyl chloride least easily, for it is known that chlorine substitution stabilizes the methyl free radical[27].

The preparation of the first member of a series of σ-bonded organochromium compounds, which is isolable crystalline, was reported by Herwig and Zeiss[28], shortly after the work on benzylchromium(III) perchlorate had been completed. The compound obtained was triphenylchromium(III), in the form of its tetrahydrofuranate.

When phenylmagnesium bromide was allowed to react with chromic chloride in tetrahydrofuran, the σ-bonded triphenylchromium(III) complex was obtained, as the tri-tetrahydrofuranate, in the form of bright red crystals. The structure of the complex has been proven by both physical and chemical methods. The magnetic susceptibility of the compound has a value almost identical with that of the chromic halides. The complex was cleaved by mercuric chloride to yield three equivalents of phenylmercuric chloride, and one equivalent of $CrCl_3(THF)_3$, per equivalent of complex.

The complex was found to be sensitive to moisture, and upon hydrolysis, yielded the green chromium(III) ion. In the presence of diethyl ether, it underwent irreversible

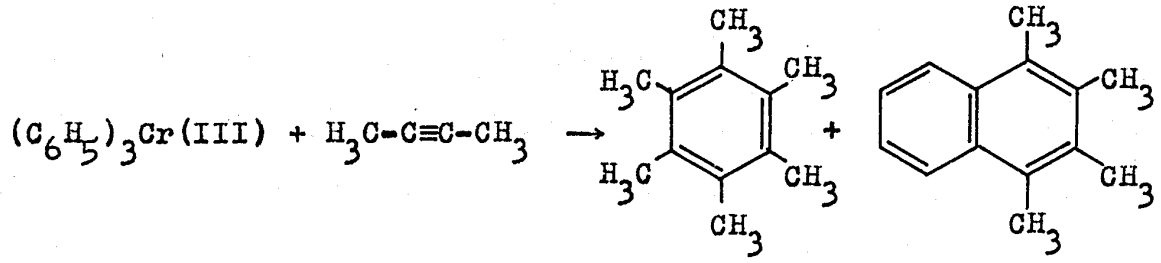
rearrangement to a mixture of π-complexes. The rearrangement takes place when the coordinating tetrahydrofuran molecules are washed away by ether, or removed under vacuum. It is believed that triphenylchromium(III) is incapable of existence, unless stabilized by molecules such as tetrahydrofuran, which are sufficiently basic to effectively coordinate trivalent chromium.

The existence of triphenylchromium(III), as a fully coordinated chromium(III) compound[29], allows the assumption that its molecular geometry is that of the octahedron, such as occurs in the coordinated chromium(III) salts and in chromium hexacarbonyl, due to d^2sp^3 type bonding to chromium. The assumption of σ-bonding[28], rather than ionic bonding of phenyl to chromium, is based on the experimental fact of the failure of trimesitylchromium(III) or dimesitylchromium(II), to undergo rearrangement to π complexes, indicating that an important steric factor, arising from close bonding between carbon and chromium, is involved. In fact, dimesitylchromium(II), violet, and trimesitylchromium(III), blue, are isolable, and do not rearrange, even when their coordinating tetrahydrofuran molecules are removed[30].

Recently, the existence of trimethyl and of triethylchromium(III), in the forms of the tritetrahydrofuranate derivative, has also been reported[31], and their

preparation is effected similarly to that of their triphenylchromium(III) analogue.

Triaryl and trialkyl-chromium(III) compounds have been found to react with disubstituted acetylenes, yielding as cyclic condensation products, benzene derivatives, and polynuclear aromatic hydrocarbons[29]. When triphenylchromium(III) reacts with 2-butyne under heterogeneous conditions, approximately equal amounts of hexamethylbenzene and 1,2,3,4-tetramethylnaphthalene are produced.



The participation of the phenyl groups of triphenylchromium(III) in this condensation, leading to the naphthalene derivative, through the interaction of phenyl with two molecules of 2-butyne in the π-complex, followed by ortho-ring closure, opens new avenues for the syntheses of various condensed aromatic ring systems, through the appropriate choice of triarylchromium(III) and substituted acetylenes. In this way, substituted phenanthrenes and anthracenes, as well as naphthalenes, have been produced.

In all of these reactions, it has been shown that the aryl groups bonded to chromium have participated in the cyclizations, and substituted hydrogen has been abstracted from them. It has therefore been concluded that organochromium(III) is a powerful hydrogen acceptor[31].

Triethylchromium(III) was found to condense tolane to hexaphenylbenzene, and also to contribute an ethyl group, in a mixed condensation with tolane*, yielding 1,2,3,4-tetraphenylbenzene, again demonstrating its hydrogen acceptor capacity, by dehydrogenating the dihydrobenzene ring. When trimethylchromium(III) was used as the organochromium reagent with tolane, a mixed condensation again took place, yielding as product, 1,2,3,4-tetraphenylcyclopentadiene, in addition to the normal product hexaphenylbenzene.

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* Diphenylacetylene

EXPERIMENTAL

Chromium(II) perchlorate was prepared by electrolytic reduction of a solution of chromium(III) perchlorate in perchloric acid, at a mercury cathode. A carbon anode, separated from the cathode by a porous porcelain pot containing dilute perchloric acid, was used. The chromium(II) perchlorate was prepared as a 0.4M solution in 1M perchloric acid, and it is this concentration which is used throughout the experimental work, unless otherwise stated. The preparation, storage, and use of the chromium(II) reagent was effected under an atmosphere of oxygen-free nitrogen. The nitrogen used was purified by bubbling through six solutions of chromous chloride containing amalgamated zinc, followed by a water wash. The chromium(III) perchlorate was prepared[32] by the reduction of reagent grade chromium trioxide with formic acid in dilute perchloric acid, and was recrystallized from a small amount of dilute perchloric acid.

A Beckmann D.K.2 spectrophotometer was used to obtain all spectra in the visible and ultra-violet regions. In the infrared region, spectra were taken using a Perkin-Elmer Infracord, model 137. Vapor phase chromatography was done on a Perkin-Elmer Vapor Fractometer, model 154 C, using a silver nitrate in propylene glycol column. Melting points of compounds were taken on a hot-stage microscope melting point apparatus, and are uncorrected.

A REDUCTION OF α-HALOKETONES

Reduction of Phenacyl Chloride in Methanol

Experiment I

Phenacyl chloride (0.0527 g, 0.34 millimoles) was dissolved in 12 ml. of methanol, and a slow stream of nitrogen was passed through the solution to remove oxygen. A three-fold excess of chromium(II) perchlorate (5 ml, 2 millimoles) was added under nitrogen, and the reaction mixture was allowed to stand under nitrogen overnight. At the end of this time, the excess chromous ion was destroyed by shaking in air, and the reaction mixture was treated directly with a twenty-five per cent excess of 2,4-dinitrophenylhydrazine reagent.

A 2,4-dinitrophenylhydrazone derivative (0.1030 g) was obtained, which had a melting point of 178-180°. (The 2,4-dinitrophenylhydrazone derivatives of the ketonic products will be designated by the name of the ketone followed by DNP, the abbreviated form of 2,4-dinitrophenylhydrazone).

The hydrazone derivative was chromatographed on a fifty per cent mixture of Merck neutral and acid washed alumina, on a column (30 cm x 2 cm), using benzene as eluent. The mixture separated into three bands, two main fractions which could be eluted, and one minor fraction, which was rigidly held on the top of the column.

The first fraction (0.0382 g) had a melting point of 250-252°, when recrystallized from methanol, and did not depress the melting point of known acetophenone DNP[33]. The yield of acetophenone was 38%.

The second fraction (0.0546 g) had a melting point of 200-202°, after recrystallization from methanol, and did not depress the melting point of known ω-methoxyacetophenone DNP, m.p. 200-202°. Yates[34] reports the melting point of ω-methoxyacetophenone as 192-194°, after two recrystallizations from ethanol-ethyl acetate. A carbon-hydrogen analysis of this product gave the following result:

Calc. for $C_{15}H_{14}O_5N_4$: C, 54.4; H, 4.24%.

Found: C, 54.3; H, 4.23%.

The infrared spectra of this fraction and of known ω-methoxyacetophenone DNP, taken as a Nujol mull, were identical. The yield of ω-methoxyacetophenone was 48%.

Phenacyl chloride was again reduced in the same manner, but the organic products were extracted into ether. The ether extract was washed repeatedly with water to remove all methanol, and was dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the organic residue was taken up in carbon tetrachloride.

An NMR spectrum, run on this solution, showed three main bands in addition to those of the aromatic ring systems. One band, having a τ value of 7.5, was found to

be due to the methyl group of acetophenone. The other two bands were in the rough proportion of three to two, and were due to the methoxy group ($\tau = 5.6$) and the methylene group ($\tau = 6.7$) of -methoxyacetophenone, respectively.

Experiment II

Phenacyl chloride (0.0527 g, 0.34 millimoles) was reduced with a three-fold excess of chromium(II) perchlorate (5 ml, 2 millimoles) in 12 ml of methanol, the reaction time being shortened to three minutes. The pH of the solution, taken after reaction, was found to be 1.2. The excess chromous ion was oxidized with air, and the solution was treated with a twenty-five per cent excess of 2,4-dinitrophenylhydrazine reagent, and produced on standing, 0.0933 g of a DNP derivative.

Chromatography gave 0.0390 g of acetophenone DNP, a 38% yield, and 0.0468 g of ω-methoxyacetophenone DNP, representing a 42% yield.

Experiment III

Phenacyl chloride (0.0258 g, 0.167 millimoles) was dissolved in 6 ml of methanol, and 1.2 ml of chromium(II) perchlorate (0.318M, 0.38 millimoles), a fifteen per cent excess, was added under nitrogen to the oxygen-free solution. After oxidation of the excess chromous ion, the solution was treated directly with 2,4-dinitrophenylhydrazine reagent, and

0.0466 g of derivative were obtained.

Chromatography on alumina yielded 0.0062 g of acetophenone DNP, a 30% yield, and 0.0120 g of ω-methoxyacetophenone DNP, representing a 45% yield.

Reduction of Phenacyl Chloride in a Large Excess of Methanol

Phenacyl chloride (0.026 g, 0.168 millimoles) was dissolved in 100 ml of methanol, and a 150% excess of chromium(II) perchlorate (1.25 ml, 0.5 millimoles) was added under nitrogen to the oxygen-free solution. The reaction mixture was stoppered under nitrogen for a period of twenty-four hours, to assure completion of the reduction at such high dilution.

The 2,4-dinitrophenylhydrazone derivative (0.0459 g) was obtained by direct treatment of the solution, after removal of the excess methanol under vacuum, with a 25% excess of 2,4-dinitrophenylhydrazine reagent, and chromatography on alumina yielded 0.0055 g, 11% of acetophenone DNP, and 0.0312 g of ω-methoxyacetophenone DNP, representing a 55% yield.

Reduction of Phenacyl Chloride in the Presence of Excess Perchloric Acid.

Phenacyl chloride (0.0264 g, 0.171 millimoles) was dissolved in 4 ml of methanol, and to this solution was added 3 ml of 70% perchloric acid. Chromium(II) perchlorate,

150% excess (1.25 ml, 0.5 millimoles), was added under nitrogen to the above oxygen-free solution.

The 2,4-dinitrophenylhydrazone derivative (0.0467 g) of the organic products, was obtained as before, and chromatography on alumina yielded one main fraction, that of acetophenone DNP (0.043 g), which represents an 85% yield.

Phenacyl chloride, when reduced in the presence of concentrated hydrochloric acid in place of perchloric acid, gave similar results, producing acetophenone in over 80% yield.

Reduction of Phenacyl Chloride in Acetone

Phenacyl chloride was reduced by chromium(II) perchlorate, as before, using acetone as solvent. After reduction, the solution was diluted with water, and the organic product was extracted into ether. The ether extract was washed repeatedly with water to remove acetone, and after evaporation of the ether, the organic residue was treated with an excess of 2,4-dinitrophenylhydrazine reagent. The sole derivative was acetophenone DNP, m.p. 250°, and a mixed melting point, with known acetophenone DNP, showed no depression.

Reaction of Phenacyl Chloride with Methanol in the Presence of Various Cations

Phenacyl chloride (0.0258 g) was dissolved in 6 ml of methanol, and 2.5 ml of a saturated 1M perchloric acid

solution of cation was added.

The cations studied were Cu^{++}, Fe^{++}, Mn^{++}, Co^{++}, Cd^{++}, Ni^{++}, UO_2^{++}, Fe^{+++}, Zn^{++}, Cr^{+++}, Y^{+++} and ZrO^{++}.

Each sample was allowed to stand for a period of twenty-four hours, after which time a test for the presence of halide ion was made, by the addition of aqueous silver nitrate. All tests were negative.

Inorganic Products from the Reduction of Phenacyl Chloride

Phenacyl chloride (0.0290 g, 0.189 millimoles), 50% excess, was dissolved in 6 ml of solvent and reduced by 0.6 ml (0.24 millimoles) of chromium(II) perchlorate. The reaction time was one hour. The solvents used were methanol, 50% methanol-water, ethanol, acetone and t-butanol.

Visible spectra on the inorganic products were taken, and the relative amounts of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$ were calculated from these spectra, using the values of $\varepsilon = 13.9$ at $575m\mu$[12] for $Cr(H_2O)_6^{+++}$, and $\varepsilon = 17.8$ at $605m\mu$[12] for the monochlorochromium species.

The results of these analyses are presented in Table I.

Chromatography of the reaction products on Dowex 50 W-X4, resin, (200-400 mesh), using perchloric acid as eluent, showed only $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$ as the inorganic species present. No dinuclear chromium species was formed in the reaction.

TABLE I

Relative Percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$ Formed in the Reduction of Phenacyl Chloride (in excess) by Chromium(II) Perchlorate

Solvent	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_5Cl^{++}$
methanol	30	70
ethanol	30	70
acetone	30	70
t-butanol	50	50
50% methanol-water	75	25

Inorganic Products from the Reduction of Phenacyl Bromide

A fifty per cent excess of phenacyl bromide (0.0373 g, 0.187 millimoles), was reduced in 6 ml of solvent by 0.6 ml (0.24 millimoles) of chromium(II) perchlorate. Visible spectra of the inorganic products were taken, and the relative amounts of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$ were calculated, using the value of $\varepsilon = 19.9$ at 622 $m\mu$[3] for the monobromochromium ion.

The results of these analyses are in Table II.

TABLE II

Relative Percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$ Formed in the Reduction of Phenacyl Bromide (in excess) by Chromium(II) Perchlorate

Solvent	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_5Br^{++}$
methanol	60	40
ethanol	60	40
acetone	60	40
t-butanol	70	30
50% methanol-water	80	20

Reduction of Phenacyl Chloride in Ethanol at 0°C

Reduction of phenacyl chloride or bromide in ethanol at 0° produced a yellow-red coloration, indicative of the presence of an organochromium compound. The organochromium compound was unstable, and decomposed readily at room temperature and in the presence of oxygen.

A visible spectrum of the cold ethanolic solution, taken immediately after reduction, differed from that obtained by reducing phenacyl chloride in ethanol at room temperature. A transient organochromium compound was also formed, in the cold, when n-butanol was used as solvent.

Reduction of Phenacyl Chloride in t-Butanol

Phenacyl chloride (0.029 g, 0.189 millimoles, 50% excess) was reduced in t-butanol (6 ml) by chromium(II) perchlorate (0.6 ml, 0.24 millimoles), and the solution was allowed to stand under nitrogen for one hour.

A visible spectrum run after this time, was consistent with that expected of a mixture of $Cr(H_2O)_6^{++}$ and $Cr(H_2O)_5Cl^{++}$ ions. If the solution was again stoppered under nitrogen for twenty-four hours, the spectrum obtained was identical with that taken after one hour. However, if the solution was allowed to stand in the presence of oxygen for several hours, or if it was shaken with air, the spectrum was no longer constant, but showed an increase in absorption in the 360-370 mμ region.

Reduction of Chloroacetone in Excess Methanol

Chloroacetone (0.0154 g, 0.167 millimoles) was dissolved in 100 ml of methanol, and 2.5 ml (1 millimole) of chromium(II) perchlorate, a three-fold excess, was added under nitrogen to the oxygen-free solution. The reaction mixture was stoppered under nitrogen for a period of twenty-four hours.

At the end of this time, the remaining chromous ion was oxidized by shaking with air. The excess methanol was removed under vacuum, and the organic residue was

treated with a 25% excess of 2,4-dinitrophenylhydrazine reagent.

The 2,4-dinitrophenylhydrazone derivative (0.0130 g) had a m.p. of 160°, which is in agreement with that for ω-methoxyacetone, reported in the literature as 160-163°[35], and well above that for acetone DNP which has a m.p. of 128°[36].

The yield of ω-methoxyacetone, obtained as its derivative, was 27%.

Inorganic Products from the Reduction of Chloroacetone.

A fifty per cent excess of chloroacetone (0.0173 g) was reduced in 6 ml of solvent by 0.6 ml (0.24 millimoles) of chromium(II) perchlorate. Visible spectra on the inorganic products were taken, and the relative amounts of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$ were calculated.

The results of these analyses are found in Table III.

TABLE III

Relative Percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Cl^{++}$ Formed in the Reduction of Chloroacetone (in excess) by Chromium(II) Perchlorate

Solvent	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_5Cl^{++}$
methanol	46	54
ethanol	44	56
acetone	48	52
t-butanol	65	35
50% methanol-water	67	32

B REDUCTION OF HALOGENATED METHANES

Reduction of Methylene Iodide

Experiment I

Methylene iodide (2.01 g, 0.6 ml, 0.75 millimoles, 50% excess) was dissolved in 25 ml of methanol, and 2.5 ml (1 millimole) of chromium(II) perchlorate was added to the oxygen-free solution. The reaction mixture was stoppered under nitrogen for three hours. At the end of this time, the solution appeared wine-red in color, and was chromatographed on a column (10 cm x 2 cm) of Dowex 50W-X4 (200-400 mesh) cation exchange resin.

The solution was absorbed on the column, and 1M perchloric acid was used as eluent. A milky fraction (25 ml), containing unreacted methylene iodide, was eluted first, followed by a second fraction (25 ml), red-green in color, containing 40% (0.38 millimoles) of the total chromium. A colorless fraction (20 ml), containing a negligible amount of the $Cr(H_2O)_5I^{++}$ species was obtained next, followed by a yellow-red solution (160 ml) of the organochromium ion $Cr(H_2O)_5CH_2I^{++}$, containing 15% (0.146 millimoles) of the total chromium.

The only other chromium species obtained was the hexaaquochromium(III) ion, which was eluted from the column with 100 ml of 5M perchloric acid, and which contained 43% (0.426 millimoles) of the total chromium.

The chromium concentration of the hexaaquochromium(III) ion was obtained by direct spectrophotometric measurement in a 5 cm cell. The chromium content of the other two chromium containing solutions was obtained by taking known volumes of the solutions, and converting the chromium present to chromate ion, by treatment with an excess amount of sodium hydroxide and hydrogen peroxide. The chromate ion obtained was made up to a definite volume, in a volumetric flask, and the chromium content of the solution was calculated from the visible spectrum, taking $\varepsilon = 4{,}830$ at 372 mμ.[37]

Experiment II

Methylene iodide (4.02 g, 1.2 ml, 1.5 millimoles, 50% excess) was dissolved in 25 ml of methanol, and reduced by 5 ml (2 millimoles) of chromium(II) perchlorate. The reaction mixture was allowed to stand under nitrogen for fifteen hours, after which time it was chromatographed in the usual manner.

A 25 ml turbid fraction was obtained, followed by 25 ml of a red-green solution, which contained 10% (0.147 millimoles) of the total chromium. The next fraction 80 ml, consisted of the organochromium ion, and contained 25% (0.493 millimoles) of the total chromium. The remaining chromium 65% (1.26 millimoles) was in the form of the hexaaquochromium(III) ion.

Experiment III

Methylene iodide (0.42 g, 0.43 ml, 0.53 millimoles) was dissolved in 100 ml of water, and 1.5 ml (0.6 millimoles) of chromium(II) perchlorate was added. The reaction was stoppered under nitrogen for twenty-four hours, after which time, the pale-blue color of the chromous ion remained unchanged. No organochromium ion was formed, and the methylene iodide was not reduced.

Methylene iodide was reduced in N,N-dimethylformamide in a few seconds, yielding an intensely red colored solution. Reduction of methylene iodide in acetone and t-butanol was very slow, but after several hours, the solutions appeared yellow-green in color.

Reduction of Methylene Bromide

Methylene bromide (1.3 g, 0.5 ml, 0.75 millimoles 50% excess) was dissolved in 25 ml of methanol, and reduced by 2.5 ml (1 millimole) of chromium(II) perchlorate. The reaction mixture was allowed to stand for twenty hours under nitrogen, after which time it was chromatographed in the usual manner.

Unreacted methylene bromide was eluted from the column in a 50 ml colorless first fraction, which was followed by 190 ml of a clear green solution of $Cr(H_2O)_5Br^{++}$, containing 30% (0.27 millimoles) of the total chromium. The organochromium ion $Cr(H_2O)_5CH_2Br^{++}$ was eluted next, and the

100 ml fraction contained 30% (0.32 millimoles) of the total chromium.

The $Cr(H_2O)_6^{+++}$ ion was eluted from the column with 150 ml of 5M perchloric acid, and contained 40% (0.43 millimoles) of the total chromium.

Reduction of Bromoform

Experiment I

Bromoform (3.8 g, 1.3 ml, 1.5 millimoles, 100% excess) was dissolved in 25 ml of methanol, and reduced by 4 ml (1.6 millimoles) of chromium(II) perchlorate. The reaction mixture was stoppered under nitrogen for half an hour, after which time it was chromatographed in the usual manner.

The first 25 ml fraction contained unreacted bromoform, and was followed by a green-red fraction (25 ml) which contained 20% (0.302 millimoles) of the total chromium. The next colored ion to be eluted was $Cr(H_2O)_5Br^{++}$, 65 ml, which contained 30% (0.402 millimoles) of the total chromium. This was followed directly by the organochromium ion $Cr(H_2O)_5CHBr_2^{++}$, which contained 15% (0.209 millimoles) of the total chromium.

The hexaaquochromium(III) ion was eluted from the column with 5M perchloric acid, and contained 35% (0.535 millimoles) of the total chromium.

Experiment II

Bromoform (1.9 g, 0.66 ml, 0.75 millimoles, 50% excess) was dissolved in 25 ml of methanol, and reduced by 2.5 ml (1 millimole) of chromium(II) perchlorate. The reaction mixture was stoppered under nitrogen for fifteen hours.

At the end of this time, the reaction products were chromatographed in the usual manner. A first colorless turbid fraction of 50 ml, was obtained, followed by the clear green fraction of $Cr(H_2O)_5Br^{++}$ (320 ml), which contained 35% (0.355 millimoles) of the total chromium. The organochromium ion $Cr(H_2O)_5CHBr_2^{++}$ (140 ml) was eluted next, and contained 35% (0.345 millimoles) of the total chromium. The $Cr(H_2O)_6^{+++}$ ion, eluted from the column with 120 ml of 5M perchloric acid, contained 30% (0.30 millimoles) of the total chromium.

Reduction of Bromotrichloromethane

Bromotrichloromethane, in 50% excess, was reduced by chromium(II) perchlorate to give an organochromium ion, which was unstable, and which decomposed within a few minutes. Chromatography of the reduction products, after the decomposition of the organochromium ion, showed the presence of the $Cr(H_2O)_5Br^{++}$ ion, λ_{max} = 622 mμ. No $Cr(H_2O)_5Cl^{++}$, λ_{max} = 605 mμ, was formed in the reduction.

Reduction of Bromodichloromethane

Bromodichloromethane, (1.23 g, 0.6 ml, 0.75 millimoles, 50% excess) was reduced by 2.5 ml (1 millimole) of chromium(II) perchlorate in the usual manner. Chromatography of the reduction products gave only $Cr(H_2O)_5Br^{++}$, and no $Cr(H_2O)_5Cl^{++}$, along with the organochromium ion $Cr(H_2O)_5CHCl_2^{++}$ [25].

Reduction of Dibromochloromethane

Dibromochloromethane (1.5 g, 1.5 millimoles) was reduced in methanol (25 ml), by 5 ml (2 millimoles) of chromium(II) perchlorate. The reduction products were chromatographed in the usual manner, and $Cr(H_2O)_5Br^{++}$ was eluted. No $Cr(H_2O)_5Cl^{++}$ was formed. The organochromium ion formed in the reduction was $Cr(H_2O)_5CHBrCl^{++}$.

Reaction of Methyl Iodide with Chromium(II) Perchlorate

Methyl iodide (2.15 g, 0.93 ml, 1.5 millimoles) was dissolved in 25 ml of methanol, and chromium(II) perchlorate (5 ml, 2 millimoles) was added to the solution. The reaction mixture was stoppered under nitrogen for twenty-four hours, at the end of which time, the pale blue color, due to the chromous ion, remained unchanged. No organochromium ion was formed, and the methyl iodide was unreduced.

It was found that methyl chloride, methyl bromide, methylene chloride, and bromochloromethane were also

unreduced under similar reaction conditions.

Reduction of Iodoform

Iodoform (0.33 g, 0.084 millimoles) was dissolved in 25 ml of methanol, and chromium(II) perchlorate (0.28 ml, 0.11 millimoles) was added to the solution. Reduction took place within a few seconds, the solution becoming deep red in color. The red complex ion formed, decomposed within a few seconds, leaving the solution green-blue in color.

A similar reaction took place when carbon tetrachloride and 1,1,1-trichloroethane were reduced under the above conditions.

Analysis of Iodomethylpentaaquochromium(III) Perchlorate

The yellow-red organochromium fraction, obtained from the reduction of methylene iodide, was purified by rechromatographing the solution on Dowex resin, and eluting the pure ion from the column with 1M perchloric acid. The pure ion was made up to 250 ml with 1M perchloric acid, in a volumetric flask.

Several 5 ml samples of the solution were taken and converted to $CrO_4^{=}$ ion, by treatment with excess sodium hydroxide and hydrogen peroxide. The chromate ion was made up to a definite volume, and the chromium content of the solution was obtained by direct spectrophotometric measurement.

The concentration of the organochromium ion was 5.24 millimolar.

Another known volume (200 ml) of the organochromium ion was heated to boiling for five minutes with a two-fold excess of silver nitrate and potassium permanganate. The cooled solution was treated with hydrogen peroxide to dissolve the manganese dioxide, and the silver iodide was filtered off onto a sintered glass crucible. The silver iodide was washed with methanol and ether, and dried in the oven at 100°, to constant weight. The silver iodide obtained (0.2554 g) contained 1.08 millimoles of iodine, and therefore, the concentration of iodine was 5.4 millimolar.

The chromium to iodine ratio was therefore 1:00 : 1.03 The solution was not analysed for carbon content.

Analysis of Dibromomethylpentaaquochromium(III) Perchlorate

The yellow-red organochromium fraction obtained in the reduction of bromoform, was purified by rechromatographing on Dowex resin. The pure ion was eluted with 1M perchloric acid, and made up to 250 ml, with 1M perchloric acid.

The solution was analysed for chromium and halide by the same method used for the iodomethylpentaaquochromium ion.

The ratio of chromium to bromide was found to be 1.00 : 2.06.

Analysis of Bromochloromethylpentaaquochromium(III) Perchlorate

The yellow-red organochromium ion obtained from the reduction of dibromochloromethane was purified by chromatography on Dowex resin. The pure ion was eluted from the column with 1M perchloric acid, and made up to 250 ml, with 1M perchloric acid.

Analysis of the organochromium ion was performed in the manner used for the iodomethylpentaaquochromium(III) perchlorate. The analyses gave a ratio of chromium to halide of 1.00::2.00.

Molar Extinction Coefficient of Iodomethylpentaaquochromium(III) Perchlorate

The organochromium ion obtained from the reduction of methylene iodide, was purified by chromatography, in the usual manner. The purified ion was made up to a volume of 50 ml, in 1M perchloric acid, and a visible spectrum of the solution was taken. The organochromium ion had a high intensity maximum at 397 mμ, and a low intensity maximum at 523 mμ.

Several 5 ml samples of the organochromium ion were treated with excess amounts of sodium hydroxide and hydrogen peroxide, and the chromate ion obtained was made up to a definite volume. The chromium content of each sample was obtained by direct spectrophotometric measurement in a 1 cm cell. From the average value of the chromium content of each

5 ml sample, the chromium content of the solution was calculated, and found to be 2.24 millimolar.

The absorption of the organochromium ion was measured at λ_{max} = 523 mμ in a 5 cm cell, and at λ_{max} = 397 mμ in a 1 cm cell.

The molar extinction coefficient ε was calculated[38] using the formula

$$\varepsilon = \frac{A}{Md}$$

where A is the absorbance.

M is the concentration in moles per litre, and d is the thickness of solution in cm, through which the light passes.

At λ_{max} = 523 mμ

$$A\ 523\ m\mu = 0.31$$

$$\varepsilon\ 523\ m\mu = \frac{0.31}{0.00224 \times 5} = 28$$

Similarly, at λ_{max} = 397 mμ

$$A\ 397\ m\mu = 0.61$$

$$\varepsilon\ 397\ m\mu = \frac{0.61}{0.00224} = 266$$

In a similar manner, the molar extinction coefficients, at positions of maximum absorption, were calculated

for the series of pure organochromium ions obtained in the reduction of methylene bromide, bromoform, dibromochloromethane, bromodichloromethane and chloroform. The results of these calculations are presented in Table IV.

Spectra of the pure organochromium ions formed in the reduction of methylene iodide and dibromochloromethane are shown in Figure 1.

Reactions of Iodomethylpentaaquochromium(III) Perchlorate

Solutions of iodomethylpentaaquochromium(III) perchlorate, in 1M perchloric acid, were stable at room temperature for several hours, and at 0°, for several months. On heating, or after standing for a few days at room temperature, the solutions became blue, and iodide ion was liberated.

Solutions of the ion did not react with silver nitrate in the cold, but on heating, yielded a precipitate of silver iodide.

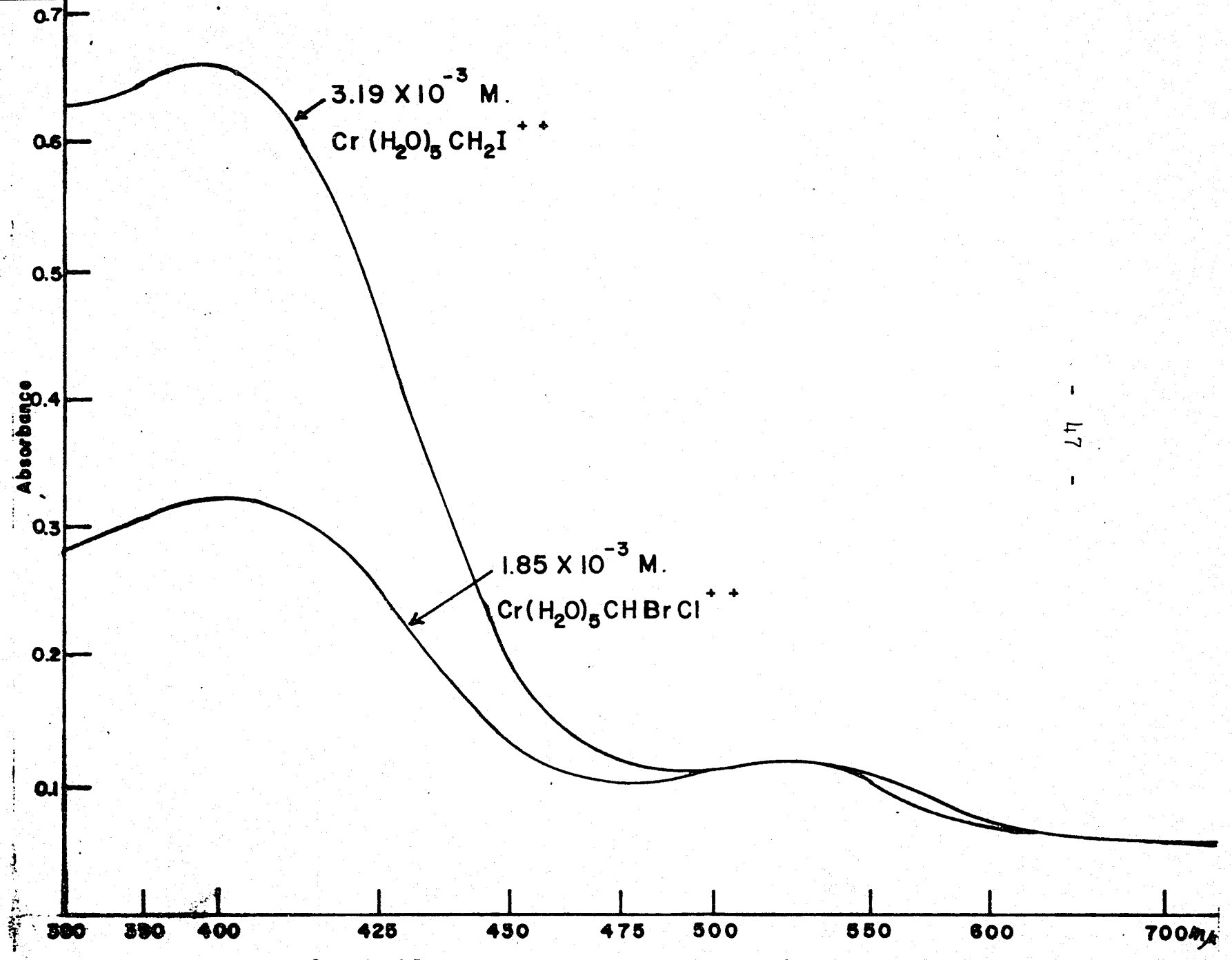
The organochromium ion did not react with mercuric chloride in the cold, but on heating, mercurous chloride was formed.

A solution of the ion was shaken with hydrogen, in the presence of palladium catalyst, for three hours. At the end of this time, the solution appeared to be lighter in color, and hydrogen had been taken up by the solution. The

TABLE IV

Molar Extinction Coefficients ε of a Series of Pure Organochromium Ions, Measured at Positions of Maximum Absorption

Compound Reduced	Organochromium Ion Formed	λ_{max}	ε	λ_{max}	ε
CH_2I_2	$Cr(H_2O)_5CH_2I^{++}$	523	28	397	266
CH_2Br_2	$Cr(H_2O)_5CH_2Br^{++}$	522	23	395	200
$CHBr_3$	$Cr(H_2O)_5CHBr_2^{++}$	524	50	403	155
$CHBr_2Cl$	$Cr(H_2O)_5CHBrCl^{++}$	519	38	400	146
$CHBrCl_2$	$Cr(H_2O)_5CHCl_2^{++}$	510	25	395	103
$CHCl_3$	$Cr(H_2O)_5CHCl_2^{++}$	510	25	395	103


0.7
0.6
0.5
0.4
0.3
0.2
0.1
Absorbance
3.19 X 10⁻³ M.
Cr (H₂O)₅ CH₂I ⁺⁺
1.85 X 10⁻³ M.
Cr(H₂O)₅CH Br Cl ⁺⁺
350
400
425
450
475
500
550
600
700mμ

solution was then chromatographed on Dowex resin, and the original organochromium ion was obtained together with hexaaquochromium(III).

Kinetics of the Reduction of Chloroform

Chloroform was reduced in a solution of 50% t-butanol-water at 18.73°, by an equivalent amount of chromium(II) perchlorate. The kinetic study of this reduction was carried out in a manner similar to that described later for meso-2,3-dibromobutane. The reduction was found to be second order. The calculated rate constants for two separate runs were 2.26×10^{-3} moles^{-1} litre second^{-1}, and 2.60×10^{-3} moles^{-1} litre second^{-1}.

C REDUCTION OF VICINAL HALIDES

Preparation of 2,3-Dibromobutanes

Meso-2,3-dibromobutane was prepared from trans-2-butene, and racemic 2,3-dibromobutane was prepared from cis-2-butene, according to the procedure of Lucas, Dillon and Young[39]. The cis-and trans-2-butene, used in the preparation, were obtained from the Matheson Company, and were described as 99% pure. Gas chromatography showed less than 1% isomer contaminent.

The meso-2,3-dibromobutane had a boiling point of 40.5° at 11.4 mm, and an NMR spectrum of the compound showed it to be free of impurities[40].

Racemic 2,3-dibromobutane had a boiling point of 44-44.5° at 10.6 mm, and an NMR spectrum of the compound showed it to be of high purity.

Reduction of Meso-2,3-Dibromobutane by Chromium(II) in 10% Excess

Meso-2,3-dibromobutane (1.78 g, 1 ml, 8.3 millimoles) was dissolved in 30 ml of methanol, and 30 ml of chromium(II) perchlorate (0.6M, 18 millimoles, 10% excess) was added to the oxygen-free solution. The reduction took place at room temperature, and the gas evolved was swept out by a stream of nitrogen into a bromine trap. Gas evolution appeared to cease after one hour, but the reaction was allowed to

continue for a further three hours to ensure completion.

The dibromobutane from the bromine trap was washed with an aqueous solution of sodium bisulfite to destroy the excess bromine, and the dibromobutane was extracted into ether. The ether extract was washed with a solution of sodium carbonate and water, and was dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the dibromobutane residue was further purified by distillation.

An infrared spectrum of the distilled dibromobutane, run as a liquid film, showed the presence of racemic as well as meso-2,3-dibromobutane.

Reduction of Meso-2,3-dibromobutane in 50% Excess

Meso-2,3-dibromobutane (0.625 g, 0.35 ml, 2.9 millimoles, 50% excess) was dissolved in 30 ml of ethanol, and 10 ml of chromium(II) perchlorate (0.388 M, 3.88 millimoles) was added under nitrogen to the oxygen-free solution, which was maintained at a temperature of 25°.

The gaseous product formed was removed from the reaction flask by the passage of a slow stream of nitrogen, and was caught in a trap immersed in liquid nitrogen.

The gaseous product was chromatographed, using nitrogen as carrier gas, and showed the presence of a mixture of only two gases. These were cis- and trans-2-butene, and

their respective positions were identified by chromatographing pure known samples of these gases.

From the calculations of areas under the curve, approximate relative ratios of cis-and trans-2-butene were obtained.

The product obtained from this reduction consisted of 70% trans-2-butene and 30% cis-2-butene.

Reduction of Meso-2,3-dibromobutane in Five-fold Excess

Meso-2,3-dibromobutane (0.535 g, 0.30 ml, 2.5 millimoles, a five-fold excess) was dissolved in 28 ml of a 50% solution of ethanol-water, and 2 ml of chromium(II) perchlorate (0.8 millimoles) was added under nitrogen to the oxygen-free solution. The reaction mixture was stoppered under nitrogen, and was allowed to shake for a period of fifteen hours at room temperature.

At the end of this time, the organic products were removed by the passage of a slow stream of nitrogen, and were received into a trap immersed in liquid nitrogen.

The gas obtained was chromatographed, and was found to contain 60% trans-2-butene and 40% cis-2-butene.

Reduction of Meso-2,3-dibromobutane in the Presence of 150% Excess of Chromium(II) Perchlorate

Meso-2,3-dibromobutane (0.178 g, 0.1 ml, 0.8 millimoles) was reduced by 10 ml of chromium(II) perchlorate,

(4 millimoles, 150% excess) in a solution of 15 ml of ethanol and 5 ml of water. The reduction took place at room temperature, and the butenes were removed from the reaction mixture as quickly as possible.

The butenes obtained were chromatographed, and consisted of 70% trans-2-butene and 30% cis-2-butene.

Reduction of Racemic 2,3-Dibromobutane by Chromium(II) in 10% Excess

Racemic 2,3-dibromobutane (1.79 g, 1 ml, 8.3 millimoles) was dissolved in 30 ml of methanol, and 30 ml of chromium(II) perchlorate (0.6M, 18 millimoles, 10% excess) was added to the oxygen-free solution. The reduction took place at room temperature, and the gas evolved was swept out by a slow stream of nitrogen into a trap containing bromine. The total reaction time was four hours.

The dibromobutane, from the bromine trap, was washed with an aqueous solution of sodium bisulfite, and the dibromobutane was extracted into ether. The ether extract was washed with an aqueous solution of sodium carbonate and water, and was dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the dibromobutane residue was further purified by distillation.

An infrared spectrum of the distilled dibromobutane, run as a liquid film, showed the presence of meso- as

well as racemic 2,3-dibromobutane.

Reduction of Racemic 2,3-dibromobutane in 50% Excess

Racemic 2,3-dibromobutane (0.625 g, 0.35 ml, 2.9 millimoles, 50% excess) was dissolved in 30 ml of oxygen-free ethanol, and 10 ml of chromium(II) perchlorate (0.388M, 3.88 millimoles) was added under nitrogen. The temperature of the reaction was maintained at 25°.

The gaseous organic products were obtained as before, and chromatography showed that 60% trans-2-butene and 40% cis-2-butene had been formed in the reduction.

Reduction of Racemic 2,3-dibromobutane in Five-fold Excess

Racemic 2,3-dibromobutane (0.535 g, 0.3 ml, 2.5 millimoles, a five-fold excess) was dissolved in 28 ml of a 50% solution of ethanol-water, and 2 ml of chromium(II) perchorate (0.8 millimoles) was added under nitrogen to the oxygen-free solution. The reaction mixture was stoppered under nitrogen, and was allowed to shake at room temperature for a period of four hours.

Chromatography of the gaseous products of the reduction showed the presence of trans-2-butene to the extent of 55% and of cis-2-butene to the extent of 45%.

Reduction of Racemic 2,3-Dibromobutane (100% excess) with Rapid Removal of Gaseous Products

Racemic 2,3-dibromobutane (0.179 g, 0.1 ml, 0.8 millimoles, 100% excess) dissolved in 10 ml of ethanol, was added slowly, under nitrogen, to a solution of 2 ml of chromium(II) perchlorate (0.388M, 0.776 millimoles) in 15 ml of water and 5 ml of ethanol.

The gaseous products were removed as quickly as possible by a stream of nitrogen, and were captured in a flask immersed in liquid nitrogen.

Chromatography of the gas produced showed it to consist of 60% cis-2-butene and 40% trans-2-butene.

Reaction of Cis-2-butene in the Presence of Chromium(II) Perchlorate

Cis-2-butene was bubbled into a solution of chromium(II) perchlorate in 30 ml of a 50% ethanol-water solution, and the reaction flask was stoppered.

The resulting mixture was allowed to shake for a period of two hours at room temperature, after which time, the pale blue color, due to the chromous ion present, remained unchanged.

The gas was removed in the usual manner, and chromatography showed some 98% cis-2-butene present.

Reduction of 1,2-Dibromocyclohexane by Chromium(II) Perchlorate in the Presence of Cis-2-butene

Cis-2-butene was shaken with a solution of chromium(II) perchlorate (2ml, 0.8 millimoles), in 30 ml of 50% ethanol-water, containing 0.1 ml (0.73 millimoles) of 1,2-dibromocyclohexane. The stoppered reaction flask was allowed to shake for one hour at room temperature. At the end of this time, the reduction of the 1,2-dibromocyclohexane did not appear to be complete, and the reaction mixture was allowed to shake for an additional time of twelve hours. At the end of this time, the gas was removed in the usual manner, and the vapor-phase chromatogram, showed that the gas consisted of 70% cis-2-butene and 30% trans-2-butene.

If cis-2-butene was shaken with a mixture of the reduction products of 1,2-dibromocyclohexane, after the reduction had been completed, no isomerization took place, and only cis-2-butene was obtained.

Reduction of Styrene Dibromide by Excess Chromium(II) Perchlorate

Styrene dibromide (0.01694 g, 0.0643 millimoles) was reduced in 10 ml of methanol by 2 ml of chromium(II) perchlorate (0.34M, 0.68 millimoles, a three-fold excess). Reduction took place very quickly, and the reduction mixture was diluted with water, and steam distilled.

The distillate was made up to a volume of one litre with distilled water in a volumetric flask, and the ultra violet spectrum of the solution taken. The ultra violet spectrum was identical with that of styrene, and the concentration of styrene in the solution was calculated using the value of $\varepsilon = 12{,}500$ at 244 mμ[41]. Although the value for styrene refers to a spectrum taken in methanol, it is assumed to be similar for the aqueous methanol distillate obtained in this reaction. The solution was found to contain 0.0613 millimoles of styrene, representing a yield of ninety-five per cent.

Inorganic Products from the Reduction of Meso-2,3-Dibromobutane by Chromium(II) Perchlorate

Meso-2,3-dibromobutane, in equivalent concentration, or in two-fold, four-fold, eight-fold and sixteen-fold excess, was reduced by chromium(II) perchlorate in a series of various solvents.

Meso-2,3-dibromobutane was dissolved in 6 ml of solvent, and nitrogen was passed through the solution for a one minute period. Chromium(II) perchlorate (0.6 ml, 0.24 millimoles) was added under nitrogen, and the solution was stoppered under nitrogen for two hours at room temperature. At the end of this time, the visible spectrum of the solution was taken, and the relative quantities of $Cr(H_2O)_6^{++}$ and $Cr(H_2O)_5Br^{++}$ were calculated from the spectrum. The solvents used were

ethanol, acetone and 50% t-butanol-water, and the results obtained, appear in Table V.

The spectrum of the reduction products of meso-2,3-dibromobutane in ethanol, at various dibromide concentrations, is shown in Figure 2.

It was also found that when meso-2,3-dibromobutane was reduced in the presence of excess 1,4-dibromobutane or n-propyl bromide, (neither of which is reduced by chromous ion), that the absorption maximum of the visible spectrum of the reduction products, was shifted to lower wavelengths, when compared with the spectrum of the reduction products in the absence of these two substances.

Chromatography of representative solutions on Dowex-50 resin showed $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_6^{+++}$ to be the only chromium species present. No dinuclear species was formed in these reductions.

TABLE V

Relative Percentage of $Cr(H_2O)_6^{+++}$ in the Mixture of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$, Formed in the Reduction of Meso-2,3-Dibromobutane

Molar Proportion of Dibromobutane Per Two Moles of Chromium(II) Ion	Solvent		
	Ethanol	Acetone	50% t-Butanol-H_2O
	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_6^{+++}$
16			57
8	25	38	80
6		43	
4	38	57	90
2	60	69	100
1	75	73	

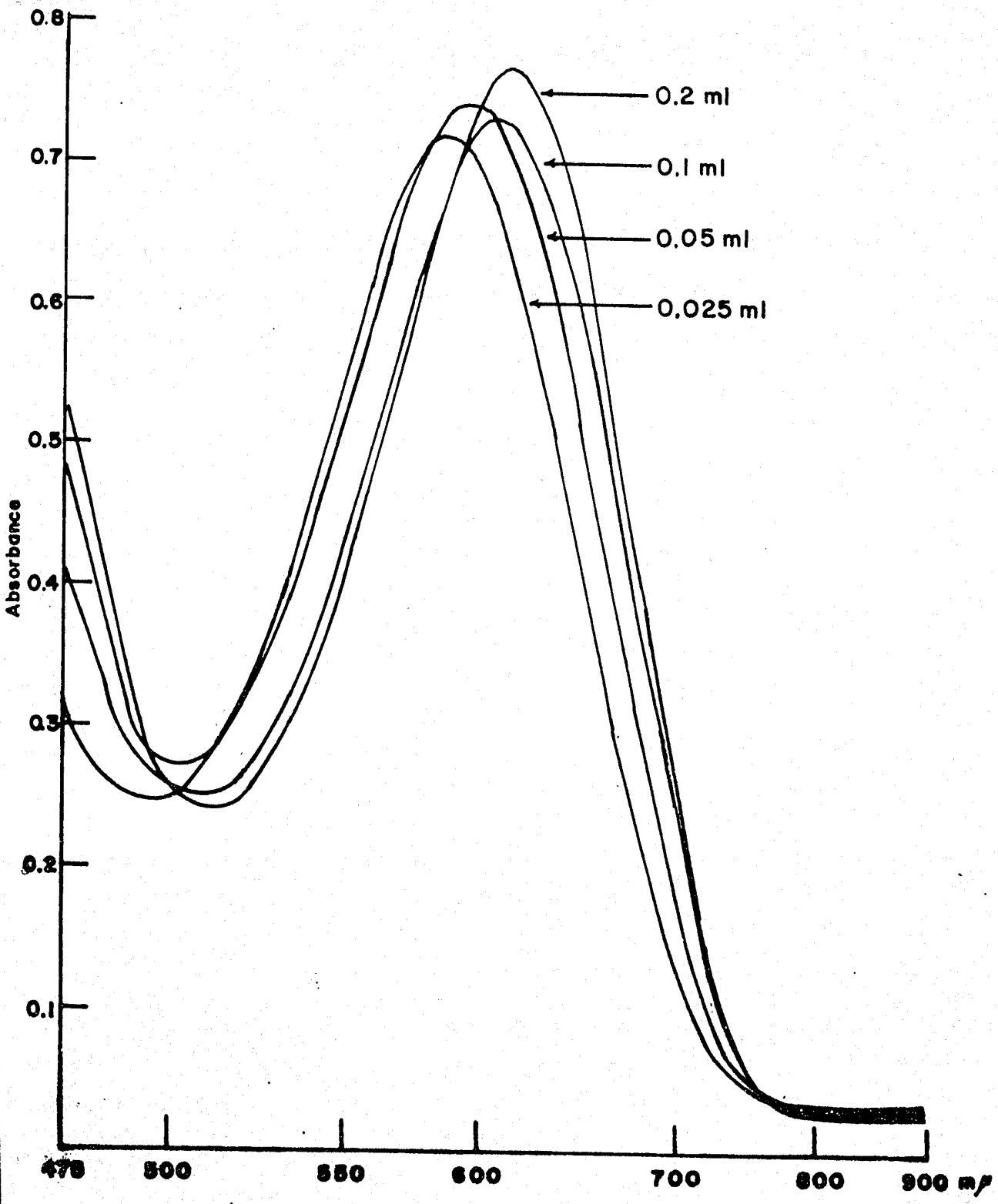


Fig. 2 Spectra of the inorganic products formed in the reduction of different amounts of meso-2,3-dibromobutane by chromous ion, under otherwise identical conditions.

Inorganic Products from the Reduction of 2-Methyl-2,3-dibromobutane

Excess amounts of 2-methyl-2,3-dibromobutane were reduced in acetone by chromium(II) perchlorate in a similar manner to that of meso-2,3-dibromobutane. The solutions were allowed to stand at room temperature for two hours, after which time the visible spectra were obtained, and the relative percentage quantities of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$ were calculated. The results appear in Table VI.

TABLE VI

Relative Percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$ Formed in the Reduction of 2-Methyl-2,3-Dibromobutane in Acetone

Molar Proportion of Dibromobutane Per Two Moles of Chromium(II) Ion	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_5Br^{++}$
8	0	100
4	7	93
2	28	72
1.6	40	60

Inorganic Products from the Reduction of 1,2-Dibromo-2-Methylpropane

Excess amounts of 1,2-dibromo-2-methylpropane were reduced in a similar manner to meso-2,3-dibromobutane, using 50% t-butanol-water as solvent. The relative percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)Br^{++}$ in the solution, was calculated from the visible spectra of the reduction products. The results appear in Table VII.

TABLE VII

Relative Percentage of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$ Formed in the Reduction of 1,2-Dibromo-2-Methylpropane

Molar Proportion of Dibromide Per Two Moles of Chromium(II) Ion	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_5Br^{++}$
16	35	65
8	46	54
4	56	44
2	75	25

Inorganic Reduction Products of a Series of Substituted Ethanes

A four-fold excess of the organic halogen compound was reduced in 6 ml of solvent, with 0.6 ml of chromium(II) perchlorate (0.24 millimoles), by the method previously described for meso-2,3-dibromobutane.

The visible spectra of the solutions were taken, and the percentage composition of the solution, with respect to the two inorganic species $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$, was calculated. These results are presented in Table VIII. The solvents used were methanol, acetone and t-butanol.

Under the conditions of the experiment, it was found that the reduction of 1,2-dibromoethane, 2-bromopropane and 1,2-dibromopropane, was incomplete.

TABLE VIII

Relative Percentage of $Cr(H_2O)_6^{+++}$ in the Mixture of $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5Br^{++}$, Formed in the Reduction of a Four-fold Excess of Halogenated Substituted Ethanes

COMPOUND	SOLVENT		
	Methanol	Acetone	t-Butanol
	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_6^{+++}$	% $Cr(H_2O)_6^{+++}$
1,2-dibromo-2-methylpropane	0	17	68
sym-tetrabromoethane	0	17	37
2,3-dibromobutane (meso-)	0	66	80
2,3-dibromobutane (rac,)	0	66	80
2-methyl-2,3-dibromobutane	0	7	52
2,3-dimethyl-2,3-dibromobutane	0	7	

Inorganic Products of the Reduction of Styrene Dibromide

Styrene dibromide (0.0495 g, 0.188 millimoles) in excess, was reduced in 6 ml of methanol by 0.6 ml of chromium(II) perchlorate (0.24 millimoles). The reduction products gave a spectrum in the visible region with a maximum absorption at 622 mμ, showing the presence of 100% $Cr(H_2O)_5Br^{++}$.

Kinetics of the Reduction of Meso-2,3-Dibromobutane

Water (15 ml), and t-butanol (30 ml) were placed in a 250 ml distilling flask immersed in a constant temperature bath at 20°. Nitrogen was passed over the solution by a connection attached to the side arm, and also into the solution by a second connection inserted through the neck of the flask, in order to remove all oxygen. To this oxygen-free solution, 15 ml of chromium(II) perchlorate (0.15M approximately) was added under nitrogen, and the solution was allowed to stand for a period of fifteen minutes, to reach the equilibrium temperature. The solution was kept under an atmosphere of oxygen-free nitrogen at all times.

A one ml sample of the solution was pipetted up under nitrogen, and was transferred, under nitrogen, to an oxygen-free solution of excess ferric ammonium sulfate. The ferrous ion formed was titrated against standard potassium dichromate solution, using diphenylamine as indicator, in

the presence of a few drops of phosphoric acid, to obtain a sharp end-point.

The excess amount of dibromide to be added was calculated on the concentration of chromous ion present. The dibromide was added under nitrogen, and a slow stream of nitrogen was bubbled through the solution for a few seconds to effect stirring and to insure the homogeneity of the solution. Five ml samples of solution were removed at various time intervals, and the normality of the unreacted chromous ion was obtained.

A second order plot of $\log \frac{b-x}{a-x}$ against time was linear, and the rate constant was calculated from the equation

$$k = \frac{2.3}{t(b-a)} \log \frac{a}{b} \frac{b-x}{a-x}$$

where a = initial concentration of chromous ion in moles per litre

$b = 4a$ = initial concentration of 2,3-dibromobutane in moles per litre

$a-x$ = concentration of chromous ion at time "t"

$b-x$ = concentration of dibromide at time "t"

A sample calculation is shown in Table IX, as well as a plot of $\log \frac{b-x}{a-x}$ vs. "t", in Figure 3.

TABLE IX

Determination of the Second Order Rate Constant For the Reduction of Meso-2,3-Dibromobutane, in Four-fold Excess, by Chromium(II) Perchlorate, in 50% t-Butanol-water

$a = 0.0374$ mole litre^{-1}, $b = 0.1496$ mole litre^{-1}, $\frac{a}{b} = \frac{1}{4}$

t min	a-x mole litre^{-1}	x mole litre^{-1}	b-x mole litre^{-1}	$\log \frac{b-x}{a-x}$	$\frac{2.3}{b-a} \log \frac{a}{b} \frac{(b-x)}{(a-x)}$ mole^{-1} litre	k litre mole^{-1} sec^{-1}
0	0.0374	0	0.1496	0.603	0	
12.5	0.0290	0.0084	0.1412	0.688	1.74	0.00232
28	0.0214	0.0160	0.1336	0.796	3.97	0.00234
38	0.0175	0.0199	0.1297	0.871	5.50	0.00241
49	0.0138	0.0237	0.1259	0.960	7.34	0.00248
61	0.0120	0.0254	0.1242	1.015	8.47	0.00231
73	0.0092	0.0282	0.1214	1.122	10.60	0.00246
86	0.0074	0.0300	0.1196	1.209	12.45	0.00242
104	0.0051	0.0323	0.1173	1.360	15.50	0.00248
120	0.0040	0.0334	0.1162	1.465	17.70	0.00246
					k average	0.00241

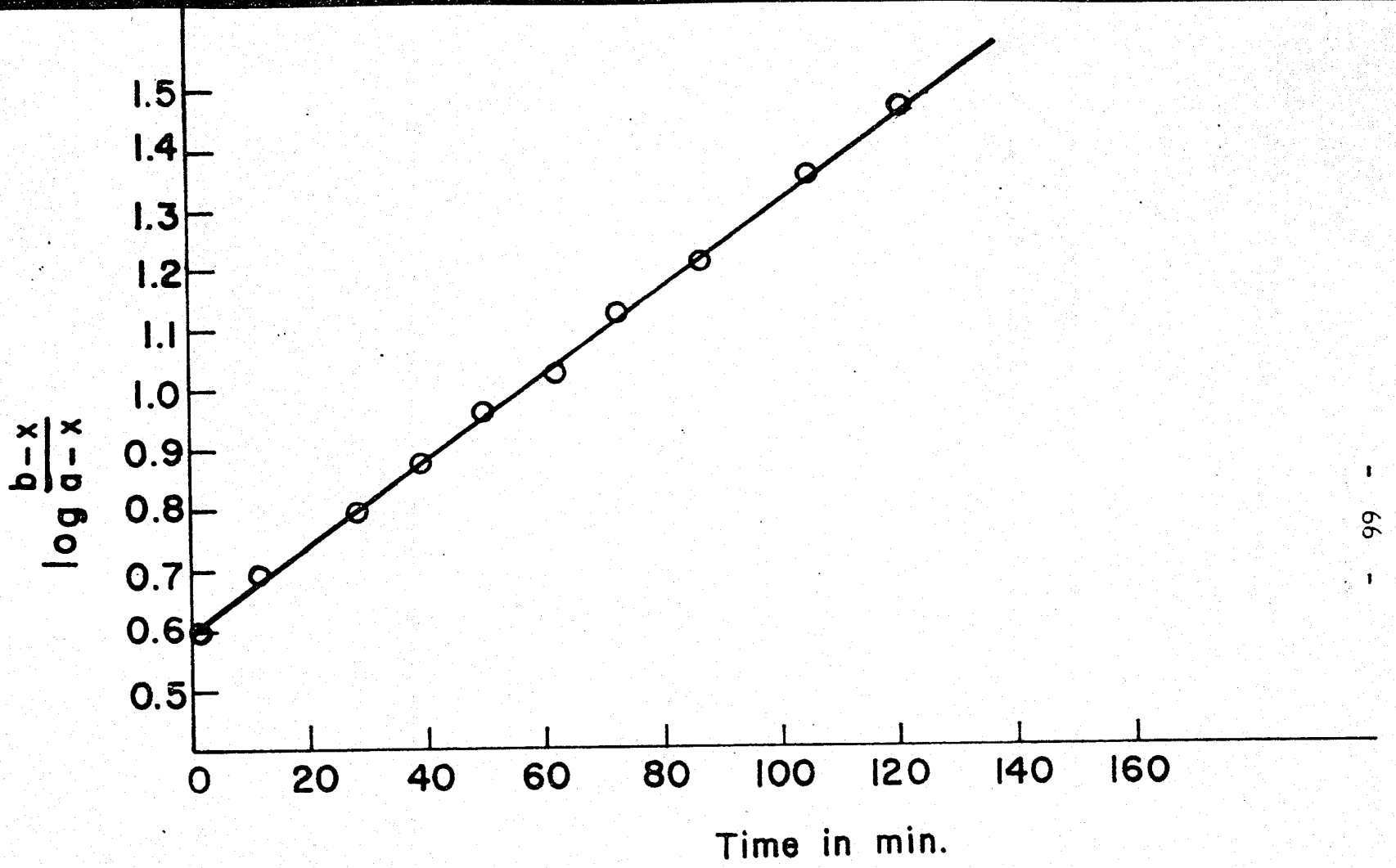


Fig. 3 Second order plot of the reduction of meso-2,3-dibromobutane, in four-fold excess, by chromous ion, at 20°, in 50% t-butanol-water.

Rate Determination Studies on the Reduction of Meso-2,3-Dibromobutane by Chromium(II) Perchlorate

Meso-2,3-dibromobutane was reduced as previously described, in sixteen-fold, eight-fold, four-fold, two-fold excess, and in equivalent amount, by chromium(II) perchlorate in 50% t-butanol-water at 20°.

These same quantities of meso-2,3-dibromobutane were also reduced using 75% t-butanol-water as solvent. These reactions were found to follow second order kinetics.

Reduction, in 50% t-butanol-water, of an eight-fold excess of meso-2,3-dibromobutane, in the presence of an eight-fold excess of 1,4-dibromobutane, which is unreduced by chromous ion, was found to be second order, as was the reduction of a four-fold excess of meso-2,3-dibromobutane in 0.5M sodium chloride.

The calculated rate constants for these reductions are presented in Table X.

The reaction mixtures from the reduction of meso-2,3-dibromobutane, containing a sixteen-fold and eight-fold excess of dibromide, were each extracted with ether, and the ether extracts washed with water and dried over anhydrous magnesium sulfate. The ether was removed under vacuum, and the dibromide residues were distilled.

Infrared spectra of the two samples, run as a liquid film, showed only meso-2,3-dibromobutane to be present.

TABLE X

Rate Constants Calculated for the Reduction of Meso-2,3-Dibromobutane at 20° by Chromium(II) Perchlorate

Molar Proportion of Dibromobutane per Two Moles of Chromium(II) Ion	In 50% t-butanol k in $mole^{-1}$ $litre\ sec^{-1}$	In 75% t-butanol k in $mole^{-1}$ $litre\ sec^{-1}$
1	0.00339	0.00359
2	0.00282	0.00334
4	0.00242	0.00325
8	0.00217	0.00294
16	0.00142	0.00228
4 (in 0.5N NaBr)	0.00183	
8 + 8-fold excess of 1,4-dibromobutane	0.00140	

Kinetics of the Reduction of Racemic 2,3-Dibromobutane.

Rate studies were carried out for racemic 2,3-dibromobutane, in a manner similar to that for meso-2,3-dibromobutane. The reactions were found to follow second order kinetics, and the calculated rate constants for the reduction, at different concentrations of dibromide, are presented in Table XI.

TABLE XI

Rate Constants for the Reduction of Racemic 2,3-Dibromobutane in 50% t-Butanol-water at 20°C

Molar Proportion of Dibromobutane per Two Moles of Chromium(II) Ion	k mole^{-1} litre sec^{-1}
1	0.00110
2	0.00156
4	0.00130
8	0.00102
16	0.00087

The reaction mixture from the reduction containing a sixteen-fold excess of racemic 2,3-dibromobutane, was extracted with ether, and the ether extract was washed with water and dried. The ether was removed under vacuum, and the organic residue was distilled.

An infrared spectrum taken on the recovered dibromobutane, run as a liquid film, showed only racemic 2,3-dibromobutane to be present.

Rate Determination for the Reduction of 1,2-Dibromo-2-Methylpropane by Chromium(II) Perchlorate

Reduction of 1,2-dibromo-2-methylpropane in 50% t-butanol-water, at 20°, using a two-fold excess of dibromide, was carried out in a manner similar to that of meso-2,3-dibromobutane.

The reaction was found to be second order, and the calculated value of the rate constant for the reaction was found to be

$$k = 0.0236 \text{ mole}^{-1} \text{ litre sec}^{-1}.$$

DISCUSSION

A REDUCTION OF α-HALOKETONES

Phenacyl chloride was found to be reduced readily by chromium(II) perchlorate in a number of solvents, the reaction time being of the order of a few minutes.

When phenacyl chloride was reacted with chromium(II) perchlorate in methanolic solution, the expected product, acetophenone, was found not to be the sole organic product of the reaction. This became apparent when the 2,4-dinitrophenylhydrazone derivative of the reaction products was prepared. This derivative was found to have a melting point of 178-180°, well below the melting point of acetophenone DNP*, which is reported in the literature as 250° [33].

The DNP derivative of the reaction products was therefore chromatographed on alumina, and gave two main fractions. The first fraction eluted, was recrystallized from methanol, and had a melting point of 250°. A mixed melting point of this fraction with known acetophenone DNP was also 250°.

The identity of the second fraction proved more difficult to establish. The melting point of this fraction, after recrystallization from methanol, was 200-202°.

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* The 2,4-dinitrophenylhydrazone derivatives of the ketonic products are designated by the name of the ketone followed by DNP, the abbreviated form of 2,4-dinitrophenylhydrazone.

Phenacyl chloride was again reduced in methanol, and the reduction products were extracted into ether. After removal of the ether, an NMR spectrum of the reduction products was run in carbon tetrachloride solution containing 1% tetramethylsilane.

The spectrum showed three major peaks, in addition to those of the aromatic ring systems. One peak was identified as the methyl group of acetophenone, and had a τ value of 7.50. The two other peaks had τ values of 5.60 and 6.70.

A possible compound possessing the above requirements was ω-methoxyacetophenone. A calculated carbon-hydrogen content of the DNP derivative of this substance was almost identical with that for fraction II, and the melting point of ω-methoxyacetophenone DNP is reported in the literature[34] as 192-194°, after recrystallization from ethanol-ethyl acetate.

A sample of ω-methoxyacetophenone was prepared according to the method of Newman and Beal[42], by the reaction of diazoacetophenone with methanol in the presence of a small amount of boron trifluoride, and was converted directly to the 2,4-dinitrophenylhydrazone.

The DNP derivative was purified by chromatography on alumina, and after recrystallization from methanol, had a melting point of 200-202°. A mixed melting point of known ω-methoxyacetophenone DNP with fraction II was also 200-202°.

Infrared spectra of known ω-methoxyacetophenone DNP and of fraction II, taken as a Nujol mull, were identical.

ω-Methoxyacetophenone was again prepared by the method of Newman and Beal; The product was purified by distillation, and gave a main fraction of constant boiling point 110° at 10 mm. An NMR spectrum of this distillate, in carbon tetrachloride containing 1% tetramethylsilane, (Figure 4), showed several peaks in addition to those expected of ω-methoxyacetophenone. The τ values of these additional peaks, excluding those of the aromatic ring systems, were 6.50, 6.88 and 6.98. The impurities in this constant boiling fraction were not identified. An NMR spectrum of methyl phenylacetate, a possible contaminent, had two bands, excluding those due to the aromatic ring, with τ values of 6.73 and 6.80, and was therefore not an impurity in the above mixture.

Another sample of ω-methoxyacetophenone was prepared according to the method of Kaelin[43], by the chromic acid oxidation of methoxymethylphenylcarbinol. An NMR spectrum of the distilled product showed two main peaks, in addition to those of the aromatic ring system. The two bands, having intensities in the rough proportion of two to three, had τ values of 5.60 and 6.70 respectively, identical in position and relative intensity to those of the reduction products of phenacyl chloride. These two bands, with τ values of 5.60 and 6.70, were due to the methylene group and the

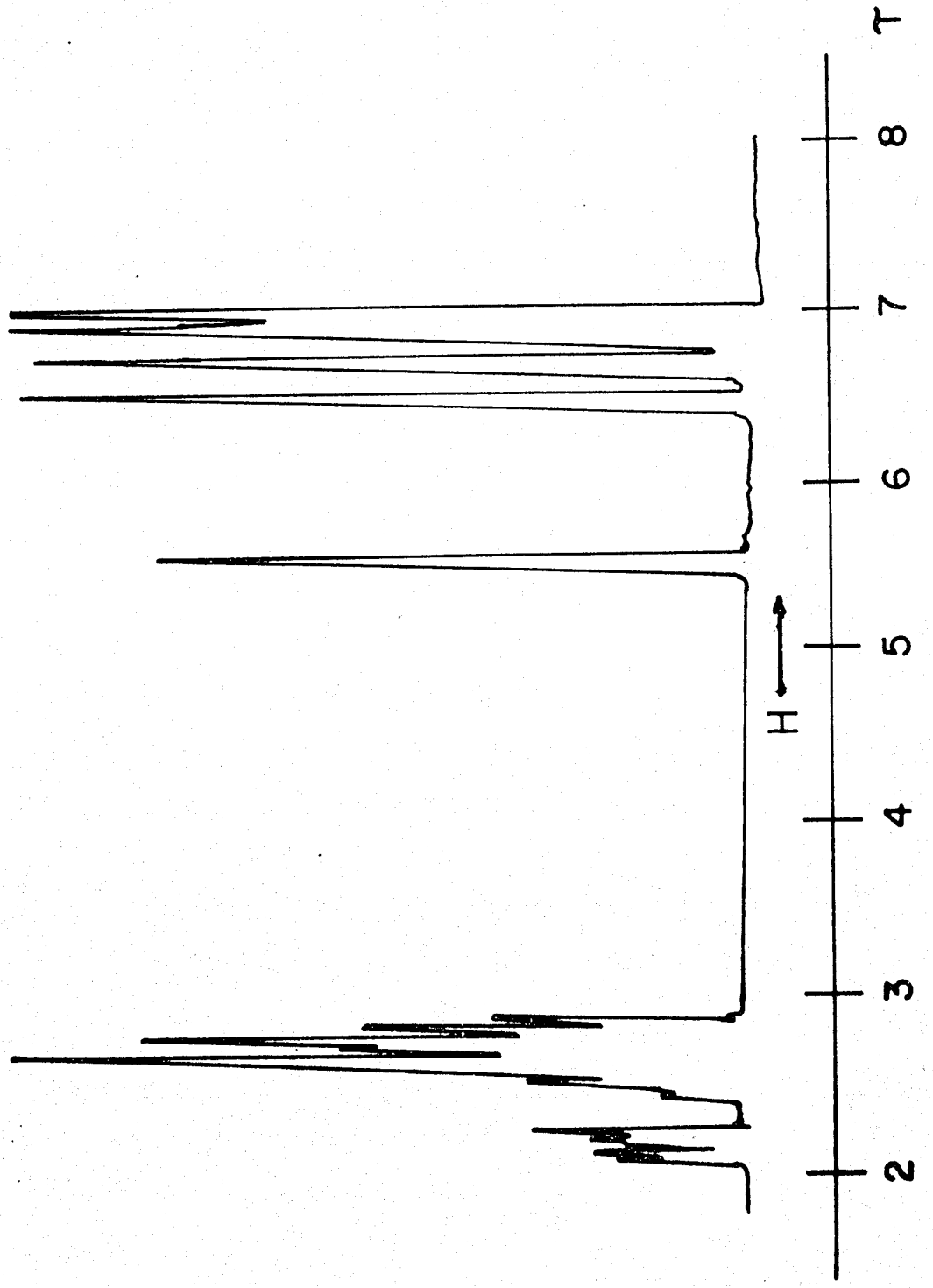


Fig. 4 NMR spectrum of impure ω-methoxyacetophenone, prepared by the method of Newman and Beal.

methoxyl group of ω-methoxyacetophenone, respectively.

The two main products of the reaction of phenacyl chloride, with chromium(II) perchlorate in the presence of methanol, were therefore, acetophenone and ω-methoxyacetophenone.

A study of the reaction conditions under which these substances were formed was undertaken, and it was found that by varying certain of these conditions, different ratios of the two products could be obtained.

When phenacyl chloride was reacted with a three-fold excess of chromium(II) perchlorate, in a small amount of methanol, and the solution stoppered under nitrogen overnight, the yield of acetophenone was 38%, and that of ω-methoxyacetophenone was 48%. If the time of reaction, at these concentrations, was shortened to three minutes, acetophenone was obtained in 38% yield and ω-methoxyacetophenone in 42% yield. If only a 10% excess of chromium(II) perchlorate was used, acetophenone was formed in 30% yield, and ω-methoxyacetophenone in 45% yield.

In these reactions, only small changes in the relative yields of the two products were observed, and these differences are probably not significant. However, when phenacyl chloride reacted with 150% excess of chromium(II) perchlorate in a large volume of methanol, a significant change in the relative yields was observed, that of acetophenone decreasing to 11%, and that of ω-methoxyacetophenone increasing

to 55%. If, on the other hand, phenacyl chloride was reduced in a methanolic solution containing a high concentration of perchloric or hydrochloric acid, acetophenone was formed in over eighty-five per cent yield, along with trace quantities of ω-methoxyacetophenone.

When phenacyl chloride was reduced in ethanol and t-butanol, the DNP derivatives of the reduction products had melting points of 245-248°, indicating, that although mixed with impurities, acetophenone was the main product of the reaction. The reduction of phenacyl chloride in acetone gave only acetophenone, identified as its DNP derivative.

It would appear therefore, that when the reaction of phenacyl chloride with chromium(II) perchlorate is carried out in methanolic solution, increased acidity favors the formation of acetophenone, whereas decreased acidity favors the formation of ω-methoxyacetophenone.

ω-Methoxyacetophenone is, in fact, a product of the solvolysis of phenacyl chloride in methanol. However, since phenacyl chloride is known to be resistant to solvolysis in acidic methanol, a simple solvolysis mechanism for the formation of ω-methoxyacetophenone must be excluded, as the solutions, after reduction, were found to have pH values very close to one. It would therefore appear that chromous ion acts as a catalyst in the solvolysis of phenacyl chloride under these conditions.

Evans[22] has proposed a mechanism for the reduction of α-bromoketones by chromous ion, which involves a two-electron transfer process, yielding a chromium(IV) species after reaction.

$$Cr^{++} + Br\text{-}\overset{|}{C}H\text{-}\overset{|}{C}{=}O + H^{+} \longrightarrow [CrBr]^{+++} + -CH{=}\overset{|}{C}\text{-}OH$$

According to the recent work of Ardon and Plane[9], it is proposed that such a chromium(IV) species, if formed, would react with chromous ion, to yield a dinuclear chromium species.

In the above reactions of chromium(II) with phenacyl chloride, chromatography of the inorganic products showed only the presence of $Cr(H_2O)_6^{+++}$ ion and $Cr(H_2O)_5Cl^{++}$ ion. No dinuclear species was formed. It would appear, therefore, if these assumptions are correct, that the reduction of phenacyl chloride, by chromous ion, occurs by a one-electron transfer process, rather than by a process involving the simultaneous transfer of two electrons.

When phenacyl chloride was reduced in ethanol or t-butanol, acetophenone was found to be the main product of the reaction. This is not unexpected, since the greater size of these two molecules would hinder their ability to complex with chromium(II) in the manner suggested for methanol.

It was also found that when phenacyl chloride was reacted with chromous ion in ethanol at 0°, the solution became yellow in color, indicating the possible presence of an organochromium ion. This reaction was not investigated further, as the ion formed was unstable.

In order to ascertain whether other cations could catalyse the solvolyses of phenacyl chloride in methanol, experiments employing a series of cations were performed in methanol, both in the presence and in the absence of dilute perchloric acid. The cations used in this study were Cu^{++}, Fe^{++}, Mn^{++}, Co^{++}, Cd^{++}, Ni^{++}, UO_2^{++}, Fe^{+++}, Zn^{++}, Cr^{+++}, Y^{+++} and ZrO^{++}. The solutions were allowed to stand for a period of twenty-four hours, after which time, the sharp odor of phenacyl chloride remained, and tests for the presence of halide ion, using silver nitrate, were negative.

In order to determine whether the reaction to form an α-ketoether was a property peculiar to aromatic α-ketohalides, the reduction of chloroacetone was studied. The reduction was performed in a large excess of methanol. After a twenty-four hour period, the excess methanol was removed under vacuum, and presumably, any acetone formed in the reduction, would also have been removed at this time. The DNP derivative of the organic residue, obtained in 27% yield, had a melting point of 160°, very close to that of ω-methoxyacetone DNP, reported in the literature as

160-163° [35], and well above that of acetone DNP, m.p. 128° [36]. Chloroacetone had also been found to be resistant to solvolysis in acidic methanol, and therefore, any ω-methoxyacetone formed in the reaction could not be accounted for by a simple solvolysis process.

It was therefore established by analogy that in the aliphatic series, as well as in the aromatic series, α-haloketones react with chromium(II) perchlorate, in the presence of methanol, to give the respective ω-methoxy derivative of the parent ketone, as well as the parent ketone, under certain reaction conditions.

When phenacyl chloride, phenacyl bromide and chloroacetone reacted with chromium(II) perchlorate, the α-haloketones being in excess, the only inorganic products formed were the hexaaquochromium(III) ion and the monohalochromium(III) ion. No dinuclear species was formed in the reduction.

Reaction of phenacyl chloride (in excess), with chromium(II), in methanol, ethanol and acetone, gave approximately the same ratio of the inorganic products, 30% of the hexaaquochromium(III) ion, and 70% of the monochlorochromium(III) ion. When phenacyl chloride was reduced in t-butanol, a 50% mixture of the two ions was formed, and when 50% methanol-water was used as solvent, 75% $Cr(H_2O)_6^{+++}$ was formed, together with 25% $Cr(H_2O)_5Cl^{++}$ ion.

The same trend occurred also in the reaction of phenacyl bromide and chloroacetone with chromium(II). Reaction of phenacyl bromide (in excess), with chromium(II) in methanol, ethanol cr acetone, yielded 60% $Cr(H_2O)_6^{+++}$ and 40% $Cr(H_2O)_5Br^{++}$. Reduction in t-butanol gave 70% $Cr(H_2O)_6^{+++}$ and 30% $Cr(H_2O)_5Br^{++}$, and in 50% methanol-water, gave 80% $Cr(H_2O)_6^{+++}$ and 20% $Cr(H_2O)_5Br^{++}$.

Similarly, when chloroacetone (in excess) was reacted with chromium(II) in methanol, ethanol or acetone, approximately 46% $Cr(H_2O)_6^{+++}$ was formed together with 54% $Cr(H_2O)Cl^{++}$. In t-butanol and in 50% methanol-water, approximately 65% $Cr(H_2O)_6^{+++}$ was formed, together with 35% $Cr(H_2O)_5Cl^{++}$ ion.

The percentage composition of the two ions $Cr(H_2O)_6^{+++}$ and $Cr(H_2O)_5X^{++}$, where X is halogen, was calculated from the visible spectra of the solutions, obtained after the reaction of the α-haloketones (in excess) with chromous ion. The results of these calculations are not extremely accurate, as the spectra of these two ions are rather similar, λ_{max} for $Cr(H_2O)_6^{+++}$ being 575 mμ, and that for $Cr(H_2O)_5X^{++}$ being 605 mμ and 622 mμ, where X is Cl and Br, respectively.

Although no simple explanation for these observed results can be put forward, they are however significant, insofar as they were found to be reproducible.

B REDUCTION OF HALOMETHANES

In reductions employing chromous ion as the reducing agent, the inorganic products of the reaction, as well as the reducing agent itself, are highly colored. This factor is useful in qualitatively determining the nature, as well as the extent, of the reaction.

Chromous ion itself is clear blue in color. In the reduction of organic halogen compounds by chromous ion, four chromium containing species may be formed as reaction products. These include the hexaaquochromium(III) ion, blue-violet, the monohalopentaaquochromium(III) ion, green-yellow, a dinuclear chromium species, gray-green in color, and an organochromium(III) ion, varying in color from red to yellow. Solutions containing mixtures of these ions have their own distinctive colors, but in general, a deep red or yellow coloration, is indicative of the presence of an organochromium ion.

It has been found[24] that in the reaction of chloromethanes and of substituted chloromethanes with chromium(II) perchlorate, 1,1,1-trichloromethane, carbon tetrachloride and chloroform are reduced by chromous ion to yield deep red solutions, whereas methylene chloride and methyl chloride are not reduced. While 1,1,1-trichloroethane and carbon tetrachloride reduce in a matter of seconds, the

organochromium ions formed are not stable, and decomposition takes place after a few minutes, yielding a green-blue solution.

However, the pure organochromium ion isolated from the chloroform reduction is stable and was assigned the structure $Cr(H_2O)_5CHCl_2^{++}$ [25].

When the reduction reactions of the iodomethanes with chromium(II) perchlorate were studied, it was found that both iodoform and methylene iodide were reduced to form organochromium ions, whereas methyl iodide did not react. However, unlike the organochromium ion formed from chloroform, that formed from iodoform was unstable, and decomposed in a matter of a few minutes.

When methylene iodide reacted with chromous ion in methanol, reduction took place after a few hours, and the solution obtained varied in color from green-red to red-blue, depending upon the length of time allowed for the reduction.

The solution of the reduction products of methylene iodide was chromatographed on Dowex 50 cation exchange resin. Perchloric acid (1M) was used as eluent, and a first fraction, green-red in color, was eluted as a sharp band, moving with the solvent front.

The next fraction eluted contained traces of the ion $Cr(H_2O)_5I^{++}$, and was followed by a fraction, also eluted

with 1M perchloric acid, yellow-red in color, containing the organochromium ion $Cr(H_2O)_5CH_2I^{++}$. The fact that this ion was easily eluted with 1M perchloric acid suggests that it possesses two positive charges, as King and Dismukes[26] have found that the minimum concentrations of perchloric acid required to easily elute chromium species of charges +1, +2 and +3 from Dowex 50 resin are 0.1M, 1M and 5M respectively.

The ion was analysed for chromium and iodine, and the Cr:I ratio was very close to 1:1. The ion was found to be stable for several hours at room temperature in the presence of oxygen, and for several months at 0°.

These properties of the ion suggest that it is an octahedral complex of chromium(III), having a structure of the type $Cr(H_2O)_5CH_2I^{++}$, analogous to those of the two ions $Cr(H_2O)_5CHCl_2^{++}$ and $Cr(H_2O)_5CH_2Ph^{++}$, which had been previously investigated[24,25]. The stability of the organochromium ion is due to the substitution-inertness of chromium(III) complexes[10]. This organochromium ion, as well as others formed in methanolic solution, may contain methanol in the coordination sphere of chromium ion. This factor may be of importance in the reaction of methylene iodide with chromous ion, since it was found that the reaction to yield the stable organochromium occurs readily in methanol, but does not take place if water is used as solvent.

When the reaction time of methylene iodide with chromous ion was three hours, three chromium containing fractions were obtained. Fraction I, a green-red solution contained 40% of the total chromium, and fraction II, the organochromium ion $Cr(H_2O)_5CH_2I^{++}$, contained 15% of the total chromium. The remainder of the total chromium 45%, was in the form of the hexaaquochromium(III) ion. If the reaction time was increased to fifteen hours, these same three chromium containing fractions were obtained, but the chromium content of each differed from those values obtained after the shorter reaction time. Fraction I contained only 10% of the total chromium, and fraction II, consisting of the stable organochromium ion $Cr(H_2O)_5CH_2I^{++}$, contained 25% of the total chromium. The remaining chromium, 65%, was in the form of the hexaaquochromium(III) ion. No dinuclear chromium species was formed in either reaction.

The organochromium ion obtained in the first fraction eluted was very unstable. Although a study of the nature of this ion was not undertaken, it is thought to be an intermediate species, which on decomposition, yields the more stable, 'normal', organochromium ion. This is supported by the fact that as the chromium concentration if this fraction decreases, the yield of the stable organochromium ion increases. This complex is thought to consist of chromium bonded to the halogen and the organic fragment, as

the rapidity with which it is eluted from Dowex resin with 1M perchloric acid, strongly suggests that it possesses only one positive charge. The visible spectrum of this solution showed positions of maximum absorption at 644 mμ and 523 mμ, similar to those of the monohalohexaaquochromium(III) and the stable organochromium ion respectively. This chromium species is not formed in the reaction of halomethanes with chromous ion in aqueous solution. However, when methanol is used as solvent, this ion is formed. The possible complexing of the chromium with the methanol of the solvent may also play a role in the formation of this species.

In the reduction of chloroform by chromous ion in aqueous solution, the reaction was postulated to go by a one-electron process according to the following mechanism:

$$CHCl_3 + Cr^{++} + 5H_2O \xrightarrow{\text{slow}} Cr(H_2O)_5Cl^{++} + \cdot CHCl_2$$

$$\cdot CHCl_2 + Cr^{++} + 5H_2O \xrightarrow{\text{fast}} Cr(H_2O)_5CHCl_2^{++}$$

This mechanism would require that the kinetics of the reaction be second order, the rate of the reaction depending upon the concentration of both chloroform and chromous ion. This was indeed found to be the case in the present investigation, when chloroform was reduced by chromium(II) perchlorate in 50% t-butanol-water as solvent.

Since no dinuclear species is formed the reduction of methylene iodide, it may be assumed that a similar type of one-electron process might occur. Such a process would require that the chromium be equally divided between the two ions $Cr(H_2O)_5CH_2I^{++}$ and $Cr(H_2O)_5I^{++}$. Because of the instability of the $Cr(H_2O)_5I^{++}$ ion[3], it would be expected for it to dissociate into $Cr(H_2O)_6^{+++}$ and I^-, thus accounting for the presence of $Cr(H_2O)_6^{+++}$ ion in the solution. The hexaaquochromium(III) ion might also be formed by the partial decomposition of the organochromium ion, which would perhaps be less stable in methanolic solution, than in an aqueous solution of 1M perchloric acid.

Iodomethylpentaaquochromium(III) ion was found not to react with silver nitrate in the cold, but on heating, or after standing for several days at room temperature, iodide ion was liberated. The organochromium ion did not react with mercuric chloride in the cold, but on heating, mercurous chloride was formed. Attempts to obtain methylpentaaquochromium(III), by the catalytic hydrogenation of iodomethylpentaaquochromium(III) were unsuccessful.

In the reaction of the bromomethanes with chromous ion in methanol, it was found that, both bromoform and methylene bromide were reduced to give stable organochromium ions. Methyl bromide, however, was not reduced.

The organochromium ion, formed from bromoform, was found to have a Cr:Br ratio of 1:2, and is analogous to the $Cr(H_2O)_5CHCl_2^{++}$ ion, having the structure $Cr(H_2O)_5CHBr_2^{++}$.

If the reaction time of bromoform with chromous ion was one-half hour, four chromium containing species were obtained, after chromatographing the reduction products on Dowex resin, using 1M perchloric acid as eluent. A first red-green fraction, containing 20% of the total chromium, was eluted as a sharp band moving with the solvent front. The second fraction, clear green-yellow in color, was identified as the ion $Cr(H_2O)_5Br^{++}$, and contained 30% of the total chromium. The third fraction, yellow-red in color, was shown to consist of the organochromium ion $Cr(H_2O)_5CHBr_2^{++}$, and contained 15% of the total chromium. The remainder of the chromium, 35%, was in the form of the hexaaquochromium(III) ion.

If the reaction time was lengthened to fifteen hours, only three chromium containing species were obtained. The first fraction consisted of the $Cr(H_2O)_5Br^{++}$ ion, and contained 35% of the total chromium. The second fraction consisted of the organochromium ion, and also contained 35% of the total chromium. The remainder of the chromium, 30%, was in the form of the hexaaquochromium(III) ion.

The reason for these anomalous results is not known.

The organochromium ion formed in the reduction of methylene bromide with chromous ion, is analogous to the reduction product of methylene iodide, having the structure $Cr(H_2O)_5CH_2Br^{++}$.

The reduction of methylene bromide appeared to take place more slowly than that of methylene iodide. After a reaction time of twenty hours, the reduction products of methylene bromide were chromatographed, and three chromium containing species were obtained. The first two fractions, consisting of the ions $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_5CH_2Br^{++}$, each contained 30% of the total chromium. The remaining chromium, 40%, was in the form of the hexaaquochromium(III) ion.

The reduction of several halomethanes, containing both bromine and chlorine, was investigated. The halomethanes studied were bromotrichloromethane, dibromochloromethane, bromidichloromethane, and bromochloromethane. Bromochloromethane was not reduced by chromous ion. Bromotrichloromethane was reduced quickly, but the organochromium ion formed on reduction was unstable, and decomposed within a very short time. Chromatography of this solution, after decomposition had taken place, gave only two chromium containing species, $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_6^{+++}$. No $Cr(H_2O)_5Cl^{++}$ was formed.

Dibromochloromethane gave a stable organochromium ion on reduction. This ion was found to have a chromium to halogen ratio of one to two, where the halogen was an equimolecular mixture of chlorine and bromine. The structure of the organochromium ion was, therefore, $Cr(H_2O)_5CHBrCl^{++}$. Monobromopentaaquochromium(III) was also formed in this reduction, but no $Cr(H_2O)_5Cl^{++}$ was obtained.

Bromodichloromethane also gave a stable organochromium ion on reduction, identical with that obtained in the reduction of chloroform, together with $Cr(H_2O)_5Br^{++}$ as the only monohalopentaaquochromium(III) species. No $Cr(H_2O)_5Cl^{++}$ was formed in the reduction.

It would appear, therefore, that in the reduction of these halomethanes, attack of the chromous ion takes place preferentially at a bromine atom, rather than at a chlorine atom, when both are present.

The molar extinction coefficients of the stable organochromium ions, obtained in the reduction of the various halomethanes, taken at the positions of maximum absorption, are presented in Table IV.

For the organochromium ions formed in the reduction of the trihalomethanes, it was found that the position of maximum absorption shifts to shorter wavelengths, and the molar extinction coefficients, at these positions of maximum absorption, decrease in the order

$$Cr(H_2O)_5CHBr_2^{++} > Cr(H_2O)_5CHBrCl^{++} > Cr(H_2O)_5CHCl_2^{++}.$$

For the organochromium ions, formed in the reduction of dihalomethanes, it was found that the positions of maximum absorption for the ion $Cr(H_2O)_5CH_2I^{++}$ are at longer wavelengths than those of the $Cr(H_2O)_5CH_2Br^{++}$ ion, and the molar extinction coefficients at the positions of maximum absorption are greater for the iodomethylpentaaquochromium(III) ion than for the bromomethylpentaaquochromium(III) ion.

This relationship of the organochromium ions is not unexpected, for it is known that the positions of maximum absorption shift to shorter wavelengths, and the molar extinction coefficients, at these positions of maximum absorption, decrease in the order

$$Cr(H_2O)_5I^{++} > Cr(H_2O)_5Br^{++} > Cr(H_2O)_5Cl^{++}.$$

C REDUCTION OF VICINAL HALIDES

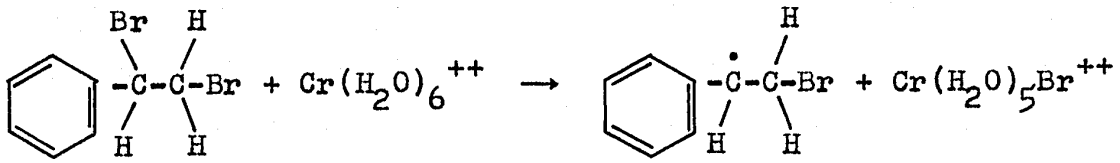
Although chromous ion has not been used very extensively as a reducing agent, in organic chemistry, it has been reported[21] that chromous ion does reduce vicinal halides to yield the olefin.

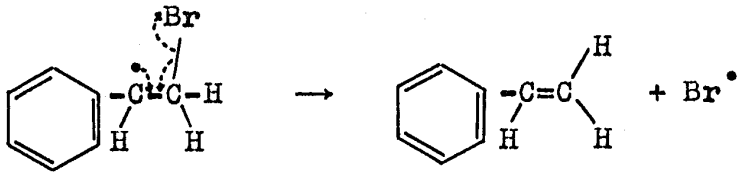
The reduction of a series of substituted dibromoethanes by chromium(II) perchlorate has been the subject of the present work. Among the compounds studied have been 1,2-dibromoethane, 1,2-dibromopropane, 1,2-dibromo-2-methylpropane, sym-tetrabromoethane, meso- and racemic 2,3-dibromobutane, 2-methyl-2,3-dibromobutane, 2,3-dimethyl-2,3-dibromobutane, and styrene dibromide. The reduction of 1,2-dibromoethane and 1,2-dibromopropane took place very slowly, and was found to be incomplete under the imposed reaction conditions. The remaining substituted dibromoethanes were reduced by chromous ion within a reasonable length of time, and the reduction of styrene dibromide, meso- and racemic 2,3-dibromobutane was studied in some detail.

Styrene dibromide was found to reduce very quickly in methanolic solution to yield styrene as the only organic product of the reduction, and the $Cr(H_2O)_5Br^{++}$ ion as the only inorganic product.

A possible mechanism for this reduction would consist in the abstraction of a bromine atom from the

styrene dibromide molecule by a chromous ion, followed by the elimination of the second bromine atom.





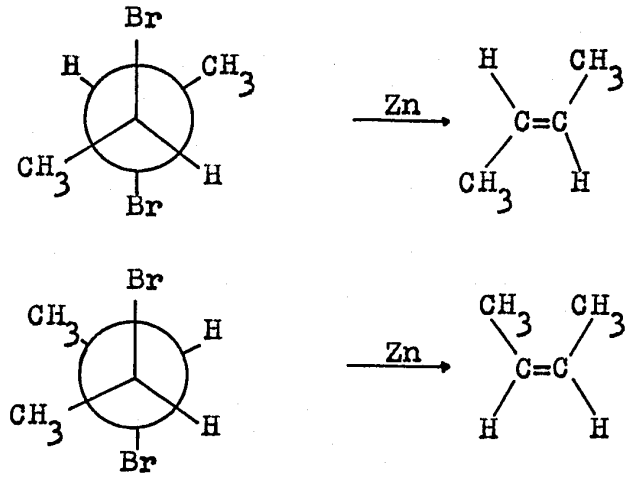
$$Cr(H_2O)_6^{++} + Br^{\bullet} \longrightarrow Cr(H_2O)_5Br^{++} + H_2O$$

It is possible that the first and second step may take place simultaneously, as a concerted process.

This mechanism explains especially well the observed fact that all of the chromium after reduction is found complexed to bromine in the form of bromopentaaquochromium(III) perchlorate, and that styrene is the only organic product of the reduction.

Although it is known that chromous ion reduces vicinal organic halogen compounds to yield the respective olefins, the stereochemistry of such reactions has not been investigated in the past. This stereochemical question did, however, become of importance when the reduction of <u>meso</u>- and

racemic 2,3-dibromobutane was studied. It is known that the reduction of the 2,3-dibromobutanes with zinc in acid[44], is stereospecific, meso-2,3-dibromobutane yielding trans-2-butene, and racemic 2,3-dibromobutane yielding cis-2-butene, the removal of the bromine thus occurring via a trans elimination process.



The reduction of meso- and racemic 2,3-dibromobutane by chromium(II) perchlorate, was found to be non-stereospecific, mixtures of cis- and trans-2-butene being formed when either isomer of the 2,3-dibromobutanes was reduced. The relative ratios of cis- and trans-2-butene, formed as products of the reaction, were calculated from the vapor phase chromatograms.

When meso-2,3-dibromobutane was reduced by chromium(II) perchlorate, with either the dibromobutane or the chromous ion in excess, the reduction products were found

to consist of approximately 70% trans-2-butene and 30% cis-2-butene.

When racemic 2,3-dibromobutane was reduced with either the dibromobutane or chromous ion in excess, approximately 60% trans- and 40% cis-2-butene were obtained. However, if racemic 2,3-dibromobutane was reduced by chromous ion, and the gaseous products removed as quickly as possible, this mixture was found to consist of 60% cis-2-butene and 40% trans-2-butene.

When cis-2-butene was shaken with an aqueous ethanolic solution of chromous ion, no isomerization took place. However, when 1,2-dibromocyclohexane was reduced by chromous ion in the presence of pure cis-2-butene, isomerization took place, the recovered 2-butene consisting of 70% cis-2-butene and 30% trans-2-butene. If cis-2-butene was shaken with the reduction products of 1,2-dibromocyclohexane, after reduction had taken place, no isomerization occurred.

When meso- and racemic 2,3-dibromobutane in sixteen-fold excess, were reduced by chromous ion in 50% t-butanol-water as solvent, the recovered 2,3-dibromobutanes, from the reaction mixture, were found not to have undergone isomerization.

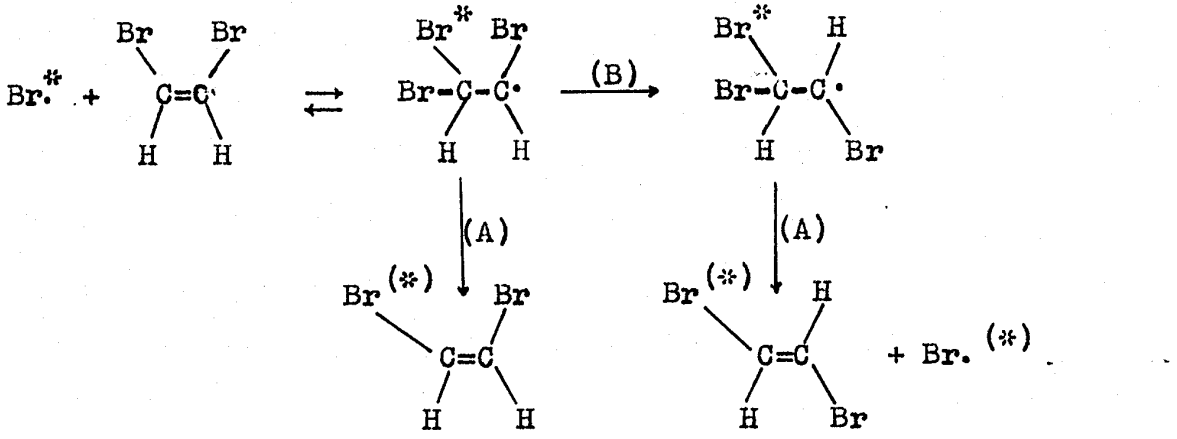
These results, involving the isomerization of the cis-2-butene, and the nonstereospecific reduction of the

2,3-dibromobutanes by chromous ion, strongly suggest the presence of a free radical intermediate, probably a bromine atom, formed during the reduction.

It is known that bromine atoms can cause isomerization of ethylene derivatives, and cases are known where such atoms are generated by way of oxidation-reduction processes[45].

It is possible that isomerization might occur by the reversible addition of a bromine atom to the double bond. The intermediate radical formed would then be free to undergo both inversion and rotation about the carbon-carbon bond. Loss of the halogen atom could then lead to either isomer.

The bromine catalysed isomerization of cis-dibromoethylene in carbon tetrachloride at 39.59°, was investigated by Noyes and Steinmetz[46]. Radioactive bromine was used, and bromine atoms were allowed to form by way of thermal decomposition of the bromine. The following mechanism has been proposed to explain isomerization arising from rotation about the carbon-carbon bond.



By measuring the relative rates of exchange and isomerization, they concluded that the rate constant for dissociation, process A, is about twice that for rotation, process B, but that the two processes have almost identical activation energies, of something greater than three kilocalories.

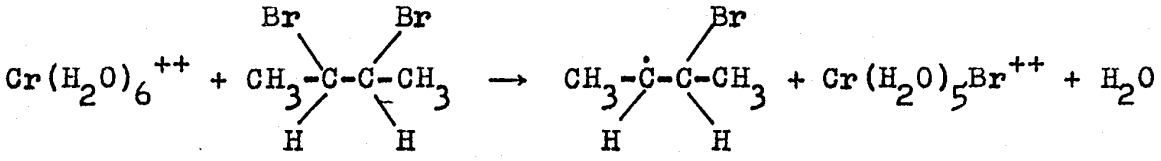
The kinetics of the reduction of meso- and racemic 2,3-dibromobutane by chromous ion at 20° were studied. The solvents used were 50% t-butanol-water and 75% t-butanol-water. These reductions were found to follow second order kinetics, good straight line plots being obtained. However, the calculated rate constants for these reactions, presented in Tables X and XI, show some discrepancy in different experiments, decreasing as the concentration of the dibromobutane is increased.

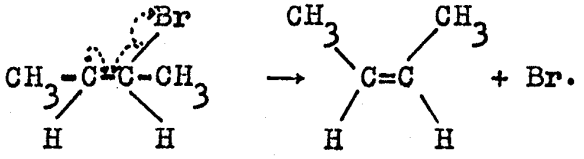
The reason for these anomalous results is not known. Kinetic studies involving chromous ion as one of the

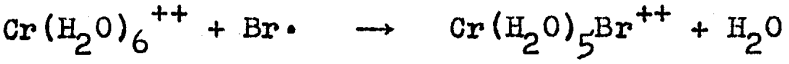
reactants, possess inherent difficulties, the major one being the affinity of this reagent for oxygen. Because of this property of chromous ion, it is necessary that all reactions be done in the presence of oxygen-free nitrogen. Although precautions were taken to insure the absence of oxygen during all stages of these kinetic studies, the possibility of contamination by atmospheric oxygen cannot be completely excluded.

The possibility of competing mechanisms in these reductions must also be considered. Reduction of the 2,3-dibromobutanes might conceivably occur by two mechanisms, a one-electron process, Mechanism A, or a two-electron process, Mechanism B.

Mechanism A

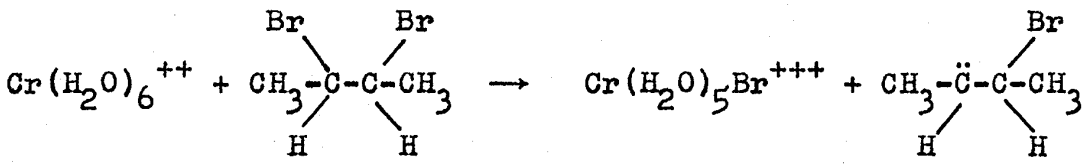


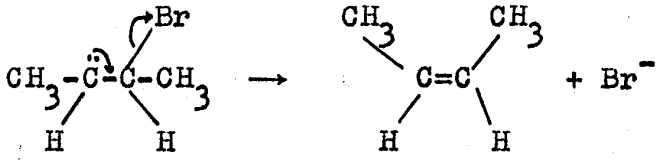




This mechanism would require that all the chromium be bonded to bromine in the form of the monobromohexaaquo-chromium(III) ion, after reduction. This is indeed found to be the case when either meso- or racemic 2,3-dibromobutane, in four-fold excess, is reduced in methanol.

Mechanism B





$$Cr(H_2O)_5Br^{+++} + H_2O \longrightarrow Cr(H_2O)_6^{++++} + Br^-$$

or

$$Cr(H_2O)_5Br^{+++} + Cr(H_2O)_6^{++} \longrightarrow Cr(H_2O)_6^{+++} + Cr(H_2O)_5Br^{++}$$

$$Cr(H_2O)_6^{++++} + Cr(H_2O)_6^{++} + H_2O \longrightarrow [(H_2O)_5Cr\text{-}O\text{-}Cr(H_2O)_5]^{++++} + 2H_3O^+$$

If the dissociation of the $Cr(H_2O)_5Br^{+++}$ complex were fast, the dinuclear chromium species would be the sole expected inorganic product of the reduction. If on the other hand, dissociation of this complex were slow, it could undergo reduction by chromous ion, yielding the $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_6^{+++}$ ions in equivalent amounts.

Neither of these two proposed mechanisms, however explains fully the observed results. The $Cr(H_2O)_6^{+++}$ ion, found as a product in these reactions, might conceivably be partially formed by the dissociation of the $Cr(H_2O)_5Br^{++}$ ion, since the stability of this latter ion, in the solvents used, is not known.

In the reduction of meso-2,3-dibromobutane in methanol, acetone and 50% t-butanol-water, it was found that $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_6^{+++}$ were the only products of the reduction. It was also found in these reductions, that as the concentration of the 2,3-dibromobutane was increased, the formation of the $Cr(H_2O)_5Br^{++}$ ion also increased. This same tendency was also found to occur in the reduction of 1,2-dibromo-2-methylpropane in acetone, and in the reduction of 2-methyl-2,3-dibromobutane in 50% t-butanol-water. It was also found that in the reactions of meso- and racemic 2,3-dibromobutane, as well as in those of the other substituted dibromoethanes, the yield of $Cr(H_2O)_6^{+++}$ ion was least

in methanol, greater in acetone, and largest in 50% t-butanol-water.

The reason for these variations is not known, but the possibility of the two competing mechanisms, including one and two-electron processes, cannot be excluded, if the latter mechanism gives rise to equivalent amounts of the two ions $Cr(H_2O)_5Br^{++}$ and $Cr(H_2O)_6^{+++}$.

Because of the reproducibility of these experimental values, any acceptable mechanism for the reduction of <u>meso</u>- and racemic 2,3-dibromobutane must include the explanation of all of these apparently anomalous results.

CLAIMS TO ORIGINAL RESEARCH

1. The reaction of phenacyl chloride with chromium(II) perchlorate was studied in some detail. The products of this reaction in methanol, were found to be ω-methoxyacetophenone and acetophenone.
2. Solvolysis of phenacyl chloride to yield ω-methoxy-acetophenone was favored in the presence of a large excess of methanol.
3. At high acid concentrations, reduction was favored, yielding acetophenone as product.
4. Reduction of phenacyl chloride in ethanol, acetone or t-butanol, gave acetophenone as the main product.
5. Chloroacetone reacted with chromium(II) perchlorate, in a large excess of methanol, to yield ω-methoxy-acetone.
6. A series of organochromium ions was prepared by the reduction of dihalo- and trihalomethanes, in methanol.
7. The ions prepared had the following probable structures:

   $Cr(H_2O)_5CH_2I^{++}$, $Cr(H_2O)_5CH_2Br^{++}$,

   $Cr(H_2O)_5CHBr_2^{++}$, $Cr(H_2O)_5CHBrCl^{++}$.

8. Reduction of a halomethane containing both bromine and chlorine, resulted in the removal of bromine preferentially.
9. Reduction of chloroform in 50% t-butanol-water was found to follow second order kinetics.

10. The reduction of meso- and racemic 2,3-dibromobutane was non-stereospecific, yielding mixtures of cis- and trans-2-butene, when either isomer was reduced.
11. The non-stereospecificity of the reduction has been explained by the formation of bromine atoms during the course of the reduction, which cause isomerization of the olefin.
12. The presence of this radical was demonstrated by the isomerization of cis-2-butene, when present during the reduction of 1,2-dibromocyclohexane by chromous ion.
13. The reduction of meso- and racemic 2,3-dibromobutane was found to follow second order kinetics.
14. The reduction of 1,2-dibromo-2-methylpropane was second order.
15. Styrene dibromide was reduced by chromium(II) perchlorate in methanol to yield styrene as the only organic product.

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