THE OXIDATION OF SECONDARY AND TERTIARY AROMATIC ALCOHOLS

BY CHROMIUM(VI) AND MANGANESE(VII)

by

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Date Oct 27, 1968
The mechanism of permanganate oxidation of benzhydrol has been investigated between pH 7.00 and $H_0 = -2.46$. The deuterium isotope effect, $k_H/k_D$, obtained by studying the oxidation rate of benzhydrol $\alpha$-d, was found to fall from 7.3 at pH 7.00 to 1.08 at $H_0 = -1.22$.

Between pH 7.00 and $H_0 = 0.20$, the reaction is of second order, first order in each of the reactants. Beyond $H_0 = 0.50$ the reaction becomes first order in carbinol and zero order in permanganate, and in this region the reaction is strongly acid-catalyzed.

A study of eight substituted benzhydrols shows an excellent Hammett correlation with $\sigma^+, \rho^+$ being -1.02. The rate-determining step at higher acidities is believed to be the scission of protonated carbinol to carbonium ion, which then reacts with permanganate in a fast step. This idea is supported by the results of a study of the rate of ionization of $p$-methoxybenzhydrol under conditions similar to those of the oxidation reaction.

The mechanism of chromic acid oxidation of benzhydrol has been studied between $H_0 = 0.50$ and -4.20. The reaction is acid-catalyzed in this region and was found to be of second order, first order in each of the reactants. The deuterium isotope effect with benzhydrol $\alpha$-d at $H_0 = -1.00$ is 6.81.
A Hammett plot, obtained from the study of five substituted benzhydrols, shows \( \sigma \) to be the operative substituent constant, \( \rho \) being -0.54. The rate-determining step is believed to be the unimolecular decomposition of a chromate ester.

The permanganate oxidation of triphenylcarbinol has been investigated in the region of acidity of \( H_o -0.60 \) to \(-1.93\). The reaction was found to be acid-catalyzed in this region and to produce benzophenone and phenol. The order of reaction was found to be the same as in the case of benzhydrol, i.e., first order in carbinol and zero order in permanganate.

A study of nine substituted triphenylcarbinols gave a good Hammett correlation with \( \sigma^+ , \rho^+ \) being -1.39. As in the case of benzhydrol, the rate-determining step is believed to be the ionization of the carbinols.

The chromic acid oxidation of triphenylcarbinol has been investigated between \( H_R -2.80 \) and \(-7.48\). Acid-catalysis was observed for the reaction in this region. The reaction was found to be of second order, first order in each of the reactants, as in the case of benzhydrol. The reaction gave a quantitative yield of benzophenone, phenol also being formed.

A Hammett correlation with \( \sigma^+ \) was obtained from a study of eleven substituted triphenylcarbinols, \( \rho^+ \) was found to be -0.879. The rates of oxidation of the triarylcarbinols were also studied in the presence of added manganous ions, which showed an
almost uniform reduction in rate for all the carbinols, the value of $\rho^+$ in this case being -0.906. The migration aptitudes of the substituted aryl groups were determined and $\rho^+$ for migration was found to be -1.44. A chromate ester mechanism, similar to that proposed for benzhydrol and other secondary alcohols, is believed to be operative in this case, except that the decomposition of the ester takes place by migration of the electron-rich ring. It is suggested that the chromic acid oxidation of primary and secondary alcohols may take place by an analogous rearrangement reaction of a chromate ester. In these cases the migrating group would be hydrogen.

Permanganate oxidation of benzhydrol was also studied in frozen system between pH 1.50 and 12.40. A large increase in rate, compared to that in the liquid system, was observed. The deuterium isotope effect, $k_H/k_D$, of 7.2 to 7.5 was found in this system. The reactions are of second order, as in the liquid system. The acceleration in rate appears to be due to an increase in concentration of the reactants in the liquid phase between ice crystals.
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INTRODUCTION

Potassium permanganate and chromic acid have been used extensively as oxidizing agents for both organic and inorganic substrates. The mechanisms of the reactions depend largely on the substrate and on the experimental conditions.

Permanganate Oxidation:

Manganese can exist in several oxidation states and the mechanisms of permanganate oxidation reactions vary to a great extent depending on the reaction conditions and the acidity of the medium, which determines the oxidation state to which permanganate is reduced.

The oxidation state of manganese is known to vary from +1 to +7, but only +2, +4 and +7 states are stable over a wide range of acidity. In highly alkaline solution the reduction product of permanganate is manganese(VI), in alkaline, neutral or weakly acidic solution manganese(IV) has been found to be the stable reduction product, and in strongly acidic solution permanganate can be reduced to manganese(II).

Stewart (1) has reviewed the properties and reactions of the different oxidation states of manganese in detail; a brief discussion of the same is given here.

Manganese(VI) is stable in basic solution and exists as manganate ion $\text{MnO}_4^-$. Below pH 13, it slowly disproportionates to manganese(VII) and manganese(IV), the rate of disproportionation
Increasing with acidity of the medium (2,3). Usually oxidation by manganese(VI) is slower than that by manganese(VII) (4,5). The only exception is the oxidation of aromatic aldehydes in which case the rates of oxidation by the two species are nearly same (6). The reactions of manganese(VI) with 1,2-diols, phenols and olefins have also been studied (7). Stronger oxidizing agents oxidize manganate to permanganate.

Manganese(V), or hypomanganate, is fairly stable in cold concentrated alkali solutions stronger than 10N, but below 8N alkali it disproportionates to manganese(VI) and manganese(IV) (7). Primary and secondary alcohols are oxidized slowly by hypomanganate, but alkenes, tertiary alcohols and phenols are resistant to attack.

Manganese dioxide, which is the normal form of manganese(IV), is the reduction product of permanganate in weakly alkaline or acidic solution, except in certain oxidations in acid solution, such as with oxalic acid where the ultimate product is manganese(II). Usually it is a brown insoluble powder which can exist in soluble forms under certain circumstances. The precipitation of manganese dioxide in solution is delayed by phosphate buffers due to the formation of a complex. It is also soluble in fuming sulfuric acid. Manganese dioxide, dispersed in organic solvents has been found useful as an oxidizing agent for alcohols and diarylmethanes (8-12). Such heterogeneous reactions of manganese dioxide seem to follow radical mechanisms.
Manganese(III) is stable as manganic ion in concentrated acid solution and also in weakly acidic solution when complexed with such groups as fluoride or pyrophosphate, without which it undergoes rapid disproportionation to manganese(II) and manganese(IV). However, in the presence of a large excess of manganous ion, manganese(III) is fairly stable even in 1.5M perchloric acid (14). Pyrophosphate forms a stable complex with manganese(III) and the oxidation of malonic acid (15), pinacol (16), formaldehyde and formic acid (17) by manganic pyrophosphate have been studied.

With strong reducing agents like iodide, ferrous ion or oxalic acid, the end product of permanganate oxidation in acid solution is manganous ion, where the oxidation state of manganese is +2. Permanganate reacts with manganese(II) in neutral or weakly acidic solution, which is the well known Guyard reaction used for the volumetric determination of manganese. The reaction taking place is:

$$2\text{MnO}_4^- + 3\text{Mn}^{2+} + 2\text{H}_2\text{O} \rightarrow 5\text{MnO}_2 + 4\text{H}^+$$

Ladbury and Cullis (18) have reviewed the studies made on this reaction.

In certain complexes manganese has been found to exist as manganese(I) (1).

**Permanganate Oxidation of Organic Substrates**:

Permanganate is a powerful oxidizing agent for a wide variety of organic substrates. Only the reactions related to
the present investigation are discussed here.

(i) Oxidation of Aromatic Rings: Aromatic compounds having electron donating ring substituents are readily degraded to carbon dioxide, whereas electron withdrawing groups appear to stabilise the ring. This is obvious from the reactivities of phenols and anilines. Condensed polynuclear hydrocarbons are also degraded by permanganate (19).

(ii) Oxidation of Aromatic Aldehydes: The permanganate oxidation of aromatic aldehydes such as benzaldehyde (6,20,21), acetaldehyde and formaldehyde (20,21) has been extensively studied.

Stewart and Wiberg (6) studied the oxidation of benzaldehyde and substituted benzaldehyde from pH 5 to 13. Two different mechanisms have been proposed by the authors for the reactions in basic and acidic media. In basic solution from pH 11 to 13, specific hydroxyl ion catalysis was observed according to the equation:

\[
\text{Rate} = k [\text{PhCHO}] [\text{MnO}_4^-] [\text{OH}^-]^{1/2}
\]
From pH 6.8 to 11, the rate was found to be independent of the medium. In more acidic solution, general acid catalysis was observed.

In the basic region, the deuterium isotope effect with PhCDO was very small; the effect was observed to increase with decreasing pH and in acidic medium its value was 7. In the basic region, a large positive "rho" was obtained from a Hammett plot. On the other hand, in acidic medium "rho" has a small negative value. In neutral solution, the oxygen introduced into the aldehyde, comes mainly from the oxidizing agent, whereas in basic solution the solvent contributes a major part of this oxygen.

For the reaction in basic solution, a free radical chain mechanism was suggested and for the reaction in neutral solution a fast ester formation between permanganate and aldehyde hydrate followed by rate-determining proton removal from the aldehydic hydrogen.

In solution below pH 5, an autocatalytic reaction was found to take place between permanganate and benzaldehyde.

(iii) Oxidation of Aldehyde Hydrates: Aldehydes which are extensively hydrated in aqueous solution are oxidized in a way different from ordinary aldehydes. In basic solution, anions similar to those of alcohols are generated and are oxidized rapidly although formaldehyde has been found to be oxidized slowly (23).
Stewart and Mocek (24) studied the permanganate oxidation of fluoral hydrate in solutions ranging from 46% sulfuric acid to one molar alkali. They found four different reaction paths depending on the medium although in all cases the reaction is bimolecular between a fluoral hydrate and a manganese(VII) species. The dominant reacting species, as the medium is changed from strongly basic to strongly acidic are:

\[
\begin{align*}
\text{CF}_3^- &\quad \text{C}^-\text{H} + \text{MnO}_4^- \\
\text{O}^- & \quad \text{OH} \\
\text{CF}_3^- &\quad \text{C}^-\text{H} + \text{MnO}_4^- \\
\text{O}^- & \quad \text{OH} \\
\text{CF}_3^- &\quad \text{C}^-\text{H} + \text{H}^+\text{MnO}_4^- \\
\text{OH} &
\end{align*}
\]

and

\[
\begin{align*}
\text{CF}_3^- &\quad \text{C}^-\text{H} + \text{H}^+\text{MnO}_4^- \\
\text{OH} &
\end{align*}
\]

The large isotope effect with CF$_3$CD(OH)$_2$ in all cases suggests the breaking of C-H bond in the rate-determining step. It appears that either a hydride ion or a hydrogen atom abstraction is occurring in this step. According to hydride ion transfer mechanism, the relative rate of oxidation of the different species should be:

\[
\begin{align*}
\text{CF}_3^- \quad \text{C}^-\text{H} &\quad > \quad \text{CF}_3^- \quad \text{C}^-\text{H} &\quad > \quad \text{CF}_3^- \quad \text{C}^-\text{H} \\
\text{O}^- & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]
and the oxidation by H\textsubscript{2}MnO\textsubscript{4} should be faster than MnO\textsubscript{4}\textsuperscript{-}. This is exactly what was observed.

On the other hand, the effect of substituent Z in Z-CH-CF\textsubscript{3} is much smaller than that expected for hydride ion abstraction. When Z is the strongly electron donating group O\textsuperscript{-}, the rate increases but at the same time, there is an increase in charge density on the reductant which causes an electrostatic repulsion between the similarly charged reactants. This causes a less favorable entropy of activation which is more than compensated by the lowered enthalpy of activation. This suggests that hydrogen atom abstraction also can be a probable mechanism.

The work of Halpern and Candlin (25) on the permanganate oxidation of the formate-Co(III) complex, which can only be interpreted in terms of hydrogen atom abstraction by permanganate, supports the latter mechanism as a possible route.

(iv) Oxidation of Formic Acid: Permanganate oxidation of formic acid to carbon dioxide has been extensively studied (23,26-29).

In solutions of pH above 5, the rate is almost independent of pH, since the reaction is with formate ion. Below this acidity, the rate is lower and follows the ionization of formic acid. In media containing more than 20% sulfuric acid, the rate increases due to the protonation of the permanganate ion (28,29). Above
50% sulfuric acid, the rate is still higher due to the formation of MnO$_4^-$ and MnO$_7^-$, and solvent isotope effect of 0.38 (29) with D$_2$O was observed. By using permanganate-0$^{18}$ a considerable amount of 0$^{18}$ was found in the product (28).

Hydrogen atom abstraction mechanism, similar to that suggested by Candlin and Halpern (25) for the oxidation of formate-Co(III) complex, can be considered for the oxidation of formic acid.

\[
\begin{align*}
\text{HCO}_2^- + \text{MnO}_4^- & \rightarrow \text{CO}_2^* + \text{H}^+\text{MnO}_4^- \\
\text{CO}_2^* & \xrightarrow{\text{Mn(VII) or Mn(VI)}} \text{CO}_2
\end{align*}
\]

It has been shown that both MnO$_4^-$ and MnO$_7^-$ oxidize formate anions (30).

The oxygen transfer is explained by the following mechanism:

\[
\text{CO}_2^* + \text{H}^+\text{MnO}_4^- \rightarrow \text{O}_2\text{C}^{\text{MnO}_3\text{H}^2^-} \rightarrow \text{CO}_3^{2^-} + \text{Mn}(\text{V})
\]

In weakly acid solution, the unionized formic acid reacts with permanganate, although very slowly. The solvent isotope effect and reactant isotope effect are small in such solutions.
(v) **Oxidation of Tertiary Hydrogen:** Kenyon and Symons (31) found that carboxylic acids of the general structure \( R_2CH(CH_2)_2CO_2H \) in strong alkali solution can be converted into hydroxy-\( \text{acids } R_2C(\text{OH})(CH_2)_2CO_2H \) in good yields. With dilute alkali, the reaction is slow and leads to extensive degradation. Permanganate oxidation of these acids in concentrated alkali solutions gives racemic products, whereas manganate in dilute alkali, being equally effective as oxidant, gives products with retention of optical activity. The authors suggested that in strong alkali solution, permanganate may remove a hydrogen atom through hydroxyl radical, although this does not explain the attack on the \( \gamma \)-H.

(vi) **Oxidation of Alcohols:** Primary and secondary alcohols readily undergo oxidation by permanganate but tertiary alcohols are oxidized only under drastic conditions, and degradation products are obtained.

The rates of oxidation of primary and secondary alcohols are higher in basic solutions than in neutral or weak acidic solutions, although secondary alcohols are more readily oxidized in acid solution than the primary alcohols (32). In more concentrated acid the reactions are faster, due to protonation of the oxidant and probably also due to induced oxidation involving lower oxidation states of manganese (33).

In basic solution, the rates increase with increasing pH, due to the ionization of the alcohol (4,34).
The permanganate oxidation of benzhydrol \((C_6H_5)_2CHOH\) (4), hexafluoro-2-propanol \((CF_3)_2CHOH\) (35) and fluoral hydrate \(CF_3CH(OH)_2\) (24) have been studied extensively. The last compound, although it is an aldehyde hydrate, can also be classed as a secondary alcohol; the oxidation reactions of this compound have been discussed before.

The oxidation products of secondary alcohols are ketones. Enolizable ketones undergo further reaction to give cleavage products. Ketones which do not enolize are stable in alkaline permanganate.

Primary alcohols produce aldehydes which are further oxidized to carboxylic acids when no \(\alpha\)-hydrogen is available for enolization. Enolizable aldehydes undergo degradation by permanganate. The reactions can be represented as:

\[
R_2CHOH + OH^- \xrightarrow{Mn\,\text{VII}} R_2CHO^- + H_2O
\]

\[
R_2CHO^- \xrightarrow{Mn\,\text{VII}} R_2CO
\]

\[
RCH_2CH_2OH \xrightarrow{Mn\,\text{VII}} RCH_2CHO \xrightarrow{OH^-} RCH=CHOH
\]

\[
RCH_2CO_2H \xrightarrow{Mn\,\text{VII}} RCO_2H + CO_2
\]

The oxidation of alcohols in neutral solutions is very slow, and the rate is proportional to the hydroxyl ion concentration \((4,34)\).
11. \[ \text{Rate} = k \left[ R_2\text{CHOH} \right] \left[ \text{MnO}_4^- \right] \left[ \text{OH}^- \right] \]

The aldehydes are oxidized at a much higher rate than the alcohols in neutral solution and the increase in rate with the increase in hydroxyl ion concentration is not so much as in the case of alcohols. Thus aldehydes can be isolated as the reaction product of oxidation of primary alcohols only in the basic solutions, but not in neutral or weakly acidic solutions.

Cullis and Ladbury (36) have investigated the oxidation of benzyl alcohol and of 1- and 2-phenylethanol. With benzyl alcohol ring cleavage occurs to a great extent.

It has been shown by Stewart (4) that the alcohol-perrmanate reaction involves hydrogen abstraction, either as hydride ion or as a hydrogen atom, by permanganate ion from the anion of the alcohol. The rate-controlling step is the reaction between the alkoxide and the permanganate ion. The deuterium isotope effect with \( R_2\text{CDOH} \) for the oxidation of benzhydrol and fluorinated alcohols are large, showing the rupture of C-H bond in the rate determining step, which can be represented as:

\[
\begin{align*}
\text{R}_2\text{CHO}^- + \text{MnO}_4^- & \rightarrow \text{R}_2\text{C-O}^- + \text{H}^+ \text{MnO}_4^- \\
\text{R}_2\text{CHO}^- + \text{MnO}_4^- & \rightarrow \text{R}_2\text{C-O}^- + \text{H}^+ \text{MnO}_4^- 
\end{align*}
\]

The effect of substituents in the phenyl or phenyltrifluoromethyl carbinol on the rate controlling step is very small,
showing the mechanism involving hydride ion abstraction to be unlikely.

If hydrogen atom abstraction is taking place, it would produce the radical anion $R_2\cdot\dot{C}-O^-$ which is rapidly oxidized to the ketone. This also explains the greater ease of abstraction from alkoxide ion than from neutral alcohol due to the relatively greater stability of radical anion $R_2\cdot\dot{C}-O^-$ compared to the neutral ketyl $R_2\cdot\dot{C}-OH$ (37). Kurz (38) has examined these systems in order to distinguish between different mechanisms.

**Chromic Acid Oxidation:**

Chromic acid oxidations have been reviewed in detail by Westheimer (39) and recently by Wiberg (40). Only the aspects related to the present investigation are discussed here.

Chromium is known to exist in oxidation state $+2$ to $+6$. Oxidation by chromic acid results in the reduction of chromium(VI) to the $+3$ state $Cr^{3+}$, since the intermediate chromium(V) and chromium(IV) species are unstable and chromium(II) is a very strong reducing agent under ordinary conditions.

Chromium in oxidation state of $+6$ exists as chromic oxide $(CrO_3)_n$ or chromic acid, both containing $\begin{array}{c} O \\ 0-Cr-O \\ 0 \end{array}$ units (41). In dilute aqueous solutions (less than 0.05M) the predominating species is $HCrO_4^-$, whereas at a higher concentration
dehydration occurs to a large extent according to the following equation:

\[ 2\text{HCrO}_4^- \rightarrow \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \]

Polychromates are formed at still higher concentrations (42). Alkaline chromate is devoid of oxidizing power and it has been found that \( \text{Cr}_2\text{O}_7^{2-} \) has a much weaker oxidizing power than \( \text{HCrO}_4^- \) (43). The anhydride, \( \text{CrO}_3 \) and the acid chloride \( \text{CrO}_2\text{Cl}_2 \) are strong oxidizing agents. In strong acids, cations such as \( \text{HCrO}_4^+ \) exist; this explains the solubility of \( \text{CrO}_3 \) in acetic acid. Moreover, chromium(VI) forms a new species with the anions added in solution, the reactivity of this species largely depending on the identity of the added anion (44). Thus the chlorochromate anion, \( \text{ClCrO}_3^- \), formed by the following reaction

\[
\text{H}^+ + \text{HO}^- \rightarrow \text{Cr}^{3+} + \text{Cl}^- \rightarrow \text{Cl}^{-} \rightarrow \text{Cr}^{3+} \rightarrow \text{H}_2\text{O}
\]

is of much less oxidizing power than \( \text{HCrO}_4^- \).

It has been found that in anhydrous acetic acid or in acetic anhydride incomplete reduction of chromium(VI) occurs, leading to the formation of brown insoluble complexes of chromium(III), chromium(VI) and acetate ion (46).

Chromium(V) can exist in strongly basic solutions; Baily and Symons (47) prepared green \( \text{K}_3\text{CrO}_4 \) by the action of KOH on \( \text{K}_2\text{CrO}_4 \). It has been proved that the compound contains chromium(V) (47, 48). Solutions of chromium(V) in alkali absorb oxygen to form chromium(VI) which on dilution disproportionates to chromium-
(III) and chromium(VI). Barium hypochromate \( \text{Ba}_3(\text{CrO}_4) \) is another known derivative of chromium(V) (49). The oxide \( \text{Cr}_2\text{O}_5 \) is also known (50).

The known derivatives of chromium(IV) are \( \text{CrF}_4 \), \( \text{CrCl}_4 \) (51). Chromium dioxide \( \text{CrO}_2 \) has also been prepared (52). Other known compounds of chromium(IV) are \( \text{Ba}_2\text{CrO}_4 \), \( \text{Ba}_3\text{CrO}_5 \), \( \text{Sr}_2\text{CrO}_4 \) (49b).

Westheimer et al. (39,53) have clearly shown that these intermediate chromium(V) and chromium(IV) species are stronger oxidizing agents than chromium(VI).

**Chromic Acid Oxidation of Organic Substrates:**

Chromic acid oxidizes many classes of organic compounds. The reactions related to the present investigation are given in the following discussion.

(i) **Oxidation of Hydrocarbons:** (a) Aryl alkanes: Although benzene itself is relatively resistant to oxidation by chromic acid (51) polycyclic aromatic hydrocarbons are easily oxidized to quinones (54,55). The reactivity of these compounds depends on their electron availability and this is consistent with attack by a cation such as \( \text{HCrO}_3^+ \). Chromic acid easily destroys ring systems containing electron-donating substituents such as \(-\text{OH}\) or \(-\text{NH}_2\). With acidic chromic acid solution, the alkyl group of an alkylbenzene is finally oxidized to a carboxylic group (56). In diphenylmethanes the methylene group is readily oxidized to a carbonyl group (57,58). Similarly the dibenzylbenzenes are oxidized to dibenzoylebenzoic acid (59). Further oxidation of the products leads to carboxylic acids (60). With different electron withdrawing groups rearranged products are also
obtained (61). Triarylmethane on oxidation give the corresponding tertiary alcohols, which on further oxidation lose one aryl group and produce the diaryl ketones (62,63) as will be seen later. The chromic acid oxidation products of aliphatic alkanes usually undergo further oxidation and hence the reactions are not of much use in synthesis. The primary carbon-hydrogen bonds are rather unreactive towards chromic acid. The oxidation of secondary carbon-hydrogen bonds leads to the formation of ketones which can undergo further oxidation (64). The tertiary carbon-hydrogen bonds on oxidation produce the corresponding tertiary alcohol, which also undergo further dehydration or oxidation (65).

(b) Carbon-carbon double bonds: The oxidation of alkenes generally leads to several products obtained from the cleavage of the double bond, such as epoxides, ketols, acids or ketones and thus it is not of much use in synthesis. The products of chromic acid oxidation of carbon-carbon double bonds are different in sulfuric acid than in acetic acid medium, the former giving mainly the rearrangement products, although the intermediate may be an epoxide in both the cases (66,67). In some cases, allylic oxidation occurs (68). Thus cyclohexene yields cyclohexenone along with other products. This type of oxidation is rather uncommon with straight chain alkenes.

(ii) Oxidation of Aldehydes: The kinetic studies of several aromatic aldehydes in acetic acid as well as in aqueous
solutions have been reported (69,70). The oxidation of benz­
aldehyde is of first order with respect to both $[\text{PhCHO}]$ and $[\text{HCrO}_4^-]$ and the rate constant follows the $H_0$ acidity function (69,70). Comparison with PhCDO showed the cleavage of the C-H bond to be the rate-determining step. The effect of substituents on the oxidation rate indicates a positive value of $\rho$ (70). The oxidation of aliphatic aldehydes is found to be similar to that of aromatic aldehydes (71-74).

It has been shown with both aromatic and aliphatic aldehydes that the addition of manganous or cerous ions reduces the oxidation rates by 30-50% by eliminating secondary reactions due to chromium(V) and chromium(IV) (69,72). A detailed study of such an induced oxidation and determination of the kinetics of the intermediate steps leading to the reduction of chromium(VI) to chromium(V) and chromium(IV) has been reported by Wiberg and Richardson (75), by using a competitive technique with substituted benzaldehydes. On the whole, the reactions of aldehydes are quite similar to those of alcohols, to be discussed later.

(iii) Oxidation of Ketones: Generally ketones on oxida­tion give two carboxylic acids derived from carbon-carbon bond cleavage (64,65). The kinetics of the chromic acid oxidation of cyclohexanone have been studied in detail (76,77). The rate of reaction was found to be proportional to the concentrations of
ketone, acid chromate ion and acid. A kinetic isotope effect of 5.5 was obtained by comparison with cyclohexanone-d₄ and a solvent isotope effect of 4-5 was observed by using D₂O (76). An enol intermediate has been suggested for the reaction (76-78).

(iv) Oxidation of Alcohols: The chromic acid oxidation of alcohols has been investigated in considerable detail. The reactions have been studied in different solvents such as water, aqueous acetic acid, aqueous acetone; mineral acids have also been used as catalysts.

The chromic acid oxidation of isopropyl alcohol in different solvents has been studied extensively (43-45, 79-82). In the absence of any other oxidizable group, a quantitative yield of the corresponding ketone was obtained from secondary alcohols.

The oxidation of primary alcohols is complicated due to the formation of oxidizable products namely aldehydes (83). However, the reaction can give satisfactory results if the products can be removed from the reaction mixture as soon as they are formed.

Westheimer and Novick (43) suggested the following rate law for the oxidation of isopropyl alcohol:

\[ v = k_a \left[ \text{HCrO}_4^- \right] \left[ R_2\text{CHOH} \right] \left[ \text{H}^+ \right] + k_b \left[ \text{HCrO}_4^- \right] \left[ R_2\text{CHOH} \right] \left[ \text{H}^+ \right]^2 \]

This rate law has also been found to be applicable to the reactions of other alcohols (45, 76, 84).

Comparison with the rate of oxidation of isopropyl-α-d-alcohol showed that the reaction has a considerable kinetic isotope
effect (82), proving the cleavage of carbon-hydrogen bond in
the rate determining step. The existence of a pre-equilibrium
step has been shown by the fact that the reaction is faster in
\( \text{D}_2\text{O} \) than in \( \text{H}_2\text{O} \). In the presence of a large excess of manganous
ion the rate of reaction was decreased by a factor of two (85),
and one mole of manganese dioxide was produced for each mole of
acetone formed. From these observations, the following steps
were suggested for the oxidation in the presence of manganese(II):

\[
\begin{align*}
R_2\text{CHOH} + \text{Cr}^\text{VI} & \rightarrow R_2\text{CO} + \text{Cr}^\text{IV} \\
2\text{Cr}^\text{IV} + \text{Mn}^\text{II} & \rightarrow \
\text{MnO}_2 + 2\text{Cr}^\text{III}
\end{align*}
\]

Hence the probable reaction scheme is:

\[
\begin{align*}
R_2\text{CHOH} + \text{Cr}^\text{VI} & \rightarrow R_2\text{CO} + \text{Cr}^\text{IV} \\
\text{Cr}^\text{IV} + \text{Cr}^\text{VI} & \rightarrow 2\text{Cr}^\text{V} \\
R_2\text{CHOH} + \text{Cr}^\text{V} & \rightarrow R_2\text{CO} + \text{Cr}^\text{III}
\end{align*}
\]

Since it is possible to prepare the chromate ester of
isopropyl alcohol, Westheimer et al. suggested the following
mechanism for the oxidation:
The decomposition of the chromate ester was thought to occur by proton loss to any available base with elimination of a chromium(VI) ion:

\[
\begin{align*}
R_2CHOH + HCRO_4^- + H^+ & \rightarrow R_2CHOCrO_3H + H_2O \\
R_2CHOCrO_3H + H^+ & \rightarrow R_2CHOCrO_3H^+ \\
R_2CHOCrO_3H & \rightarrow R_2CO + H_2CrO_3 \\
R_2CHOCrO_3H^+ + H_2O & \rightarrow R_2CO + H_2CrO_3 + H_3O^+
\end{align*}
\]

This mechanism was questioned by Roček (79) who pointed out that the evidence indicating the participation of external base in the reaction was inconclusive. He also suggested that since water, which is the only base present, participates, it is unlikely that the reaction will follow the \( \text{p}_\text{H}_2 \) acidity function.
Graham and Westheimer (87) showed that if the two rate expressions are written, including the activity of the activated complexes, they become equal. This happens since water is formed in the first step of the ester mechanism. Thus the activity of water that is introduced in rate expression will be cancelled by the one as a result of the last equation.

Evidence for ester formation was also obtained from an investigation of the oxidation of the sterically hindered alcohol 38-28-diaetoxy-68-hydroxy-188-12-oleanen (40). Recently Wiberg and Schafer (88) have reported the direct spectrophotometric observation of the formation of the intermediate chromate ester.

Another objection to the ester mechanism is the effect of substituents on the oxidation of phenylmethyl carbinols. Kwart and Francis (94b) have reported the reaction constant for such an oxidation to be -0.37 to -1.01, depending on the reaction conditions. Roček obtained $\rho^* = -1.11$ for the oxidation of aliphatic secondary alcohols (79) and -1.06 for primary alcohols (86). Similar results were obtained for a series of aryltrifluoromethyl carbinols by Stewart and Lee (89) who found $\rho = -1.01$, and the recently reported oxidation of isopropyl alcohol in aqueous acetone gives the value of $\rho$ to be -1.16 (90). The results show a relatively electron poor reacting carbon in the activated complex.

According to Stewart and Lee (44,89,91) the proton abstraction should have a positive $\rho$, since the base catalyzed decomposition of analogous nitrate ester has a $\rho$ value of +3.6.
This was also suggested by Roček (79). However, the $\rho$ value for elimination reactions is known to vary widely depending on the degree of bond breaking in the transition state.

The effect of ring size on the rate of oxidation has been studied by Kuivila and Becker (84). It was observed that the 5-, 7-, and 8-membered ring alcohols are more reactive than cyclohexanol. This is due to the ease of change from tetrahedral to a trigonal arrangement about the reacting carbon. In a recent publication (92) it has been shown that the rates of oxidation of cyclic alcohols depend mainly on the relief of strain present in the reactant molecule.

The mechanism originally proposed by Roček et al. (79) involves a hydride transfer from alcohol to chromic acid or to its conjugate acid, with a simultaneous proton loss from the hydroxyl group as the carbon-hydrogen bond was cleaved.

$$\begin{align*}
\text{ROH} & \rightarrow \text{RO}^- + \text{H}^+ \\
\text{RCH}_2\text{OH} + \text{H}^+ & \rightarrow \text{RCH}_2\text{O}^- + \text{H}_2\text{O} \\
\text{ROH} + \text{H}^+ & \rightarrow \text{RO}^- + \text{H}_2\text{O}
\end{align*}$$

The solvent isotope effect obtained from the rate constant in D$_2$O, shows this mechanism to be unlikely. The rate of oxidation in D$_2$O is much faster than that in H$_2$O which arises from the greater acidity of D$_3$O$^+$ compared to H$_3$O$^+$ and the consequent larger concentration of the reactive conjugate acid. In the Roček
mechanism the primary kinetic isotope effect due to the cleavage of oxygen-hydrogen bond should at least cancel the solvent isotope effect, since the rapid exchange of hydroxyl protons with the solvent produces deuterated hydroxyl groups.

These observations show that the oxygen-hydrogen bond can neither be intact nor be broken in the transition state, since ethers are relatively inert to chromium(VI) and because of the positive solvent isotope effect. Hence it can be reasonably concluded that the ester is an intermediate in the oxidation path. Roček et al. have found supporting evidence for the ester mechanism from the study of the oxidation of highly hindered secondary alcohol 3β,28-diacetoxy-6β-hydroxy-18β-12-oleanen (93). It was observed that the isotope effect in 80% acetic acid is 1.0 and in less acidic solution, where the reaction is slower, it is 2.0. Presumably in the former case, ester formation becomes the rate-controlling step. Considering a unimolecular decomposition mechanism for the chromate ester, the following rate controlling step is possible:

\[
\begin{align*}
R & \quad O \\
C & \quad \text{CrO}_2\text{H}_2^+ \\
R & \quad H \\
\end{align*}
\]

\[
\begin{align*}
R & \quad O \\
C & \quad \text{CrO}_2\text{H}_2^+ \\
R & \quad H \cdots O \\
\end{align*}
\]

Transition state $+ \text{H}_3\text{CrO}_3^+$
Kwart and Francis have also proposed a similar transition state (94a). Further support for an ester intermediate has been obtained by Wilberg and Shaefer (88) (see p 20). Stewart and Lee consider that this transition state involves electron transfer to chromium through the C-H-O bonds as well as through the C-O-Cr bonds, i.e., partial bonds bind the hydrogen to both carbon and oxygen in the transition state (90). Thus the transition state becomes electron deficient and the developing carbonyl group will be stabilized by electron donating groups. This explains the observed negative value of $\rho$. Kwart et al. do not believe that the developing group has any influence on the reaction (94c).

Tertiary alcohols are relatively resistant to chromic acid oxidation but this can be effected in the presence of sulfuric acid. Sager (95) has reported the oxidation of triethylcarbinol which proceeds by prior dehydration to the olefin, the final product being a ketone.

When the tertiary alcohol is unable to dehydrate, it undergoes oxidative cleavage (96-98).

\[
\begin{align*}
(C_6H_5)_3COH & \xrightarrow{\text{CrVI, HOAc}} (C_6H_5)_2CO \\
(C_6H_5)_3CHOH(C_6H_5) & \xrightarrow{\text{CrVI, HOAc}} (C_6H_5)_3COH + C_6H_5CHO
\end{align*}
\]

Cleavage products also appear in the case of phenyl-t-butyl carbinol (85,99); here the cleavage product consisting of
t-butyI alcohol and benzaldehyde is 60-70%, the phenyl-t-butyl ketone being the minor product.

\[
\begin{align*}
\text{C}_6\text{H}_5\text{C} & \text{—C}(\text{CH}_3)_3 \quad \text{Cr}^{VI} \quad \text{C}_6\text{H}_5\text{C} —\text{C}(\text{CH}_3)_3 \\
& + \text{C}_6\text{H}_5\text{CHO} + (\text{CH}_3)_3\text{COH}
\end{align*}
\]

An interesting feature of this type of oxidation is the virtual elimination of cleavage products in the presence of manganous or cerous ions, which catalyze the disproportionation of chromium(IV) and chromium(V) (85). This shows that the ketone is the oxidation product of the alcohol by chromium(VI) whereas the chromium species of intermediate valence produce the cleavage products.

**Oxidation of Alcohols by Other Reagents:**

**Vanadium(V):** Pentavalent vanadium in acid solutions exists as pentavanadyl ion $\text{VO}_2^+$. It has been shown by Waters and his group (100) that the reactions of the oxidant with primary alcohols are the same as those with secondary alcohols, although the tertiary alcohols are much more resistant to attack. There is evidence (101) that in acid solution vanadium(V) forms a complex of the formula $\text{ROH},\text{V(OH)}_3$ with an alcohol. The rate-determining step in the oxidation of cyclohexanol to ketone is the decomposition of the complex, as shown by the existence of
an isotope effect in the oxidation of cyclohexanol-1-d. The kinetic equation corresponding to this slow decomposition of the complex to vanadium(IV) and an alcohol radical is:

\[
\frac{d[V(\text{V})]}{dt} = k \left[ \text{ROH} \right] [V_{\text{O}}^+][H_3O^+] 
\]

It is evident from the polymerization of added acrylonitrile in such systems that the homolytic scissions, shown in the following equation, take place:

\[
\text{VO}_2^+ + H_3O^+ + \text{OH} \xrightarrow{\text{slow}} \text{V(OH)}^+ 
\]

\[
\text{H} \xrightarrow{\text{fast}} \text{V(OH)}^+ + \text{DOH} 
\]

The presence of even small amounts of bromide ion changes the course of the oxidation of alcohols. The rate controlling step in this case is the production of bromine atoms which act as the active oxidant (102):

\[
\text{V(\text{V})} + \text{Br}^- \xrightarrow{\text{fast}} \text{V(\text{IV})} + \text{Br}^+ 
\]

\[
\text{R}_2\text{CHOH} + \text{Br}^+ \xrightarrow{\text{fast}} \text{R}_2\text{COH} + \text{Br}^- + \text{H}^+ 
\]
With certain alcohols, carbon-carbon bond fission giving rise to a stable radical is more favored than a carbon-hydrogen bond cleavage. Thus t-butylphenylcarbinol on oxidation produces benzaldehyde, instead of t-butyl phenyl ketone. The ready formation of the t-butyl radical assists in the scission of the carbon-carbon bond, which may accompany the homolytic cleavage of metal-oxygen bond (103).

\[
\begin{align*}
\text{C}_6\text{H}_5 - & \text{C} - \text{t-Bu} \quad \xrightarrow{\text{V}^\text{V}} \quad \left[ \begin{array}{c}
\text{C}_6\text{H}_5 - & \text{C} - \text{t-Bu} \\
\text{H} & \text{H}
\end{array} \right] \\
& \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{t-Bu}^* \\
& \rightarrow \text{C}_6\text{H}_5\text{CHO} + \text{t-BuOH}
\end{align*}
\]

Such carbon-carbon bond fission provides a route for the oxidation of tertiary alcohols and occurs when one group is split off as a stable radical.

**Cobalt(III):** Unlike vanadium(V) and cerium(IV), the oxidation of alcohols by cobalt(III) is faster than that of ketones. In all the cases of oxidation of alcohols, the rate of the main reaction varies inversely with the acid concentration and with cyclohexanol-1-d, a small isotope effect, \(k_H/k_D = 1.72\) at \(10^\circ\), was observed (104). The inverse acid dependence of the rate is explained to be due to the rapid exchange of a ligand with an alcohol molecule, occurring with the ion \(\text{Co(OH)}(\text{H}_2\text{O})^2^+\) but not with the ion \(\text{Co(H}_2\text{O})^3^+\).
According to Hoare and Waters (104) the initially formed complex between cobalt(III) and the alcohol decomposes to a radical which is oxidized rapidly:

\[
\begin{array}{cccc}
\text{Co(H}_2\text{O)}^3_+ & \rightleftharpoons & \text{Co(OH)}^+ (\text{H}_2\text{O})^2_+ & + \text{H}^+ \\
\end{array}
\]

The small kinetic isotope effect is suggested to be due to the concerted breaking of a carbon-hydrogen group and the removal of an electron from the oxygen atom of alcohol by cobalt(III).

**Cerium(IV)**: The oxidation of alcohols by ceric ions involves the formation of a cerium(IV)-alcohol complex which undergoes slow decomposition to products (105, 106):

\[
\begin{array}{cccc}
\text{Ce}^{IV} (\text{H}_2\text{O})^8_{4+} & + & \text{C}_2\text{H}_5\text{OH} & \rightleftharpoons & \text{Ce}^{IV} (\text{H}_2\text{O})_7 (\text{C}_2\text{H}_5\text{OH})^4_{4+} & + & \text{H}_2\text{O} \\
\end{array}
\]

\[
\begin{array}{cccc}
\text{Ce}^{IV} (\text{H}_2\text{O})_7 (\text{C}_2\text{H}_5\text{OH})^4_{4+} & \rightarrow & \text{products} \\
\end{array}
\]

The deuterium isotope effect, \( k_H / k_D \) for ceric sulfate oxidation of \( \alpha \)-deutero-cyclohexanol was found to be 1.9, indicating
the cleavage of carbon-hydrogen bond in the rate-determining step (107). The low value of the isotope effect has been explained by a cyclic activated complex (107, 108).

For the kinetics of the oxidation of formaldehyde by ceric ion in acid the following mechanism has been proposed (106):

\[
\begin{align*}
\text{Ce}^{IV} + \text{CH}_2(\text{OH})_2 & \xrightarrow{\text{slow}} \text{Ce}^{III} + \text{CH}_2 \text{OH} + \text{H}^+ \\
\text{CH}_2 \text{OH} + \text{Ce}^{IV} & \xrightarrow{\text{fast}} \text{HCO}_2\text{H} + \text{Ce}^{III}
\end{align*}
\]

**Lead Tetraacetate:** Because the hydrolysis of lead tetraacetate is a fast reaction and because the exchange of acetate groups with other carboxylate groups takes place readily, it can be anticipated that similar equilibria might be established with other substances having acidic hydrogens. Thus the observed oxidations with lead tetraacetate are probably effected by the species in equilibrium with the reagent. Although alcohols are stable in lead tetraacetate-acetic acid solution, (since the equilibria lie on the side of the reactants), good yields of aldehydes or ketones have been obtained by the oxidation of alcohols in boiling benzene (109, 110). The following scheme has been suggested as a possible path:
The heterolysis of the bond between the alcohol oxygen and the lead is caused by the great electron affinity of the lead. This leads to a simultaneous breaking of the carbon-hydrogen bond to replace the electron pair lost by oxygen. This mechanism also agrees with the fragmentation which can occur during the oxidation of alcohols (111-114).
SCOPE OF THE PRESENT RESEARCH

The permanganate oxidation of alcohols has previously been studied in basic and weakly acidic regions. In the case of the secondary alcohol, benzhydrol, the reaction was found to be of second order, first order in each of the reactants, and the product was found to be benzophenone (4). No work has been reported on the permanganate oxidation of alcohols in highly acidic regions. Hence in the present investigation an attempt has been made to determine the course of the permanganate oxidation of benzhydrol and substituted benzhydrols by studying the kinetics and the products of reaction.

The chromic acid oxidation of a number of secondary alcohols in various media has been studied (43-45, 79-82, 85-91), but not of diarylcarbinols. There has been controversy about the exact mode of transfer of the hydrogen atoms removed from the alcohol during chromic acid oxidation. In some cases, both oxidation and cleavage products have been obtained (99). In order to ascertain the mechanism of chromic acid oxidation of diarylcarbinols, the kinetics and the products of the reaction of benzhydrol and its derivatives with chromic acid were studied.

No work has been reported on the permanganate oxidation of triarylcarbinols. These compounds lack a hydrogen atom on the alcoholic carbon and any oxidation must produce carbon-carbon
bond cleavage, possibly via aryl migration. It seemed worthwhile to examine this reaction closely.

The chromic acid oxidation of triphenylcarbinol in acetic acid has been shown to produce benzophenone and phenol (96,97). This reaction may occur via phenyl migration from carbon to electron-deficient oxygen and in order to investigate this and other possibilities, the reaction kinetics, substituent effects and the products of the reaction were examined. It has been reported that the addition of manganous ion reduces the rate of chromic acid oxidation of carbinols and in some cases changes the course of the reaction. These effects have been attributed to the scavenging action of manganous ion on the powerful oxidants chromium(V) and chromium(IV), formed as reaction intermediates (53,75). In order to find out if any of these species are involved in the chromic acid oxidation of triarylcarnbinols, the reaction was also studied in the presence of manganous ion.
SECTION I

OXIDATION OF DIARYLCARBINOLS
EXPERIMENTAL

Materials:

Benzhydrol and benzhydrol α-d, prepared previously in these laboratories, were crystallized from carbon tetrachloride. Both showed the constant melting point 64-65° (4).

4-Methylbenzhydrol, 4,4'-dimethylbenzhydrol, 4-chlorobenzhydrol and 4,4'-dichlorobenzhydrol were prepared from the corresponding benzophenones by sodium borohydride reduction of the latter. The first two carbinols were crystallized from ether-ligroin and the last two from ethanol-water to constant melting points. The yields and the melting points of the carbinols prepared are given below:

4-Methylbenzhydrol: yield 90.5%; m.p. 50°; lit. 49° (115a).
4,4'-Dimethylbenzhydrol: yield 90.1%; m.p. 68°; lit. 69° (115b).
4-Chlorobenzhydrol: yield 95%; m.p. 59-60°; lit. 59-61° (116).
4,4'-Dichlorobenzhydrol: yield 91.2%; m.p. 90.5°; lit. 89-90° (115c).

Using the same method, 9-fluorenone was reduced to 9-fluorenol, crystallized from water; yield 91.2%, m.p. 157-8°, lit. 158-9° (115b).

4,4'-Dimethoxybenzophenone was reduced to 4,4'-dimethoxybenzhydrol by lithium aluminium hydride. The product was
crystallized from ethanol-water mixture to constant melting point 70-71°, lit. 72° (117). The yield was 96%.

Dimesityl carbinol and 4-methoxybenzhydrol, previously prepared in these laboratories, were crystallized from ethanol-water to constant melting points 150° and 68° respectively.

Benzhydrol-4-carboxylic acid was prepared by Mr. J.A. MacPhee in these laboratories by sodium borohydride reduction of the corresponding ketone. It was crystallized from chloroform-ethanol to constant melting point 165-6°.

Potassium permanganate solutions were standardised by titration against aliquots of 0.1N sodium oxalate, both being prepared according to Vogel (118). Concentrated sulfuric acid (0.5 ml) was added to the flask along with sodium oxalate solution and permanganate was added to it until the pink end point was obtained.

Standard potassium dichromate solution was prepared by direct weighing of reagent grade potassium dichromate into a stoppered volumetric flask and then made up to the mark with distilled water.

**Kinetic Methods:**

The kinetics of permanganate oxidation were followed by two procedures, namely titration and measurement of light absorption.

In the first method an aqueous solution of approximately 0.006M benzhydrol was prepared by dissolving a weighed quantity
of benzhydrol in hot distilled water which had been boiled to remove dissolved gases. In a typical experiment 10 ml of this solution, 20 ml of 1M $\text{KH}_2\text{PO}_4$ buffer adjusted to the desired pH, and 68 ml distilled water were taken in a 125 ml stoppered red Erlenmeyer flask which was then immersed in a constant temperature bath, the temperature of which was adjusted to $25 \pm 0.02^\circ$. Two ml of standard potassium permanganate solution was added to it to start the reaction. The aliquots were withdrawn with a fast delivery pipette and added to a quenching solution containing 10 ml of 2M sulfuric acid, 3 ml of 5% sodium bicarbonate solution and an excess of potassium iodide. The liberated iodine was titrated with an appropriate thiosulfate solution using Thyodene as indicator. The titration method was used for reactions in solutions of acidity less than $H_\circ 0.20$, above which the reactions were too fast to be followed by this method, and hence the spectrophotometric methods were used to study the reactions. The ratio of substrate to permanganate used in the reactions studied by titration method was 3:2. This corresponds to the three equivalent change from Mn(VII) to Mn(IV) and two equivalent change of the substrate.

In the spectrophotometric method the reaction was followed by observing the disappearance of permanganate at 526 m$. Solu-

tions of the alcohols were prepared by accurately weighing out the compounds directly into 10 ml volumetric flasks and made up to
the mark with distilled methanol. In a typical run for permanganate oxidation, 0.2 ml of $1.79 \times 10^{-2}$ M solution of benzhydrol in methanol was taken in a 10 ml volumetric flask. The solvent was evaporated under vacuum; 2 ml of 18.01 M sulfuric acid was then added to the carbinol and water was added to it slowly with constant cooling till the volume was up to the mark; 2.8 ml of this solution was taken in a cell of path length 1 cm and placed in the cell compartment of a B & L Spectronic 505 spectrophotometer, thermostated at $25 \pm 0.02^\circ$ by water circulating through the thermostatic cells. The contents of the cell were allowed to stand for 20-25 minutes in order to attain the constant temperature. Next 30 µl of 0.018 M potassium permanganate solution was injected from a 50 µl syringe into the cell, and the reaction was followed by observing the decrease in the absorbance of permanganate at 526 µm.

For the chromic acid oxidation of the diaryl alcohols only the spectrophotometric method was found to be suitable, since the reactions were too fast for the titration method. In this case the solutions were made in the same way as in the permanganate oxidations; the only difference was that 80 wt% acetic acid in water was used as the reaction medium. The reason for using acetic was to obtain a higher concentration of the carbinols in solution since the reactions were rather slow for spectrophotometric measurements. In a typical run for chromic
acid oxidation, 2 ml of $2.13 \times 10^{-2} \text{M}$ solution of benzhydrol in 80 wt% acetic acid in water and containing the required quantity of sulfuric acid was taken in a cell and placed in the cell compartment of Cary 16 spectrophotometer. The cell compartment was thermostated to $25 \pm 0.02^\circ$ by circulating water from a constant temperature bath. When the contents of the cell attained the constant temperature, 10$\mu$l of $1.42 \times 10^{-1} \text{M}$ potassium dichromate solution was injected from a 50$\mu$l syringe. The reaction was followed by observing the disappearance of Cr(VI) at 350 m$\mu$.

In all of these reactions the ratio of the oxidant to the substrate used was 3:2, since the reactions correspond to the three equivalent change from Mn(VII) to Mn(IV) and Cr(VI) to Cr(III), and two equivalent change of the substrate.

A spectrophotometric method was used to follow the rate of ionization of 4-methoxybenzhydrol by observing the increase in absorption of the corresponding carbonium ion at 466 m$\mu$. Because of the low solubility of the carbinol in water 70% methanol (by volume) in water was taken as the reaction medium. In a typical experiment 2 ml of 18.005M sulfuric acid was taken in a 10 ml volumetric flask and made up to the mark with the aqueous methanol; 2.5 ml of this solution was taken in a cell and placed in the thermostated cell compartment of a Cary 16 spectrophotometer. Next 50$\mu$l of a 2.5M solution of 4-methoxybenzhydrol
was injected to the cell from a syringe. The increase in optical density at 466 μm showed the extent of ionization.

Product Analysis:

(i) Permanganate Oxidation: A weighed quantity of diarylcarbinol (0.001 mole) was dissolved in 100 ml of 1.8M sulfuric acid. To the solution, 1.5 ml of 0.446M potassium permanganate solution was added. The mixture was allowed to stand till the color of permanganate disappeared, after which the mixture was diluted with 100 ml distilled water and then extracted several times with petroleum ether. The extract was washed with water and dried over anhydrous sodium sulfate. The solvent was removed from the extract by evaporation and the infra-red spectrum of the residue observed. The residue was weighed and the melting point was ascertained. Following this method, the products of oxidation of benzhydrol and 4-methoxy-benzhydrol were isolated and analysed. In the case of benzhydrol, the 2,4-dinitrophenyl hydrazone of the product was prepared according to Vogel (119) and this served as an additional proof of the identity of benzophenone in the product.

(ii) Chromic Acid Oxidation: The carbinol (0.001 mole) was dissolved in 100 ml of 80 wt% aqueous acetic acid containing 15.9% sulfuric acid. To the solution 1.0 ml of 0.33M potassium dichromate solution was added. The mixture was allowed to stand for several hours till the color changed to green. The products were isolated and analysed in the same way as in the case of
permanganate oxidation. Using this method, the oxidation products of benzhydrol, dimethyl carbinol and 4-methylbenzhydrol were isolated and analysed.

**Determination of Acidity Functions:**

(i) \( H_0 \) in \( H_2SO_4 \) diluted with 80 wt% aqueous acetic acid (80g. acetic acid and 20g water): The measurements were carried out with a Cary 16 spectrophotometer, provided with thermostatic materials, the temperature being kept constant at 25 ± 0.02°. The solution of acetic acid was made by mixing 100.0 ml of "Baker Analyzed Glacial Acetic Acid" (99.9%) with 26.25 ml of distilled water in a glass-stoppered flask. For each measurement, a calculated quantity of "Baker Analyzed Sulfuric Acid" (99.99%) was taken in a 10 ml volumetric flask along with the required quantity of a suitable indicator and made up to the mark with 80 wt% aqueous acetic acid. The samples with varying quantities of sulfuric acid were thermostated at 25° and the absorbances of the indicators were measured at appropriate wavelengths. The indicators used were 4-nitroaniline, 3-methoxydiphenylamine, 3,4'-dichlorodiphenylamine, 3-nitrodiphenylamine, 4-nitrodiphenylamine and 2-nitrodiphenylamine. Stock solutions of the indicators were prepared by dissolving weighed quantities of the compounds in 80 wt% aqueous acetic acid.

Hammett's \( H_0 \) function relates the equilibrium between base and protonated base as (120):

\[
H_0 = pK_{BH^+} - \log\left(\frac{C_{BH^+}}{C_B}\right)
\]  

(1)
If \( A_0 \) is the initial absorbance of free base and \( A_n \) is the absorbance at any acidity, then:

\[
\frac{(A_0 - A_n)}{A_n} = \frac{C_{BH^+}}{C_B}
\]  

(2)

and

\[
H_0 = pK_{BH^+} - \log \left[ \frac{(A_0 - A_n)}{A_n} \right]
\]  

(3)

The value of \( H_0 \) at any acidity was calculated from equation (3) by substituting the values of \( A_0 \) and \( A_n \) measured spectrophotometrically.

(ii) \( H_R \) in \( H_2SO_4 \) diluted with 80 wt% aqueous acetic acid: The stock solutions of acids and indicators were prepared and the measurements were carried out in the same way as in the case of the determination of the function \( H_0 \) in the same system. The indicators used were tri(4-tolyl)carbinol, 4,4'-dimethyltriphenylcarbinol, triphenylcarbinol and tri(4-chlorophenyl)carbinol.

The acidity function \( H_R \) is defined by the relation (121):

\[
H_R = pK_{R^+} - \log\left( \frac{C_{R^+}}{C_{ROH}} \right)
\]  

(4)

where \( C_{R^+} \) is the concentration of the carbonium ion and \( C_{ROH} \) is the concentration of the unionized alcohol. If \( A_n \) is the absorbance of the indicator at any acidity and \( A \), the absorbance of the fully ionized alcohol, it follows:

\[
\frac{C_{R^+}}{C_{ROH}} = \frac{A_n}{(A - A_n)}
\]

Thus,

\[
H_R = pK_{R^+} - \log\left( \frac{A_n}{(A - A_n)} \right)
\]  

(5)

The value of \( H_R \) at any acidity was calculated from eqn. (5) by substituting the observed values of \( A \) and \( A_n \) at that acidity.
(iii) \( H_0 \) in H\(_2\)SO\(_4\) Diluted with 70 vol\% Aqueous Methanol: The values of the acidity function were calculated by using eqn. (3) following the similar experimental procedure. The indicators used were 2-nitroaniline and 4-chloro-2-nitroaniline.

(iv) \( H_R \) in H\(_2\)SO\(_4\) Diluted with 70 vol\% Aqueous Methanol: Eqn. (5) was used to calculate the values of \( H_R \). The experimental procedures were similar to those followed for the determination of the acidity function in the previously described media. The indicator used was 4,4'-dimethoxytriphenylchloromethane.
RESULTS

Product Analysis:

(i) Permanganate Oxidation: The products of oxidation of all the diarylcarbinols contained carbonyl groups, as shown in their infra-red spectra. In the case of benzhydrol, the melting point of the product was found to be 49°, lit. 49° for benzophenone (119). The 2,4-dinitro phenylhydrazone melted at 238°, lit. 239° (119). The yield of the product was 99.2%.

4-Methoxybenzhydrol produced 4-methoxybenzophenone in 98.1% yield, m.p. 62°, lit. 61-62° (122).

(ii) Chromic Acid Oxidation: The product obtained from the oxidation of benzhydrol was found to be the same as in the case of permanganate oxidation, viz., benzophenone. The yield was 98.5%.

Dimesityl carbinol produced a compound of m.p. 139-40°, which was found to be dimesityl ketone from the analysis: calc. C, 85.7%; H, 8.27%; found C, 85.4%; H, 8.3%; and also from the infra-red spectrum which showed a strong carbonyl absorption band. The yield of dimesityl ketone was 99.7%.

The crystallizable solid product of oxidation of 4-methyl benzhydrol was found to be 4-methylbenzophenone, m.p. 52°, lit. 53° (119). The yield of the product was 96.4%. The non-crystallizable oily residue was probably a mixture of some
unreacted carbinol and the ketone produced, since its infra-red spectrum did not show the characteristic absorption bands of benzaldehyde at $2750\text{cm}^{-1}$ and $2800\text{cm}^{-1}$. Since benzaldehyde is the probable product if phenyl-migration takes place, it appears that no rearrangement due to phenyl-migration is occurring.

**Determination of Acidity Functions:**

The results of spectrophotometric measurements are given in Tables 1 to 5. The data from the first two tables are plotted in Figs. 1 and 2.

**TABLE I**

Values of $H_\circ$ in $H_2SO_4$ diluted with 80 wt% aqueous acetic acid.

(i) Indicator: 4-Nitroaniline, $pK_{BH}^+ = 1.00$, $\lambda_{max} = 370 \text{ mu}$

<table>
<thead>
<tr>
<th>$%H_2SO_4$</th>
<th>$H_\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>0.73</td>
</tr>
<tr>
<td>0.85</td>
<td>0.46</td>
</tr>
</tbody>
</table>

(ii) Indicator: 3-Methoxydiphenylamine, $pK_{BH}^+ = 0.40$, $\lambda_{max} = 282 \text{ mu}$

<table>
<thead>
<tr>
<th>$%H_2SO_4$</th>
<th>$H_\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>-0.0196</td>
</tr>
<tr>
<td>4.2</td>
<td>-0.265</td>
</tr>
</tbody>
</table>
(iii) **Indicator: 3,4'-Dichlorodiphenylamine, pK\textsubscript{BH}^+ = -1.19,**

\[
\lambda_{\text{max}} = 288 \text{ m}\mu
\]

<table>
<thead>
<tr>
<th>H\textsubscript{2}SO\textsubscript{4}</th>
<th>H\textsubscript{O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>-0.27</td>
</tr>
<tr>
<td>5.8</td>
<td>-0.74</td>
</tr>
<tr>
<td>8.3</td>
<td>-1.12</td>
</tr>
<tr>
<td>12.9</td>
<td>-1.70</td>
</tr>
</tbody>
</table>

(iv) **Indicator: 3-Nitrodiphenylamine, pK\textsubscript{BH}^+ = -1.61,**

\[
\lambda_{\text{max}} = 280 \text{ m}\mu
\]

<table>
<thead>
<tr>
<th>H\textsubscript{2}SO\textsubscript{4}</th>
<th>H\textsubscript{O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.8</td>
<td>-0.74</td>
</tr>
<tr>
<td>12.9</td>
<td>-1.66</td>
</tr>
<tr>
<td>18.0</td>
<td>-2.20</td>
</tr>
</tbody>
</table>

(v) **Indicator: 4-Nitrodiphenylamine, pK\textsubscript{BH}^+ = -3.13,**

\[
\lambda_{\text{max}} = 400 \text{ m}\mu
\]

<table>
<thead>
<tr>
<th>H\textsubscript{2}SO\textsubscript{4}</th>
<th>H\textsubscript{O}</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.0</td>
<td>-2.15</td>
</tr>
<tr>
<td>22.7</td>
<td>-2.78</td>
</tr>
<tr>
<td>35.6</td>
<td>-4.01</td>
</tr>
<tr>
<td>41.0</td>
<td>-4.50</td>
</tr>
</tbody>
</table>
(vi) Indicator: 2-Nitrodiphenylamine, $pK_{BH}^+ = -4.12$.

$\lambda_{max} = 433 \text{ } \mu\text{m}$

$$
\begin{array}{cc}
\text{%H}_2\text{SO}_4 & H_0 \\
29.3 & -3.38 \\
35.6 & -4.04 \\
39.0 & -4.37 \\
41.0 & -4.64 \\
46.8 & -5.25 \\
51.8 & -5.67 \\
\end{array}
$$

**TABLE II**

Values of $H_R$ in $H_2SO_4$ Diluted with 80 wt% Aqueous Acetic Acid.

(i) Indicator: Tri(4-tolyl)carbinol, $pK_{R}^+ = -3.56$.

$\lambda_{max} = 452 \text{ } \mu\text{m}$

$$
\begin{array}{cc}
\text{%H}_2\text{SO}_4 & H_R \\
5.9 & -2.50 \\
8.3 & -2.80 \\
12.9 & -3.55 \\
15.9 & -3.95 \\
\end{array}
$$
Fig. 1. Acidity Function $H_\circ$ in $H_2SO_4$ Diluted with 80 wt% Aqueous Acetic Acid.
(ii) Indicator: 4,4'-Dimethoxytriphenylcarbinol,

\[ pK_+ = -4.39, \quad \lambda_{\text{max}} = 456 \text{ nm} \]

<table>
<thead>
<tr>
<th>$%\text{H}_2\text{SO}_4$</th>
<th>$H_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.9</td>
<td>-3.60</td>
</tr>
<tr>
<td>15.9</td>
<td>-4.20</td>
</tr>
<tr>
<td>18.0</td>
<td>-4.40</td>
</tr>
<tr>
<td>22.7</td>
<td>-4.85</td>
</tr>
<tr>
<td>26.7</td>
<td>-5.50</td>
</tr>
</tbody>
</table>

(iii) Indicator: Triphenylcarbinol, \( pK_+ = -6.65 \),

\[ \lambda_{\text{max}} = 433 \text{ nm} \]

<table>
<thead>
<tr>
<th>$%\text{H}_2\text{SO}_4$</th>
<th>$H_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.7</td>
<td>-4.80</td>
</tr>
<tr>
<td>26.7</td>
<td>-5.50</td>
</tr>
<tr>
<td>29.3</td>
<td>-6.01</td>
</tr>
<tr>
<td>31.6</td>
<td>-6.30</td>
</tr>
<tr>
<td>35.4</td>
<td>-7.00</td>
</tr>
<tr>
<td>36.6</td>
<td>-7.20</td>
</tr>
</tbody>
</table>
(iv) Indicator: Tri(4-chlorophenyl)carbinol, \( pK_R^+ = -7.74 \),
\[ \lambda_{\text{max}} = 450 \text{ nm} \]

\[
\begin{array}{|c|c|}
\hline
\%H_2SO_4 & H_R \\
37.7 & -7.26 \\
39.6 & -7.48 \\
\hline
\end{array}
\]

**TABLE III**

Values of \( H_0 \) in \( H_2SO_4 \) Diluted with 70 vol% Aqueous Methanol

(i) Indicator: 4-Chloro-2-nitroaniline, \( pK_{BH}^+ = -1.07 \),
\[ \lambda_{\text{max}} = 423 \text{ nm} \]

\[
\begin{array}{|c|c|}
\hline
M(H_2SO_4) & H_0 \\
1.80 & -0.15 \\
2.16 & -0.38 \\
2.31 & -0.50 \\
2.88 & -0.64 \\
3.60 & -0.82 \\
\hline
\end{array}
\]

(ii) Indicator: 2-Nitroaniline, \( pK_{BH}^+ = -0.26 \), \( \lambda_{\text{max}} = 412 \text{ nm} \)

\[
\begin{array}{|c|c|}
\hline
M(H_2SO_4) & H_0 \\
1.80 & -0.14 \\
\hline
\end{array}
\]
Fig. 2. Acidity Function $H_R$ in $\text{H}_2\text{SO}_4$ Diluted with
with 30 wt% Aqueous Acetic Acid.
TABLE IV

Value of $H_R$ in $H_2SO_4$ Diluted with 70 vol% Aqueous Methanol.

Indicator : 4,4'-Dimethoxytriphenylchloromethane,

$PK_R^+ = -1.24$, $\lambda_{\text{max}} = 500\,\text{nm}$

<table>
<thead>
<tr>
<th>$M(H_2SO_4)$</th>
<th>$H_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.80</td>
<td>-0.58</td>
</tr>
<tr>
<td>2.16</td>
<td>-0.98</td>
</tr>
<tr>
<td>2.30</td>
<td>-1.25</td>
</tr>
<tr>
<td>2.88</td>
<td>-1.65</td>
</tr>
<tr>
<td>3.60</td>
<td>-1.94</td>
</tr>
</tbody>
</table>

Order of Reaction :

(i) **Permanganate Oxidation**: In a medium of low acidity the reactions are of second order (4). For a 3:2 ratio of the substrate to permanganate, the following integrated second order rate expression was used (6):

$$k_2 = \frac{1}{t[\text{alcohol}]} \times \frac{V_o - V_t}{V_t - \frac{2V_o}{5}}$$
where, \( V_0 \) = volume of thiosulfate at \( t = 0 \)
\( V_t \) = volume of thiosulfate at time \( t \)
\( \frac{2V}{5} \) = volume of thiosulfate at infinite time

\( [\text{alcohol}]_0 \) = alcohol concentration at \( t = 0 \).

Up to \( H_0 0.20 \), good second order plots were obtained, a typical of which is shown in Fig. 3.

At acidities greater than \( H_0 -0.50 \) the order of reaction changes to first order in carbinol concentration and zero order in permanganate concentration. Since the oxidant undergoes three-equivalent change whereas the substrate changes by two equivalents, which is apparent from the product analysis, it is obvious that the rate of disappearance of permanganate is two-thirds the rate of disappearance of the carbinol, and the following first order rate expression was used:

\[
\frac{2}{3} k t = 2.303 \log \frac{A_0}{A_t - A_\infty}
\]

where, \( A_0 \) = absorbance of permanganate at \( t = 0 \)
\( A_t \) = absorbance of permanganate at time \( t \)
\( A_\infty \) = absorbance of permanganate at infinite time.

For a 3:2 ratio of substrate to permanganate, \( A_\infty = 0 \). Since \( A_0 \) is a constant for a particular reaction, a plot of the logarithm of the absorbance of permanganate at any time against time gave a straight line. The first order rate constant was calculated from the slope of the line using the above equation. A typical first order rate plot is shown in Fig. 4. Fig. 5 confirms that the rate is independent of permanganate concentration.
Fig. 3. Permanganate Oxidation of Benzhydrol.

Typical Rate Plot.

$V_o - V_t$

$V_t - \frac{2}{5} V_o$

$T = 25^\circ$

Benzhydrol = $9.60 \times 10^{-4} M$

Permanganate = $6.40 \times 10^{-4} M$

$k_2 = 52.08 \text{ l.mole}^{-1}\text{min}^{-1}$. 
Fig. 4. Permanganate Oxidation of Benzydrol.

Typical Rate Plot.

$H_0 = -0.69$

$T = 25^\circ$

Benzydrol = $3.65 \times 10^{-4} M$

Permanganate = $2.43 \times 10^{-4} M$

$k_1 = 2.00 \times 10^{-3} \text{sec}^{-1}$. 
Fig. 5. Permanganate Oxidation of Benzhydrol.

Typical Rate Plot.

\[ H_0 = -0.69 \]

\[ T = 25^\circ \]

Benzhydrol = 3.65 x 10^{-4} M

Permanganate = 4.87 x 10^{-4} M

\[ k_1 = 1.99 \times 10^{-3} \text{ sec}^{-1} \]
In the intermediate region between $H_0$ 0.20 and -0.50, the kinetics appear to change gradually from second order to first order and the rate plots fail to classify the kinetics clearly. Typical rate plots of this region are shown in Figs. 6a and 6b.

(ii) **Chromic Acid Oxidation**: The rate of oxidation was studied in solutions containing 0.5 to 37.0% sulfuric acid in 80 wt% aqueous acetic acid. At these acidities the reaction was found to be of second order, first order with respect to each of the two reactants. Using the stoichiometric quantities of the substrate and Cr(VI), i.e. for the 3:2 ratio, the rate data were found to fit the integrated rate expression (1):

$$\frac{3}{2}kt = \frac{1}{[\text{Cr(VI)}]_t} - \frac{1}{[\text{Cr(VI)}]_0}$$

where $[\text{Cr(VI)}]_t = \text{concentration of Cr(VI) at time } t$

and $[\text{Cr(VI)}]_0 = \text{concentration of Cr(VI) at } t = 0$

Since $[\text{Cr(VI)}]_0$ is a constant for a particular reaction, the plot of $1/[\text{Cr(VI)}]_t$ against time gives a straight line and the second order rate constant was calculated from the observed slope of the line. A typical second order rate plot is shown in Fig. 7.

**Dependence of Rate on Acidity:**

(i) **Permanganate oxidation**: In the range of 1.4M to 5.4M aqueous sulfuric acid, the oxidation of benzhydrol is acid catalyzed. The concentration of permanganic acid is negligible
Fig. 6a. Permanganate Oxidation of Benzhydrol.

$H_0 = -0.01$

$T = 25^\circ$

First Order Rate Plot.

$k_1 = 1.93 \times 10^{-4} \text{ sec}^{-1}$
Fig. 6b. Permanganate Oxidation of Benzhydrol.

\[ H_0 = -0.01 \]

\[ T = 25^\circ \]

Second Order Rate Plot.

\[ k_2 = 9.76 \times 10^{-1}_1 \text{mole}^{-1}_1 \text{sec}^{-1} \]
Fig. 7. Chromic Acid Oxidation of Benzhydrol in 80 wt% Aqueous Acetic Acid containing Sulfuric Acid.

Typical Rate Plot.

$H_o = -0.90$

$T = 25^\circ$  

Benzhydrol = $2.50 \times 10^{-3} M$

Chromic Acid = $1.67 \times 10^{-3} M$

$k_2 = 2.22 \text{ l.mole}^{-1}\text{sec}^{-1}$
in this region and it seems reasonable to ascribe the increase
in rate to ionization of the carbinol. Table V gives the values
of the rate constants at different acidities. The plot of the
logarithm of the rate constants against acidity functions $H_0$
and $H_R$ are shown in Figs. 8 and 9 respectively.

TABLE V

Oxidation of Benzhydrol with Permanganate in Aqueous Sulfuric Acid.

Variation of Rate Constants with Acidity.

<table>
<thead>
<tr>
<th>$-H_0$ (123)</th>
<th>$-H_R$ (121)</th>
<th>$10^3 k \text{ sec}^{-1}$</th>
<th>log k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>0.70</td>
<td>1.07(*)</td>
<td>-2.997</td>
</tr>
<tr>
<td>0.50</td>
<td>1.10</td>
<td>1.21</td>
<td>-2.916</td>
</tr>
<tr>
<td>0.69</td>
<td>1.40</td>
<td>2.00</td>
<td>-2.699</td>
</tr>
<tr>
<td>0.81</td>
<td>1.55</td>
<td>3.11</td>
<td>-2.507</td>
</tr>
<tr>
<td>0.98</td>
<td>1.80</td>
<td>4.23</td>
<td>-2.374</td>
</tr>
<tr>
<td>1.00</td>
<td>1.90</td>
<td>5.52</td>
<td>-2.258</td>
</tr>
<tr>
<td>1.22</td>
<td>2.25</td>
<td>8.63</td>
<td>-2.064</td>
</tr>
<tr>
<td>1.67</td>
<td>3.20</td>
<td>18.97</td>
<td>-1.722</td>
</tr>
<tr>
<td>2.05</td>
<td>4.00</td>
<td>70.40</td>
<td>-1.152</td>
</tr>
<tr>
<td>2.46</td>
<td>4.90</td>
<td>248.40</td>
<td>-0.605</td>
</tr>
</tbody>
</table>

* - Not included in the plots in Figs. 9 and 10, because of the
poor kinetics due to contribution from second order reaction.
Fig. 8. Permanganate Oxidation of Benzhydrol.

Variation of Rate Constant with Acidity Function $H_0$.

$T = 25^\circ$

Slope = -1.13

Coeff. of Correlation = 0.996
Fig. 9. Permanganate Oxidation Benzhydrol.

Variation of Rate Constant with Acidity Function $H_R$.

$T = 25^\circ$

Slope = -0.58

Coeff. of Correlation = 0.995
From a comparison of Figs. 8 and 9, it is apparent that the operative acidity function in the range studied is $H_0$.

(ii) Chromic Acid Oxidation: The rate of oxidation of benzhydrol increases with increasing acidity of the medium in the range of 0.5% to 37.0% sulfuric acid in 80 wt% aqueous acetic acid. The variation of the second order rate constants with acidity is plotted in Figs. 10 and 11 using the acidity functions $H_0$ and $H_R$ respectively. The data for the plots are given in Table VI.

**TABLE VI**
Oxidation of Benzhydrol with Chromic Acid in 80 wt% Aqueous Acetic Acid.
Variation of Rate Constants with Acidity.

<table>
<thead>
<tr>
<th>$H_0$</th>
<th>$H_R$</th>
<th>$k_2$ l.mole$^{-1}$sec$^{-1}$</th>
<th>log $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td></td>
<td>0.088</td>
<td>-1.060</td>
</tr>
<tr>
<td>0.25</td>
<td></td>
<td>0.165</td>
<td>-0.783</td>
</tr>
<tr>
<td>-0.02</td>
<td></td>
<td>0.275</td>
<td>-0.560</td>
</tr>
<tr>
<td>-0.54</td>
<td>-2.15</td>
<td>0.740</td>
<td>-0.130</td>
</tr>
<tr>
<td>-1.12</td>
<td>-3.35</td>
<td>3.930</td>
<td>0.594</td>
</tr>
<tr>
<td>-1.70</td>
<td>-3.40</td>
<td>9.460</td>
<td>0.976</td>
</tr>
<tr>
<td>-2.00</td>
<td>-3.80</td>
<td>16.50</td>
<td>1.218</td>
</tr>
<tr>
<td>-2.15</td>
<td>-4.00</td>
<td>19.80</td>
<td>1.297</td>
</tr>
<tr>
<td>-2.70</td>
<td>-4.85</td>
<td>39.00</td>
<td>1.591</td>
</tr>
<tr>
<td>-3.00</td>
<td>-5.30</td>
<td>68.50</td>
<td>1.836</td>
</tr>
<tr>
<td>-3.30</td>
<td>-5.80</td>
<td>90.20</td>
<td>1.955</td>
</tr>
<tr>
<td>-3.40</td>
<td>-5.95</td>
<td>102.70</td>
<td>2.012</td>
</tr>
<tr>
<td>-3.60</td>
<td>-6.35</td>
<td>168.50</td>
<td>2.227</td>
</tr>
<tr>
<td>-4.20</td>
<td>-7.25</td>
<td>407.00</td>
<td>2.609</td>
</tr>
</tbody>
</table>
Fig. 10. Chronic Acid Oxidation of Benzhydrol.

Variation of Rate Constant with Acidity Function $H_o$.

$T = 25^\circ$

slope = -0.65

Slope = -1.00
Fig. 11. Chronic Acid Oxidation of Benzhydrol.

Variation of Rate Constant with Acidity Function $H_R$.

$T = 25^\circ$

Slope = -0.42

Slope = -0.69
Both Figs. 10 and 11 show a bend in the initial straight line. It appears that at acidities higher than 10% sulfuric acid in 80 wt% aqueous acetic acid the rate of increase of reaction rate with acidity is lower than that at lower acidities. However, from a comparison of the initial slopes of the two plots, it seems that the acidity function $H_Q$ gives a better correlation with the logarithm of rate-constants than $H_R$.

Substituent Effect:

(i) **Permanganate Oxidation**: The effect of different ring substituents on the rate of oxidation of benzhydrol was studied at pH 7.00 and 1.99, and $H_Q - 0.81$. The measured rate-constants are given in Table VII.

### TABLE VII

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma(124)$</th>
<th>$\sigma^+(124)$</th>
<th>$k_2$ $\text{mole}^{-1}\text{sec}^{-1}$</th>
<th>$\log k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>7.00</td>
<td>0.845</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>9.50</td>
<td>0.978</td>
</tr>
<tr>
<td>4-CO$_2$H</td>
<td>0.132</td>
<td>0.132</td>
<td>5.85</td>
<td>0.766</td>
</tr>
</tbody>
</table>
(2) \( \text{pH} 1.99 \)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \sigma(124) )</th>
<th>( \sigma^+(124) )</th>
<th>( k_{21} \text{ mole}^{-1}\text{sec}^{-1} )</th>
<th>( \log k_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>21.0</td>
<td>1.322</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>28.5</td>
<td>1.455</td>
</tr>
<tr>
<td>4-C\text{O}_2\text{H}</td>
<td>0.265</td>
<td>0.265</td>
<td>13.6</td>
<td>1.125</td>
</tr>
</tbody>
</table>

(3) \( \text{H}_0 -0.81 \)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \sigma(124) )</th>
<th>( \sigma^+(124) )</th>
<th>( 10^3 k \text{ sec}^{-1} )</th>
<th>( \log k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>3.11</td>
<td>-2.507</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>6.22</td>
<td>-2.207</td>
</tr>
<tr>
<td>4,4'-diMe</td>
<td>-0.34</td>
<td>-0.612</td>
<td>14.55</td>
<td>-1.837</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.226</td>
<td>0.112</td>
<td>2.42</td>
<td>-2.616</td>
</tr>
<tr>
<td>4,4'-diCl</td>
<td>0.452</td>
<td>0.224</td>
<td>1.46</td>
<td>-2.834</td>
</tr>
<tr>
<td>4-O\text{Me}</td>
<td>-0.268</td>
<td>-0.764</td>
<td>17.90</td>
<td>-1.747</td>
</tr>
<tr>
<td>4,4'-diO\text{Me}</td>
<td>-0.536</td>
<td>-1.528</td>
<td>98.50</td>
<td>-1.007</td>
</tr>
<tr>
<td>2,4,6,2',4',6'-hexaMe</td>
<td>1.40 (*)</td>
<td>-1.29 (**)</td>
<td>55.60</td>
<td>-1.253</td>
</tr>
<tr>
<td>4-C\text{O}_2\text{H}</td>
<td>0.265</td>
<td>0.265</td>
<td>1.43</td>
<td>-2.845</td>
</tr>
</tbody>
</table>

(*) Calculated from a comparison of pK values of benzoic acid and 2,4,6-trimethylbenzoic acid (125).

(**) Calculated from a comparison of pK\text{R}^+ values of diarylcarbinols (121).
The rate constant of the oxidation of 9-fluorenol was found to be $3.09 \times 10^{-3} \text{sec}^{-1}$, which is very close to that of benzhydrol. Because of the similar structure of 9-fluorenol and benzhydrol and their similar $pK_a^+$ values { -13.3 and -14.0 (121) }, it can be anticipated that the rates of ionization of these compounds would also be similar. The close agreement between their permanganate oxidation rates suggests that the ionization of the carbinols is the rate determining step in the permanganate oxidation of these compounds. Further evidence on this point will be discussed in a later section.

The Hammett plots are shown in Figs. 12, 13 and 14.

At lower acidities the operative substituent constant is $\sigma$, which gives a better straight line when plotted against the logarithm of rate-constants than when $\sigma^+$ is used. The plot is shown in Fig. 12. The substituted benzhydrols, other than 4-methyl and 4-carboxyl substituted ones, have very low solubilities in water and thus they were found to be unsuitable for studying the rate of oxidation in this medium.

At higher acidity, the operative substituent constant is $\sigma^+$, as shown by a comparison of Figs. 13 and 14, obtained by plotting the logarithm of the rate-constants against $\sigma$ and $\sigma^+$ respectively. The values of $\sigma$ and $\sigma^+$ for the hexamethyl substituted compounds are of opposite sign and this gives a clear indication of the operative substituent constant in this case as well as in the case of chromic acid oxidation of diarylcarbinols, discussed later.
Fig. 12. Permanganate Oxidation of Diarylcarbinols.

HANETT PLOT.

1 : pH = 7.00
2 : pH = 1.99
T = 25°

ρ = -0.78

log k₂

SIGMA
Fig. 13. Permanganate Oxidation of Diarylcarbinols.

HAMMETT PLOT.

$H_\circ = -0.81$

$T = 25^\circ$
Fig. 14. Permanganate Oxidation of Diarylcarbinols.

HAMMETT PLOT.

$H = -0.81$

$T = 25^\circ$

$\rho = -1.018$

Coeff. of Correlation = 0.998
(ii) **Chromic Acid Oxidation**: The rate constants of oxidation of substituted benzhydrols with chromic acid at $H_0 = -1.70$ are given in Table VIII. Figs. 15 and 16 show the Hammett plots, using $\sigma$ and $\sigma^+$ respectively.

**TABLE VIII**

Oxidation of Substituted Benzhydrols with Chromic Acid in 80 wt% Aqueous Acetic Acid.

$T = 25^\circ$

**HAMMETT PLOT**

$H_0 = -1.70$

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma$(124)</th>
<th>$\sigma^+$(124)</th>
<th>$k_2$, mole$^{-1}$sec$^{-1}$</th>
<th>log $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>9.46</td>
<td>0.976</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>11.20</td>
<td>1.049</td>
</tr>
<tr>
<td>4,4'-diMe</td>
<td>-0.34</td>
<td>-0.612</td>
<td>13.70</td>
<td>1.132</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.226</td>
<td>0.112</td>
<td>6.60</td>
<td>0.820</td>
</tr>
<tr>
<td>4,4'-diCl</td>
<td>0.452</td>
<td>0.224</td>
<td>4.17</td>
<td>0.620</td>
</tr>
<tr>
<td>2,4,6,2',4',6'-hexaMe</td>
<td>1.40 (*)</td>
<td>-1.29 (**)</td>
<td>1.63</td>
<td>0.212</td>
</tr>
</tbody>
</table>

(*) and (**) : Calculated in the same way as in Table VII.

It was not possible to study the chromic acid oxidations of 4-methoxybenzhydrol and 4,4'-dimethoxybenzhydrol under the same conditions as the other carbinols, since the methoxy group apparently forms
Fig. 15. Chromic Acid Oxidation of Diarylcarbinols.

HAMILTON PLOT.

\( H_0 = -1.70 \)

\( T = 25^\circ \)

\( \rho = -0.54 \)

Coeff. of Correlation = 0.993
Fig. 16. Chromic Acid Oxidation of Diarylcarbinols.

HANMETT PLOT.

$H_0 = -1.70 \quad T = 25^\circ$
a colored complex with chromium(VI). The complex was found to have a considerable absorbance at the wavelength used for kinetic studies, i.e., 350 μm. A similar complex was also found to be formed when chromium(VI) was added to an acetic acid solution of anisole.

From the two Hammett plots shown in Figs. 15 and 16, it is apparent that the better linear relation is given when the substituent constant σ is used.

Isotope Effect:

(i) Permanganate Oxidation: Benzhydrol-α-d was oxidized at different acidities ranging from pH 7.00 to H_0 = -1.22. The observed deuterium isotope effects are given in Table IX.

**TABLE IX**

Oxidation of Benzhydrol with Permanganate in Aqueous Sulfuric Acid.

\[ T = 25^\circ \]

Deuterium Isotope Effect.

<table>
<thead>
<tr>
<th>Acidity</th>
<th>[ k_1(H)/k_1(D) ]</th>
<th>[ k_2(H)/k_2(D) ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 7.00</td>
<td>-</td>
<td>7.3</td>
</tr>
<tr>
<td>pH 1.99</td>
<td>-</td>
<td>7.1</td>
</tr>
<tr>
<td>H_0 0.30</td>
<td>2.46</td>
<td>2.25</td>
</tr>
<tr>
<td>H_0 -0.01</td>
<td>1.20</td>
<td>1.08</td>
</tr>
<tr>
<td>H_0 -0.50</td>
<td>1.08</td>
<td>-</td>
</tr>
<tr>
<td>H_0 -0.81</td>
<td>1.09</td>
<td>-</td>
</tr>
<tr>
<td>H_0 -1.22</td>
<td>1.08</td>
<td>-</td>
</tr>
</tbody>
</table>
Since in the region between $H_o$ 0.20 and -0.50 the kinetics are neither first nor second order, the isotope effects were calculated in both ways, i.e. from the estimated first and second order rates.

(ii) Chromic Acid Oxidation: Benzhydrol-α-d was oxidized with chromic acid at $H_o$ -1.00; the isotope effect at 25° was found to be 6.81 at this acidity.

Activation Parameters:

(i) Permanganate Oxidation: The activation parameters of permanganate oxidation of benzhydrol at pH 13.0, 7.0, 1.5 and $H_o$ -2.05 (in sulfuric acid) were determined by studying the reaction over a wide range of temperature. The enthalpies and entropies of activation were obtained from plots of $\log(k/T)$ against $1/T$. Fig. 17 shows the plot for the reaction at $H_o$ -2.05. Table X lists the values of the activation parameters at different acidities.

**TABLE X**

<table>
<thead>
<tr>
<th>Oxidation of Benzhydrol with Permanganate.</th>
<th>Activation Parameters.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acidity</td>
<td>Reaction Order</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>pH 13.00</td>
<td>Second</td>
</tr>
<tr>
<td>pH 7.00</td>
<td>Second</td>
</tr>
<tr>
<td>pH 1.50</td>
<td>Second</td>
</tr>
<tr>
<td>$H_o$ -2.05</td>
<td>First</td>
</tr>
</tbody>
</table>
Fig. 17. Permanganate Oxidation of Benzhydrol.

Variation of Rate Constant with Temperature.

\[ H_0 = -2.05 \]

\[ \Delta H = 17.5 \text{ kcal/mole}. \]

\[ \Delta S = -13.5 \text{ e.u.} \]
The values of activation parameters obtained at pH 13.0 are in good agreement with the values of $\Delta H^\ddagger$ (5.7 kcal/mole) and of $\Delta S^\ddagger$ (-33.4 e.u.) found by Stewart (4).

The reaction at $H_0$ -2.05 is of first order and as will be discussed later, the rate determining step in the reaction is the ionization of the carbinol. Hence the activation parameters obtained for this reaction are actually those for the ionization of the carbinol rather than for the reaction with permanganate. The rate constants at $H_0$ -2.05 at different temperatures are given in Table X(a).

### TABLE X(a)

Permanganate Oxidation of Benzhydrol.

Variation of Rate Constant with Temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$10^2k$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>3.00</td>
</tr>
<tr>
<td>25</td>
<td>7.04</td>
</tr>
<tr>
<td>35</td>
<td>18.10</td>
</tr>
<tr>
<td>45</td>
<td>34.00</td>
</tr>
</tbody>
</table>

(ii) **Chromic Acid Oxidation**: The activation parameters of chromic acid oxidation of benzhydrol were determined.
for the reaction at $H^0 = -0.90$. Fig. 18 shows the plot of $\log(k'/k)$ against $1/T$. The values of $\Delta H$ and $\Delta S$ obtained are 5.9 kcal/mole and -37.1 e.u., respectively. The rate constants at different temperatures are given in Table X(b).

**TABLE X(b)**

**Chromic Acid Oxidation of Benzhydrol.**

Variation of Rate Constant with Temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$k_2$, mole$^{-1}$sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.50</td>
</tr>
<tr>
<td>25</td>
<td>2.20</td>
</tr>
<tr>
<td>27</td>
<td>2.44</td>
</tr>
<tr>
<td>43</td>
<td>4.11</td>
</tr>
</tbody>
</table>

**Ionization of 4-Methoxybenzhydrol.**

Since carbonium ion formation seems to be an important part of the oxidation route of diarylcarbinols (as will become apparent in the Discussion), it was decided to study the rate at which ionization of the carbinols to carbonium ions occurs.

The rates of ionization of 4-methoxybenzhydrol were determined in 70 vol% aqueous methanol containing sulfuric acid ranging from 1.8 to 3.6M. The reaction was found to be of first
Fig. 18. Chronic Acid Oxidation of Benzhydrol.

Variation of Rate Constant with Temperature.

$H_0 = -0.90.$

$\Delta H = 5.9 \text{ kcal/mole}$

$\Delta S = -37.1 \text{ e.u.}$
order in carbinol concentration. The following first order rate expression was used to obtain the rate constants:

$$kt = 2.303 \log \frac{A_\infty}{A_t}$$

where $A_\infty = \text{absorbance at infinite time}$,

$A_t = \text{absorbance at time } t$.

Since $A_\infty$ is a constant for a particular reaction, $\log(A_\infty - A_t)$ was plotted against time to obtain a straight line. The rate constant was calculated from the slope of the line. A typical rate plot is shown in Fig. 19.

In the range of acidity studied, the rate of ionization was found to be acid catalyzed. The variation of rate constant for ionization with acidity is shown in Figs. 20 and 21, using the acidity function $H_O$ and $H_R$ respectively. The data for the two plots are given in Table XI.

**TABLE XI**

Ionization of 4-Methoxybenzhydrol.

Variation of Rate Constant with Acidity.

\(T = 25^\circ\)

<table>
<thead>
<tr>
<th>$-H_O$</th>
<th>$-H_R(*$)</th>
<th>$-H_R(**)$</th>
<th>$10^3 k$ sec$^{-1}$</th>
<th>log $k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>0.58</td>
<td>0.63</td>
<td>3.22</td>
<td>-2.492</td>
</tr>
<tr>
<td>0.38</td>
<td>0.98</td>
<td>0.89</td>
<td>5.99</td>
<td>-2.223</td>
</tr>
<tr>
<td>0.50</td>
<td>1.25</td>
<td>1.02</td>
<td>7.94</td>
<td>-2.100</td>
</tr>
</tbody>
</table>
Fig. 19. Ionization of p-Methoxybenzhydrol in 70 vol% Aqueous Methanol Containing Sulfuric Acid.

\[ \text{H}_2\text{SO}_4 = 2.16 \text{M} \]

\[ H^0 = -0.38 \]

\[ T = 25^\circ \]

\[ \text{p-Methoxybenzhydrol} = 6.0 \text{M} \]

\[ k_1 = 5.99 \times 10^{-3} \text{sec}^{-1} \]
Fig. 20. Ionization of p-Methoxybenzhydrol.

Variation of Rate Constant with Acidity Function $H_0$.

$T = 25^\circ$

Slope = -1.00

Coeff. of Correlation = 0.998
Fig. 21. Ionization of p-Methoxybenzhydrol.

Variation of Rate Constant with Acidity Function $H_R$.

$T = 25^\circ$

Slope = -0.48

Coeff. of Correlation = 0.990
TABLE XI (Cont.)

<table>
<thead>
<tr>
<th>$-H_0$</th>
<th>$-H_R(*)$</th>
<th>$-H_R(**)$</th>
<th>$10^3 k$ sec$^{-1}$</th>
<th>log k</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.64</td>
<td>1.65</td>
<td>1.78</td>
<td>10.60</td>
<td>-1.975</td>
</tr>
<tr>
<td>0.82</td>
<td>1.94</td>
<td>2.01</td>
<td>15.90</td>
<td>-1.799</td>
</tr>
</tbody>
</table>

(*) Determined by using 4,4'-dimethoxytriphenylchloromethane as indicator (Table IV, p.49).

(**) Calculated from $A^\alpha$ values, a typical calculation is shown below:

In the solution containing 2.88M sulfuric acid in 70 vol% aqueous methanol, the final absorbance of the carbonium ion $(4-\text{CH}_3\text{O-C}_6\text{H}_4)^+\text{C-C}_6\text{H}_5$, $A^\alpha$ is 0.040. The acidity function $H_R$ is defined as (121):

$$H_R = pK^+ + \log \frac{C^+}{C_{ROH}}$$

$$C^+_R = \frac{A^\alpha}{e}$$

where $e$, the extinction coefficient of the carbonium ion in the medium used, was found to be $3.5 \times 10^4$. Thus, $C^+_R = 1.14 \times 10^{-6}$ moles. litre$^{-1}$.

$$C_{ROH} = \text{Initial concentration of the carbinol} - C^+_R \text{ (negligible)} = 1.50 \text{M}$$
\[ \frac{C_{R^+}}{C_{ROH}} = 7.60 \times 10^{-6} \]

\[ \log \frac{C_{R^+}}{C_{ROH}} = -5.12 \]

\[ \text{pK}_{R^+} = -7.90 \text{ (121)} \]

Hence, \[ H_R = -7.90 + 5.12 = -1.78 \]

From a comparison of the slopes of the lines and the correlation coefficients shown in Figs. 20 and 21, it is evident that the operative acidity function for the reaction under investigation is \( H_O \). With this function a unit slope is obtained with a correlation coefficient of 0.997. The \( H_R \) plot, on the other hand, yields a slope of -0.48 and a correlation coefficient of 0.990.
It has been shown by Stewart (4) that the permanganate oxidation of benzhydrol in basic, neutral and weakly acidic regions is of second order, first order with respect to each of the reactants. The kinetics show the presence of hydroxyl ion catalysis in the basic region.

In the present investigation the permanganate oxidation of benzhydrol and its derivatives in strongly acidic region is studied. The product analysis showed that the conversion of the diarylcarbinols to the corresponding benzophenones is quantitative, and hence the stoichiometry of the reaction is:

\[ 3\text{Ar}_2\text{CHOH} + 2\text{MnO}_4^- + 2\text{H}^+ \rightarrow 3\text{Ar}_2\text{C}=\text{O} + 2\text{MnO}_2 + 4\text{H}_2\text{O} \]

In addition, the permanganate oxidation of benzhydrol has been shown to be acid-catalyzed, with the rate of this reaction being directly proportional to the carbinol concentration but independent of permanganate concentration. Thus it appears that the acid-catalysis is not due to the formation of permanganic acid. It is likely that the increase in rate that accompanies a rise in acidity is due to the ionization of the carbinol and that this is the rate-determining step in these reactions. Furthermore,
the small isotope effect, $k_H/k_D = 1.08$, shows that the cleavage of the carbon-hydrogen bond does not occur in the rate-determining step.

The rate of ionization of 4-methoxybenzhydrol has been found to be almost equal to the rate of oxidation of the carbinol at the same acidity ($k_{\text{oxidation}} = 1.79 \times 10^{-2}\text{sec}^{-1}$, $k_{\text{ionization}} = 1.59 \times 10^{-2}\text{sec}^{-1}$ at $H_0 = -0.81$). Unfortunately, it was not possible to use the same medium in the study of both oxidation and ionization reactions. The aqueous medium used for the oxidation would not dissolve sufficient carbinol to enable the ionization study to be made and the aqueous methanolic system, used for the latter, was subject to oxidation by permanganate. However, the rates of the two reactions were compared where the two media, namely aqueous sulfuric acid and 70 vol% aqueous methanol containing sulfuric acid, have the same values of the acidity function $H_0$. Since the two rates at the same acidities were found to be reasonably close to each other, it suggests that the ionization of the carbinols is the rate-determining step in the permanganate oxidations. Moreover, both oxidation and ionization reactions of the diarylcarbinols under investigation follow the acidity function $H_0$. Since $pK_{R+}$ values of the carbinols indicate that a much higher acidity is required for a considerable extent of carbonium ion formation than that used as the reaction media in this investigation, it
is probable that the carbinol undergoes a rate-controlling scission of the protonated carbinol. The steps can be represented as:

\[ \text{Ar}_2\text{CHOH} + \text{H}_3\text{O}^+ \rightarrow \text{Ar}_2\text{CHOH}_2 + \text{H}_2\text{O} \]

\[ \begin{align*}
\text{Ar}_2\text{CHOH}_2 & \quad \text{slow} \quad [\text{Ar}_2\text{CH} \ldots \text{OH}_2] \quad \text{fast} \quad \text{Ar}_2\text{CH} + \text{H}_2\text{O} \\
\text{Transition state} & \\
\text{Ar}_2\text{CH} + \text{MnO}_4^- & \quad \text{fast} \quad \text{Ar}_2\text{CHO MnO}_3 & \quad \text{fast} \quad \text{Ar}_2\text{C} = \text{O} + \text{MnO}_3^- + \text{H}^+ \\
\end{align*} \]

The rapid decomposition of the ester may proceed as follows:

\[ \begin{align*}
\text{Ar} & \quad \text{Ar} \\
\text{CHO MnO}_3 & \quad \delta^+ \quad \delta^- \\
\text{Ar} & \quad \text{Ar} \\
\text{C} = \text{O} + \text{MnO}_3^- \\
\text{I} & \\
\text{Ar} & \quad \text{Ar} \\
\text{C} = \text{OH} & \quad \rightarrow \quad \text{C} = \text{O} + \text{H}^+ \\
\end{align*} \]
The MnO₃⁻ disproportionates to give MnO₂ and MnO₄⁻.

The manganate ester decomposition takes place after the rate-determining step and it is not possible to ascertain from the rate studies whether the hydride shift is 1,2-shift, as shown in I, or a 1,4-shift (see later discussion on the analogous chromic acid reaction, p.92).

It has been shown that the operative acidity function in this region is $H_0$. This is in agreement with the fact that the protonated alcohols, similar to oxonium ions, are involved in the rate-determining step.

It is apparent from the above mechanism that the presence of electron-donating ring substituents will facilitate the reaction by stabilizing the positive centre of the cation. This is supported by the observed value of $\rho^+ = -1.02$. The operative substituent constant in this reaction is $\sigma^+$ which shows that the positively charged reaction centre is stabilized by the electron-donating groups through resonance. It is usually found that the substituent constant $\sigma^+$ is operative in those cases where the reaction follows the acidity function $H_R$ rather than $H_0$. However, Nishida (126) has shown that the solvolysis
of monosubstituted benzhydryl chlorides also follows the substituent constant $\sigma^+$ under conditions where full ionization to carbonium ion is not possible, and hence $H_R$ cannot be the operative function. In the light of this observation of Nishida, it appears that the proposed mechanism of the present investigation, which follows the acidity function $H_0$, is not in conflict with the observation that the operative substituent constant in this case is $\sigma^+$.

In neutral and weakly acidic regions, i.e., at pH 7.00 and 1.99 respectively, the reactions are of second order, first order in each of the reactants. The operative substituent constant in these cases is $\sigma$. It has been shown that the reactions are almost independent of pH in these regions (4). In general, an alcohol molecule can ionize in two ways; in basic systems, the ionization leads to the formation of an anion:

$$R_2CHOH + OH^- \rightarrow R_2CHO^- + H_2O$$

whereas in acidic medium, protonation, sometimes followed by carbonium ion formation, takes place:

$$R_2CHOH + H^+ \rightarrow R_2CHOH_2^+ \rightarrow R_2CH^+ + H_2O$$

In neutral and weakly acidic regions, neither of the two types of ionization can take place to an appreciable extent, and hence in these regions the permanganate-alcohol reactions are very slow. A
hydride abstraction from the neutral alcohol molecule can be suggested for the reaction:

\[
\begin{align*}
\text{Ar}_2\text{C} \quad &\text{OH} \\
\text{Ar}_2\text{C} = \text{OH} + \text{HMnO}_4^– &\rightarrow \text{Ar}_2\text{C} = \text{O} + \text{H}_2\text{O} + \text{MnO}_3^- \\
\text{H} &\quad \text{MnO}_4^–
\end{align*}
\]

The kinetic isotope effects at pH 7.00 and 1.99 were found to be 7.3 and 7.1 respectively; this suggests the cleavage of carbon-hydrogen bond is the rate determining step. The Hammett \( \rho \) values for the reaction at these two acidities were found to be -0.72 and -0.78 respectively. These values are close to the observed \( \rho \) values for hydride abstraction reactions \( (86, 89, 94b, 127) \).

Between the acidities of \( \text{H}_2\text{O} \ 0.40 \) and -0.50, the kinetics change from second order to first order and this is accompanied by a gradual change in the kinetic isotope effect (Table IX).

The activation parameters, listed in Table X, reflect the changes in the reaction rates at different acidities. However, the values of \( \Delta H \) (17.5 kcal/mole) and \( \Delta S \) (-13.5 e.u.) for this reaction are somewhat different from those of the solvolysis reactions of benzhydryl chloride and bromide in acidic media, reported by Winstein and others (127a). These are also believed to proceed by \( S_{N1} \) mechanism and have higher positive values of \( \Delta H \) (~20 kcal/mole) \( \dagger \) and lower negative values of \( \Delta S \) (~6 to -10.2 e.u.) than those found
in the present investigation. This difference may be due to the difference in solvent and leaving groups. In the work of Winstein et al. the leaving group is halogen, whereas in the present case it is a water molecule. The carbon-halogen bond is more polar than carbon-oxygen bond. The work of Winstein et al. (127a) also reveals a change in $\Delta S$ when the leaving group is changed from chlorine to bromine; in the latter case a less negative value of $\Delta S$ is obtained as the bond polarity is increased. In ethanol $\Delta S$ for benzhydryl chloride solvolysis is $-7.9$ e.u. and in the case of benzhydryl bromide it is $-2.6$ e.u. Robertson has also reported activation parameters for solvolysis reactions of a large number of halides (127b). The results show a gradual decrease in the negative value of $\Delta S$ as the leaving halogen changes from fluorine to iodine. For example, the $\Delta S$ values for hydrolysis of methyl fluoride, methyl chloride, methyl bromide and methyl iodide in water are $-26.2$ e.u., $-12.3$ e.u., $-10.1$ e.u. and $-8.1$ e.u. respectively.

The chromic acid oxidation of benzhydrol has been found to be of second order, first order in each of the carbinol and chromium(VI). The product analysis showed the formation of only one product, the corresponding benzophenone, as in the case of permanganate oxidation. The stoichiometry can be represented as:

$$3\text{Ar}_2\text{CHOH} + 2\text{CrO}_4^{2-} + 10\text{H}^+ \rightarrow 3\text{Ar}_2\text{CO} + 2\text{Cr}^{3+} + 8\text{H}_2\text{O}$$
The kinetic isotope effect, $k_H/k_D = 6.81$, obtained by using benzhydrol-$\alpha$-d, shows the cleavage of carbon-hydrogen bond in the rate-determining step.

The reaction has been found to be acid-catalyzed, and a better relationship is shown between the rate constant and the acidity function $H_O$, rather than $H_R$, although a sharp change in slope is observed at $H_O = -1.12$. A similar change has been observed in the chromic acid oxidation of other secondary alcohols (44,91). According to previous workers, the mechanism of chromic acid oxidation of secondary alcohols involves the formation of a chromate ester intermediate, which decomposes unimolecularly to products (44,76,89,91,128) via the cyclic mechanism (see p.22, in "Introduction"):

\[
\text{R}_2\text{C}^\cdot\text{CrO}_2^\cdot\xrightarrow{H^+}\text{R}_2\text{C}^\cdot\text{CrO}_2^\cdot\text{H}^+\xrightarrow{\text{H}_2}\text{R}_2\text{C} = \text{O} + \text{H}_3\text{CrO}_3^+
\]

At higher acidities diprotonation of the chromate part of the ester(II) occurs, and this would cause a decrease in rate (as observed with some secondary alcohols (44,91)), since there is no unprotonated oxygen atom available for participation in the hydrogen transfer in (III) :

\[
\text{R}_2\text{C}^\cdot\text{CrO}_2^\cdot\xrightarrow{H^+}\text{R}_2\text{C}^\cdot\text{CrO}_2^\cdot\text{H}^+\xrightarrow{\text{H}_2}\text{R}_2\text{C} = \text{O} + \text{H}_3\text{CrO}_3^+
\]
It may be, however, that the intermediate chromate ester decomposes through the cyclic transition state (IV), by a 1,2-hydride shift:

\[
\begin{align*}
\text{Ar}_2\text{C} = \text{O} - \text{CrO}_3\text{H}_2 & \rightarrow \text{Ar}_2\text{C} = \delta^+ \rightarrow \text{Ar}_2\text{C} = \delta^+ \rightarrow \text{Ar}_2\text{C} = \text{OH} + \text{H}_2\text{CrO}_3 \\
\text{Ar}_2\text{C} = \text{OH} & \rightarrow \text{Ar}_2\text{C} = \text{O} + \text{H}_2\text{O}^+
\end{align*}
\]

The 1,2-hydride shifts occur with great ease in many rearrangement reactions, like Baeyer-Villiger oxidation of aldehydes (128a). The usual products are carboxylic acids, formed by hydride migration. Formate esters are formed only when the mobility of an aryl group is strongly increased by electron-releasing substituents (128b). The following mechanism has been proposed for the oxidation of carbonyl compounds to esters, or acids by means of peroxo acid (128c):

\[
\begin{align*}
\text{Ar}_2\text{C} = \text{OH} & \rightarrow \text{Ar}_2\text{C} = \text{O} + \text{H}_2\text{O}^+
\end{align*}
\]

The mechanism involves a series of steps, including deprotonation and proton transfer, leading to the formation of the ester or acid.
The probability of a 1,2-hydride shift being the mode of oxidation of secondary alcohols was suggested by the results of the study of oxidation of triarylcarbinols, to be discussed in Section II. In these cases, the evidence suggests that 1,2-aryl shifts occur.

The greater mobility of hydride ion compared to that of an aryl group for a 1,2-hydride shift agrees with the observations of the present investigation, where no detectable aryl migration, leading to the formation of aldehyde as the oxidation product of diarylcarbinols, was observed.

A comparison of Baeyer-Villiger oxidation of ketones and aldehydes and the reaction under the present investigation seems reasonable, since in both the cases there is a migration of hydride ion or aryl group from carbon to the adjacent oxygen atom carrying positive charge.

On protonation of the chromate part of ester (II), the electron attracting property of chromium increases, resulting in an
increase in the rate of oxidation.

At higher acidities, protonation of the central oxygen atom might occur, which causes a slower increase in rate, as shown in Fig. 10. Thus protonation affects the rate of oxidation in the same way as in the case of other alcohols investigated, and discussed before (44,91), i.e., by reducing the hydrogen abstracting property of the oxygen.

According to the proposed mechanism electron-donating ring substituents are likely to enhance the rate of oxidation. The negative value of $\rho = -0.54$, obtained from the Hammett plot using substituted diarylcarbinols, is in good agreement with the mechanism. Also, the value of the entropy of activation for the chromic acid oxidation of benzhydrol, $\Delta S = -37.1$ e.u. is within the range for other secondary alcohols, i.e., -35.7 to -42.0 e.u., reported by D.G. Lee (129). The value for $\Delta H$ for the present reaction was found to be 5.9 kcal/mole, whereas those reported by D.G. Lee are between 8.15 to 10.38 kcal/mole (129).
SECTION II

OXIDATION OF TRIARYLCARBOXYLIC ACIDS
EXPERIMENTAL

Materials:

Triphenylcarbinol was crystallized from petroleum ether to constant melting point 164-5°.

The following triarylcarbinols were prepared by Grignard reaction from available starting materials, as described below:

Tri(4-tolyl)carbinol: from 4,4'-dimethylbenzophenone and 4-tolylmagnesiumbromide; yield 40%, m.p. 95°, lit. 96° (130).

4,4'-Dimethyltriphenylcarbinol: from 4,4'-dimethylbenzophenone and phenylmagnesiumbromide; yield 59%, m.p. 76°, lit. 76.5 - 77.5° (131).

4-Methyltriphenylcarbinol: from 4-methylbenzophenone and phenylmagnesiumbromide; yield 56.7%, m.p. 60 - 61°, lit. 61 - 62° (132).

4-Chlorotriphenylcarbinol: from 4-chlorobenzophenone and phenylmagnesiumbromide; yield 52%, m.p. 85°, lit. 85° (133).

4,4'-Dichlorotriphenylcarbinol: from 4,4'-dichlorobenzophenone and phenylmagnesiumbromide; yield 49%, m.p. 86.5°, lit. 87 - 88° (134).

Tri(4-chlorophenyl)carbinol: from 4,4'-dichlorobenzophenone and 4-chlorophenylmagnesiumiodide; yield 70%, m.p. 93°, lit. 93.5 - 94° (121).
Tri(3-chlorophenyl)carbinol: from 3-chlorophenylmagnesium-iodide and ethyl carbonate; yield 35%, the product after purification was found to be an oil which tends to decompose on heating, and hence its boiling point could not be ascertained. The ultraviolet spectrum of concentrated sulfuric acid solution of the oil showed a maximum at 412 µm, $e_{\text{max}} = 2.92 \times 10^4$, lit. $2.95 \times 10^4$ (121). Analysis: calc. C, 62.78%; H, 3.58%; Cl, 29.35%; found C, 62.69%; H, 3.60%; Cl, 29.40%.

4-Fluorotriphenylcarbinol: from 4-fluorobenzophenone and phenylmagnesiumbromide; yield 53%, m.p. 122°C, lit. 121 - 122°C (135).

Tri(4-biphenylyl)carbinol: from ethyl carbonate and 4-biphenylylmagnesiumbromide; yield 41%, m.p. 211°C, lit. 212°C (136).

3-Trifluoromethyl-4'-methyltriphenylcarbinol: from 4-methylbenzophenone and 3-trifluoromethylphenylmagnesiumbromide; yield 41%, b.p. 184°C/0.8mm. Analysis: calc. C, 73.7%; H, 4.97%; F, 16.7%; found C, 73.5%; H, 5.11%; F, 16.9%.

The following compounds were prepared by Mr. I. Beheshti in these laboratories:

4-Nitrotriphenylcarbinol: following the method of Starnes (114), yield 70%, m.p. 96°C, lit. 97 - 100°C (114).

3-Trifluoromethyltriphenylcarbinol: from benzophenone and 3-trifluoromethylphenylmagnesiumbromide; yield, 61%, b.p. 120°C/0.2mm. Analysis: calc. C, 73.17%; H, 4.57%; F, 17.37%; found C, 73.14%; H, 4.87%; F, 17.14%.
Standard solutions of potassium permanganate and potassium dichromate were prepared in the same way as mentioned in Sec. 1.

A standard solution of manganous acetate was prepared by dissolving a weighed quantity of manganous carbonate in acetic acid. Manganous carbonate was prepared by adding a solution of sodium carbonate to that of manganous chloride in water till the precipitation of manganous carbonate was complete. The precipitate was washed with water, dried under vacuum and tested for its purity by dissolving a known quantity of it in dilute sulfuric acid and titrating the solution with standard potassium permanganate solution in presence of fluoride ions, following Zvenigorodskaya's method (137).

**Kinetic Methods**:

The methods employed were essentially the same as those used in the case of the diarylcarbinols, described in Sec. 1. In the case of permanganate oxidations, the reactions appeared to speed up with time due to the consumption of permanganate by phenol produced during reaction (1). For this reason only the initial slopes of the rate plots were taken into consideration.

The solutions for chromic acid oxidation of triarylcarbinols were prepared in the same way as the diarylcarbinols, the only difference was that the reactions were studied as pseudo first order reactions, using an excess of carbinol. This was done
in order to avoid the following complications, as mentioned by Cohen and Westheimer (45): the chromic acid oxidation reactions consume hydrogen ions, and thus the concentration of these ions changes as the reaction proceeds. This consumption of hydrogen ions occurs due to the reaction of acetic acid with chromium(III) which is obtained as the reduction product of chromic acid:

$$2\text{HCrO}_4^- + 2\text{R}_2\text{CHOH} + 8\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{R}_2\text{CO} + 8\text{H}_2\text{O}$$

$$\text{Cr}^{3+} + 3\text{HOAc} \leftrightarrow \text{Cr(OAc)}_3 + 3\text{H}^+$$

In the presence of a large quantity of acid or buffer, the hydrogen ion concentration remains almost constant during the reaction. With low concentration of chromic acid, the change in acidity is very small; moreover, unlike the case of diarylcarbinols, oxidation of triarylcarbinols produces phenols (as shown later) which also consume chromium(VI) and thus increase the concentration of chromium(III) in the system. For these reasons, an excess of carbinol was used. Most previous workers have used similar method (44, 45, 90, 91). The true second order rate constants were obtained by dividing the observed rate constants by the initial concentration of the carbinol.

The extinction coefficient of \(\text{CrO}_4^{2-}\) at 350\(\mu\)m is \(3.33 \times 10^3\), whereas that of \((\text{C}_6\text{H}_5)_3\text{C}^+\) at the same wavelength is \(1.03 \times 10^2\), hence
it is apparent that the change of concentration of \((\text{C}_6\text{H}_5)_3\text{C}^+\) has very small effect on the decrease in absorbance at 350\text{m}u. All the other triarylcarbinols investigated had a similar absorbance at 350\text{m}u.

**Product Analysis:**

(i) **Chromic Acid Oxidation**: A weighed quantity (0.001 mole) of the carbinol under investigation was dissolved in 85ml of 80 wt% aqueous acetic acid in a 250ml Erlenmeyer flask. To the solution 15ml of 99.9% sulfuric acid was added slowly and with constant stirring. This gave a solution containing approximately 23% sulfuric acid. Next 0.10g potassium dichromate dissolved in 3ml of 80 wt% acetic acid in water containing 0.5ml of 99.9% sulfuric acid was added. A slight excess of chromic acid was used in order to ensure complete oxidation of the carbinol, since some of the oxidant is consumed by the phenols produced. The mixture was allowed to stand for several days till the yellow color of the solution changed to green. After this time the mixture was diluted with water and extracted several times with ligroin. The extract was treated with dilute sodium bicarbonate solution to remove acid. Next the extract was washed with 10% sodium hydroxide solution to remove any phenol formed. The ligroin extract was evaporated to dryness and the infra-red spectrum of the residue was taken. In the case of the unsubstituted carbinol, i.e. tri-phenylcarbinol, the residue of the ligroin extract was dissolved
in a small quantity of ether and treated with 2,4-dinitrophenylhydrazine and the derivative was separated and purified according to Vogel (119). The 2,4-dinitrophenylhydrazone was weighed and its melting point was determined.

For the unsymmetrically substituted triphenylcarbinols the residue of the ligroin extract was dissolved in ether and transferred quantitatively to a volumetric flask, the capacity of which depended on the quantity of the product. The ether solution was analyzed by vapor-phase chromatography using "Aerograph: Autoprep model A-700" equipped with a stainless steel column 5 ft. x 25 in. (o.d.), packed with SE-30 (15%) on chromosorb W (45-60 mesh). The carrier gas used was helium. Column temperature was varied according to the constituents of the samples. The following list shows the maximum column temperature employed to analyze the products from the different triarylcarbinols:

<table>
<thead>
<tr>
<th>Triarylcarbinol</th>
<th>Column Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Methyltriphenylcarbinol</td>
<td>230°</td>
</tr>
<tr>
<td>4,4'-Dimethyltriphenylcarbinol</td>
<td>230°</td>
</tr>
<tr>
<td>4-Chlorotriphenylcarbinol</td>
<td>200°</td>
</tr>
<tr>
<td>3-Trifluoromethyl-4'—methyltriphenylcarbinol</td>
<td>200°</td>
</tr>
<tr>
<td>4-Nitrotriphenylcarbinol</td>
<td>225°</td>
</tr>
<tr>
<td>3-Trifluoromethyltriphenylcarbinol</td>
<td>170°</td>
</tr>
</tbody>
</table>
The exact quantities of each component of the products were determined by measuring the areas of the peaks and comparing them with those obtained from known quantities of the corresponding compounds.

The alkali washings of the ligroin extract were acidified with dilute hydrochloric acid and extracted with ether. The ether extract was analyzed for phenols by preparing the corresponding bromo-derivatives, according to Vogel (119). Since phenols are known to react with chromic acid to some extent, only a qualitative estimate of their presence was possible, and this showed the existence of the predominating species only.

Chromic acid oxidations were also carried out in the presence of added manganous ions. The products were isolated and analyzed in the same way as in the case of chromic acid oxidation without any added salt.

(ii) Permanganate Oxidation: Since both the expected products of oxidation of triarylcarbinols react with permanganate to a certain extent, an exact quantitative determination of the products was not possible. However, a qualitative estimate was made. A weighed quantity (approx. 0.0002 mole) of triarylcarbinol was dissolved in 40ml of 18.01M sulfuric acid in a 500ml Erlenmeyer flask, kept immersed in an ice-bath. Water was added slowly to the solution with continuous stirring until the final volume was 200ml.
Next 0.011 M potassium permanganate solution was added to it slowly until the solution attained a faint pink color, indicating that the carbinol had reacted completely. The products were extracted with ligroin and the ketones produced were identified as their 2,4-dinitrophenylhydrazones, although in this process only the predominating ketones were identified, the minor fractions being eliminated during the process of purification. Moreover, benzophenones with different substituents react with permanganate at different rates, which made the quantitative estimation of the products more difficult. The identification of the predominating benzophenone was also done by dissolving a small quantity of the residue of ligroin extract in concentrated sulfuric acid and observing the ultra-violet spectrum of the protonated species.

The phenol fraction of the products was not possible to isolate and identify because of the rapid reaction of phenols with permanganate (1).
RESULTS

Product Analysis:

(i) **Chromic Acid Oxidation**: The 2,4-dinitrophenyl-hydrazone of the ketone produced from triphenylcarbinol melted at 238°, and it was identified to be the derivative of benzo-phenone, m.p. 239° (119). The bromo derivative of the phenol produced melted at 94-5°, identified as the trihromo derivative of phenol, m.p. 95° (119).

The results of vapor phase chromatographic analysis of the ketones produced from unsymmetrically substituted triphenylcarbinols are shown in the following table. A typical chromatogram is shown in Fig. 22.

**TABLE XII**

Analysis of Chromic Acid Oxidation.

Product of Triarylc-arbinols.

<table>
<thead>
<tr>
<th>Substituted Triphenylcarbinols</th>
<th>Benzophenones</th>
<th>Molar Ratio of Benzophenones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(a) Without Mn⁺⁺</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b) With Mn⁺⁺</td>
</tr>
<tr>
<td>A. 4,4'-diMe</td>
<td>(i) 4,4'-diMe</td>
<td>(ii)/(i) (a) 6.60</td>
</tr>
<tr>
<td></td>
<td>(ii) 4-Me</td>
<td>(b) 6.55</td>
</tr>
</tbody>
</table>
Fig. 22. VPC Analysis of the Chronic Acid Oxidation Product of 4-Chlorotriphenylcarbinol.

Column: SE 30

T = 200°
<table>
<thead>
<tr>
<th>Substituted Triphenylcarbinols</th>
<th>Benzophenones</th>
<th>Molar Ratio of Benzophenones</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(i)</td>
<td>(ii)/(i)</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
<td>(a)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(b)</td>
</tr>
<tr>
<td><strong>B. 4-Me</strong></td>
<td>4-Me</td>
<td>(a) 1.70</td>
</tr>
<tr>
<td></td>
<td>Unsubstituted</td>
<td>(b) 1.72</td>
</tr>
<tr>
<td><strong>C. 4-Cl</strong></td>
<td>4-Cl</td>
<td>(a) 0.38</td>
</tr>
<tr>
<td></td>
<td>Unsubstituted</td>
<td>(b) 0.37</td>
</tr>
<tr>
<td><strong>D. 4-NO₂</strong></td>
<td>4-NO₂</td>
<td>(a) 0.039</td>
</tr>
<tr>
<td></td>
<td>Unsubstituted</td>
<td>(b) 0.031</td>
</tr>
<tr>
<td><strong>E. 3-CF₃</strong></td>
<td>3-CF₃</td>
<td>(a) 0.18</td>
</tr>
<tr>
<td></td>
<td>Unsubstituted</td>
<td>(b) 0.17</td>
</tr>
<tr>
<td><strong>F. 3-CF₃-4'-CH₃</strong></td>
<td>3-CF₃</td>
<td>(i) : (ii) : (iii)</td>
</tr>
<tr>
<td></td>
<td>3-CF₃-4'-CH₃</td>
<td>(a) 3.1 : 1 : 0.34</td>
</tr>
<tr>
<td></td>
<td>4-CH₃</td>
<td>(b) 3.0 : 1 : 0.35</td>
</tr>
</tbody>
</table>

The migration aptitudes of the substituted phenyl groups compared to the unsubstituted ones were calculated from the molar...
ratios of the different products. The calculations are shown below and the results are listed in Table XIII.

A. 4,4'-Dimethyltriphenylcarbinol: The migrating groups are two p-tolyl and one phenyl; hence the probability of formation of 4-methylbenzophenone due to the migration of a p-tolyl group is twice as much as the probability of formation of 4,4'-dimethylbenzophenone which is the result of migration of a phenyl group. The apparent migration aptitude of p-tolyl compared to phenyl group, obtained from the molar ratio of the corresponding product is 6.6, and on correction by the statistical factor of 2, following the above arguments, it becomes 3.3.

B. 4-Methyltriphenylcarbinol: The migrating groups are two phenyl and one p-tolyl. Following the same arguments as in the case of "A", the apparent migration aptitude of p-tolyl compared to phenol should be multiplied by the statistical factor of 2, and thus it becomes 1.7 x 2 = 3.4.

C, D and E. 4-Chlorotriphenylcarbinol, 4-nitrotriphenylcarbinol and 3-trifluoromethyltriphenylcarbinol: In all these cases there are two unsubstituted and one substituted phenyl group that migrate. As in the case of "B", the migration aptitudes are corrected by multiplying the apparent values, obtained from the molar ratios of the products by the statistical factor of 2.

F. 3-Trifluoromethyl, 4'-methyltriphenylcarbinol: In this case there are three different migrating groups, hence there
is no statistical correction required and the migration aptitudes were directly obtained from the molar ratio of the products, i.e. the quantity of the disubstituted benzophenone produced was directly proportional to the migration aptitude of the unsubstituted phenyl group. The values for the other groups were similarly proportional to the quantities of the two other products.

The addition of manganous ion was found to have very little effect on the relative migration of the aryl groups. The results obtained were very close to those obtained without the added ion, and hence separate calculations were not done for these.

**TABLE XIII**

Migration Aptitudes of Aryl Groups for Chromic Acid Oxidation of Triarylcarbinols.

<table>
<thead>
<tr>
<th>Substituent X</th>
<th>$\sigma^+$ (124)</th>
<th>Mig.Apt. $X-C_6H_4/C_6H_5$</th>
<th>Log (Mig.Apt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0.0</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.306</td>
<td>3.3, 3.4, Av. 3.35 (3.1*)</td>
<td>0.525</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.112</td>
<td>0.76</td>
<td>-0.143</td>
</tr>
<tr>
<td>3-CF$_3$</td>
<td>0.415</td>
<td>0.36, (0.34*)</td>
<td>-0.444</td>
</tr>
<tr>
<td>4-NO$_2$</td>
<td>0.778</td>
<td>0.078</td>
<td>-1.102</td>
</tr>
</tbody>
</table>
* - Values obtained from "F", 3-trifluoromethyl, 4'-methyltriphenylcarbinol, Table XIII.

Fig. 23 shows the plot of the logarithm of the migration aptitudes against the corresponding $\sigma^+$ values. The slope of the line is $-1.44$, which gives the value of $\rho^+$ for the migration.

In all the cases discussed above, almost quantitative yields of the corresponding ketones were obtained.

The bromo derivatives of the phenols produced were isolated and identified. The results are listed below:

<table>
<thead>
<tr>
<th>Substituted Triphenylcarbinols</th>
<th>M.p. of the bromo derivatives of products</th>
<th>Identified Phenols</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>Lit. (119)</td>
<td></td>
</tr>
<tr>
<td>Unsubstituted</td>
<td>94°-95°</td>
<td>95°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unsubstituted</td>
</tr>
<tr>
<td>4-Me</td>
<td>48.5°</td>
<td>49°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Me</td>
</tr>
<tr>
<td>4-Cl</td>
<td>95°</td>
<td>95°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unsubstituted</td>
</tr>
<tr>
<td>4,4'-diCl</td>
<td>94°</td>
<td>95°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Unsubstituted</td>
</tr>
</tbody>
</table>

(ii) Permanganate Oxidation: The products of oxidation of triarylcariibinols apparently consist only of ketones since the other possible product, phenols, are readily oxidized to carbon-dioxide and water by permanganate (1). The evolution of carbon-dioxide from reaction mixtures has been observed and a
Fig. 23. Chronic Acid Oxidation of Triarylcyanins.

Hermott Equation Applied to the Migration of Aryl Groups.

\[ H_R = -3.95 \]

\[ \rho = -1.44 \]

Coeff. of Correlation = 0.994
quantitative estimate of the gas was made by passing the evolved gas into barium hydroxide solution and observing the increase in weight of the system. This showed the production of six moles of carbon dioxide from each mole of triphenylcarbinol used. This indicates complete degradation of the phenol produced from the carbinol.

The ketone from triphenylcarbinol was identified as benzophenone in the same way as in the case of chromic acid oxidation, although a quantitative yield was not obtained because of further oxidation of benzophenone by permanganate. With unsymmetrically substituted triphenylcarbinols the molar ratios of the ketones produced are rather inaccurate since the ketones with an electron-releasing group in the ring are destroyed by permanganate at a rate higher than those without. For this reason, a quantitative measurement of the migratory aptitudes of the different groups in this reaction could not be made. However, the spectrophotometric method and the identification of the 2,4-dinitrophenylhydrazones of the ketones produced showed that the ring containing the more electronegative group migrated preferentially. The results are given below:
TABLE XIV

Analysis of Permanganate Oxidation Product of Triarylcarbinols.

<table>
<thead>
<tr>
<th>Substituted Tri-phenylcarbinols</th>
<th>M.p. of 2,4-DNPH*</th>
<th>$\lambda_{\text{max}}$ of conc. H$_2$SO$_4$ soln. of products</th>
<th>Identified Benzophenones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs.</td>
<td>Lit.(119)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4-Me</td>
<td>238°</td>
<td>239°</td>
<td>344 my*</td>
</tr>
<tr>
<td>4-Cl</td>
<td>184°</td>
<td>185°</td>
<td>299 my, 367 my#</td>
</tr>
</tbody>
</table>

* DNPH Dinitrophenylhydrazone

# The conjugate acid of benzophenone absorbs at 344 my (138).

The conjugate acid of 4-chlorobenzophenone absorbs at 300 my and 367 my (138).

Order of Reaction:

(i) **Chromic Acid Oxidation**: As in the case of the diarylcarbinols, discussed in Sec. I, a 3:2 ratio of the substrate to oxidant is applicable and the reaction can be represented as:

$$3\text{Ar}_3\text{COH} + 2\text{H}_2\text{CrO}_4 \rightarrow 3\text{Ar}_2\text{CO} + 3\text{ArOH} + \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O}$$

For the reasons mentioned earlier in this section, the reactions were studied as pseudo-first order reactions, using an excess of the carbinols. Chromic acid oxidation of triarylcarbinols
unlike that of the diarylcarbinols, produces phenols, and this complicates the study because of their further oxidation by chromic acid. For this reason, only the initial reaction (about 60%) was taken into account in the measurement of rate. A typical pseudo first order rate plot is shown in Fig. 24. The true second order rate constant was obtained by dividing the observed first order rate constant by the initial concentration of the carbinol. This method gave satisfactorily reproducible results over a wide range of initial concentration. The following equation was used to calculate the rate constants:

$$k_2 = \frac{2.303 \times \text{slope (obs.)}}{[\text{carbinol}]_0}$$

where $[\text{carbinol}]_0$ is the initial concentration of the carbinol.

(ii) Permanganate Oxidation: As in the case of the diarylcarbinols, a 3:2 ratio of substrate to permanganate is the stoichiometry in this case, provided the initial reaction products undergo no degradation. The reaction can be represented as:

$$3\text{Ar}_3\text{COH} + 2\text{KMnO}_4 + \text{H}_2\text{O} \rightarrow 3\text{Ar}_2\text{CO} + 3\text{ArOH} + 2\text{KOH} + 2\text{MnO}_2$$

When this stoichiometric ratio is used the plot of the logarithm of the absorbance at any time against time gives straight
Fig. 24. Chromic Acid Oxidation of Triphenylcarbinol.

Typical Rate Plot.

$H_R = -3.55$

Triphenylcarbinol = $7.44 \times 10^{-4} M$

Slope = $1.85 \times 10^{-4}$

$k_2 = 0.249 \text{ l.mole}^{-1}\text{sec}^{-1}$
line for approximately 50-60% reaction. A typical first order rate plot is shown in Fig. 25. As in the case of the diaryl-carbinols, discussed in Sec. I, the rate of disappearance of permanganate is two-thirds that of the carbinol, and hence the rate constant was calculated from the same equation as before:

\[ \frac{3}{2} \cdot 2.303 \cdot \text{slope} \]

For the permanganate oxidation of tri(o-tolyl)carbinol at higher acidities a second order rate equation was found to be suitable when the stoichiometric ratio (3:2) of substrate to permanganate was used. The rate data were found to fit the second order rate expression (1):

\[
\frac{3}{2} \cdot k_t = \frac{1}{[\text{Mn}^{\text{VII}}]_t} - \frac{1}{[\text{Mn}^{\text{VII}}]_0}
\]

Since \([\text{Mn}^{\text{VII}}]_0\), the permanganate concentration at zero time, is a constant, a plot of \(t\) against \(1/[\text{Mn}^{\text{VII}}]_t\) gives a straight line, the slope being equal to \(3k/2\). The reciprocal of the absorbance of permanganate at any time was plotted against time, and in this case the following equation is valid:

\[
k_2 = \frac{2e}{3} \times \text{slope}
\]
Fig. 25. Permanganate Oxidation of Triphenylcarbinol

Typical Rate Plot.

$H_0 = -1.50$

$T = 25^\circ$

$k_1 = 1.14 \times 10^{-2} \text{sec}^{-1}$
where \( \varepsilon \) is the molar extinction coefficient of \( \text{Mn}^{\text{VII}} \). A typical rate plot for the oxidation of tri(p-tolyl)carbinol is shown in Fig. 26.

**Dependence of Rate on Acidity:**

(i) **Chromic Acid Oxidation**: The rate of chromic acid oxidation of triphenylcarbinol in 80 wt% aqueous acetic acid containing sulfuric acid increases with increasing acidity of the medium in the range of 8.3% to 39.6% sulfuric acid. The variation of second order rate constant with acidity at 25° is shown in Table XV, and plotted in Figs. 27 and 28, using the acidity functions \( H_Q \) and \( H_R \) respectively.

**TABLE XV**

<table>
<thead>
<tr>
<th>(-H_O)</th>
<th>(-H_R)</th>
<th>(k_2 \text{ l. mole}^{-1}\text{sec}^{-1})</th>
<th>(\log k_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.12</td>
<td>2.80</td>
<td>0.031</td>
<td>-1.506</td>
</tr>
<tr>
<td>1.15</td>
<td>3.20</td>
<td>0.078</td>
<td>-1.106</td>
</tr>
<tr>
<td>1.70</td>
<td>3.55</td>
<td>0.249</td>
<td>-0.604</td>
</tr>
<tr>
<td>2.00</td>
<td>3.95</td>
<td>0.548</td>
<td>-0.261</td>
</tr>
<tr>
<td>2.25</td>
<td>4.10</td>
<td>0.645</td>
<td>-0.191</td>
</tr>
</tbody>
</table>
Fig. 26. Permanganate Oxidation of Tri(p-tolyl)carbinol.

Typical Rate Plot.

$H_R = -3.10$
$T = 25^\circ$

Substrate $= 1.12 \times 10^{-5} \text{M}$
Permanganate $= 7.44 \times 10^{-6} \text{M}$

$k_2 = 35.20 \text{ l.mole}^{-1}\text{sec}^{-1}$
Fig. 27. Chromic Acid Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Acidity Function $H_0$

$T = 25^\circ$

Slope = -1.34
Coeff. of Correlation = 0.996
Fig. 28. Chronic Acid Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Acidity Function $H_R$.

$T = 25^\circ$

Slope = -0.923
Coeff. of Correlation = 0.998
TABLE XV (Cont.)

<table>
<thead>
<tr>
<th>$-H_o$</th>
<th>$-H_R$</th>
<th>$k_2$ (1 mole$^{-1}$sec$^{-1}$)</th>
<th>log $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.70</td>
<td>4.85</td>
<td>2.810</td>
<td>0.449</td>
</tr>
<tr>
<td>3.10</td>
<td>5.50</td>
<td>9.350</td>
<td>0.971</td>
</tr>
<tr>
<td>3.35</td>
<td>6.01</td>
<td>26.250</td>
<td>1.419</td>
</tr>
<tr>
<td>3.60</td>
<td>6.30</td>
<td>62.640</td>
<td>1.797</td>
</tr>
<tr>
<td>4.05</td>
<td>7.00</td>
<td>215.300</td>
<td>2.333</td>
</tr>
<tr>
<td>4.15</td>
<td>7.20</td>
<td>456.000</td>
<td>2.659</td>
</tr>
<tr>
<td>4.25</td>
<td>7.30</td>
<td>608.000</td>
<td>2.784</td>
</tr>
<tr>
<td>4.35</td>
<td>7.48</td>
<td>1023.000</td>
<td>3.010</td>
</tr>
</tbody>
</table>

In both Figs. 27 and 28, the plots of log $k_2$ against the two acidity functions give straight lines, but a comparison of the two shows a somewhat better correlation in Fig. 28, the slope $-0.923$ being closer to unity than $-1.34$. This suggests that an acidity function closely related to $H_R$ is operative.

(ii) **Permanganate Oxidation:** The oxidation of triphenylcarbinol by permanganate is acid catalyzed in the range of 12.1% to 33.5% sulfuric acid in water. The concentration of permanganate acid is negligible in this region, and for this reason, as mentioned in the case of diarylcarbinols in Sec. 1, it is likely that the increase in rate is due to the ionization of the carbinol. Table XVI lists the data for the variation of the rate constant with acidity in the region studied.
Permanganate Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Acidity.

\[ T = 25^\circ \]

<table>
<thead>
<tr>
<th>(-H_o) (123)</th>
<th>(-H_R) (121)</th>
<th>(10^3 k) sec(^{-1})</th>
<th>(\log k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.60</td>
<td>1.00</td>
<td>1.76</td>
<td>-2.755</td>
</tr>
<tr>
<td>0.67</td>
<td>1.15</td>
<td>2.04</td>
<td>-2.691</td>
</tr>
<tr>
<td>0.84</td>
<td>1.55</td>
<td>2.85</td>
<td>-2.545</td>
</tr>
<tr>
<td>1.00</td>
<td>2.00</td>
<td>4.14</td>
<td>-2.383</td>
</tr>
<tr>
<td>1.47</td>
<td>2.90</td>
<td>10.87</td>
<td>-1.964</td>
</tr>
<tr>
<td>1.93</td>
<td>3.75</td>
<td>31.05</td>
<td>-1.508</td>
</tr>
</tbody>
</table>

The plots of the logarithm of rate constants against acidity are shown in Figs. 29 and 30, using the acidity functions \(H_o\) and \(H_R\) respectively. Although both the plots gave reasonably good straight lines, only in the first case was a line of slope close to unity obtained. This indicates that the operative acidity function in this region is \(H_o\).

In order to study the oxidation of a triarylcarbinol at acidities near and beyond its \(pK_R^+\) tri(p-tolyl)carbinol was investigated. Triphenylcarbinol has a much higher value of \(pK_R^+\) than that of the trimethyl substituted compound and its rate of oxidation is too high to be measured at the acidities required to give a high degree of ionization.
Fig. 29. Permanaganate Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Acidity Function $\text{H}_0$.

$T = 25^\circ$

Slope $= -0.934$

Coeff. of Correlation $= 0.999$
Fig. 30. Permanganate Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Acidity Function $H_R^*$. 

$T = 25^\circ$

Slope = -0.45

Coeff. of Correlation = 0.997
At lower acidities the rate of oxidation of tri(p-tolyl)-carbinol is first order in carbinol and zero order in permanganate, as in the case of triphenylcarbinol. As the acid approaches the concentration for maximum ionization of the carbinol, the reaction changes to second order, first order in each of the reactants, the stoichiometry remaining the same as before. Second order rate plots were obtained by using the 3:2 ratio of the substrate to permanganate.

The rate of the oxidation was studied in the range of 4.20M to 9.08M sulfuric acid. The data showing the variation of rate constant with acidity are given in Table XVII and plotted in Fig. 31.

TABLE XVII
Permanganate Oxidation of Tri(p-tolyl)carbinol.

Variation of Rate Constant with Acidity.

\[ T = 25^\circ \]

<table>
<thead>
<tr>
<th>(-H_R)</th>
<th>(k_2 \text{ l.mole}^{-1}\text{sec}^{-1})</th>
<th>(\log k_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.60</td>
<td>13.3</td>
<td>1.123</td>
</tr>
<tr>
<td>3.00</td>
<td>25.0</td>
<td>1.398</td>
</tr>
<tr>
<td>3.10</td>
<td>35.2</td>
<td>1.546</td>
</tr>
<tr>
<td>3.50</td>
<td>60.8</td>
<td>1.784</td>
</tr>
<tr>
<td>3.88</td>
<td>73.6</td>
<td>1.867</td>
</tr>
<tr>
<td>5.00</td>
<td>90.0</td>
<td>1.954</td>
</tr>
<tr>
<td>6.53</td>
<td>118.8</td>
<td>2.075</td>
</tr>
</tbody>
</table>
Fig. 31. Permanganate Oxidation of Tri(p-tolyl)carbinol.

Variation of Rate Constant with Acidity.

$T = 25^\circ$
TABLE XVII (Cont.)

<table>
<thead>
<tr>
<th>$-H_R$</th>
<th>$k_2 \text{ l.mole}^{-1}\text{sec}^{-1}$</th>
<th>$\log k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.80</td>
<td>120.1</td>
<td>2.080</td>
</tr>
<tr>
<td>7.20</td>
<td>121.0</td>
<td>2.083</td>
</tr>
<tr>
<td>8.00</td>
<td>158.6</td>
<td>2.200</td>
</tr>
<tr>
<td>8.20</td>
<td>246.0</td>
<td>2.391</td>
</tr>
</tbody>
</table>

Fig. 31 shows that the rate increases steadily with increasing acidity up to $H_R = -3.50$, the slope of the plot of the logarithm of rate constant against the acidity function $H_R$ being very close to unity, and rises relatively slowly after this. The $pK_{R^+}$ of the carbinol is $-3.56$ (121). Assuming that the alterations in rate up to $H_R = -7.0$ are following an ionization curve, one can take the rate at full ionization to be anti-log $k_2 = 2.40$. The rate at half-ionization will be $2.08 - 0.30 = 1.78$. This corresponds to an $H_R$ of $-3.50$, which is very close to the reported $pK_{R^+}$ value of the carbinol. That is, the rate constant at $H_R = -6.90$ is in good agreement with what is expected from its value at $H_R = -3.50$. However, the rates at the intermediate acidities are somewhat lower than what is expected from an ideal ionization curve.
Beyond $H_R = -6.90$, the rate remains almost constant up to $H_R = -7.20$, since the carbinol is essentially fully ionized. At still higher acidities the rate rises again, probably because of the formation of permanganic acid. Permanganate is half-protonated in 61% sulfuric acid (1), corresponding to $H_R = -9.20$ (121), forming permanganic acid, which is believed to be a stronger oxidizing agent than permanganate ion.

Substituent Effect:

(i) Chromic Acid Oxidation: The effects of ring substituents on the rate of chromic acid oxidation of triphenylcarbinol were studied. The effect was also studied in presence of $3.045 \times 10^{-4}$ manganous ion, in order to effect the induced oxidation of the added ion by chromium species of valence V and IV, formed as intermediates in the reduction of chromic acid (53, 75, 99). A decrease in the rates of oxidation of the carbinols was observed. Table XVIII lists the rate constants of oxidation of triarylcarbinols with, and without, added manganous ion. The data are plotted in Figs. 32 and 33, using the substituent constants $\sigma$ and $\sigma^+$ respectively.
<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma(124)$</th>
<th>$\sigma^*(124)$</th>
<th>$10^2 k_2 \text{ mole}^{-1} \text{ sec}^{-1}$</th>
<th>$\log k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\text{Mn}^{2+}$ absent</td>
<td>$\text{Mn}^{2+}$ present*</td>
</tr>
<tr>
<td>$H$</td>
<td>0</td>
<td>0</td>
<td>54.81</td>
<td>37.77</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>108.21</td>
<td>71.39</td>
</tr>
<tr>
<td>4,4'-diMe</td>
<td>-0.34</td>
<td>-0.612</td>
<td>209.61</td>
<td>129.01</td>
</tr>
<tr>
<td>4,4';4''-triMe</td>
<td>-0.51</td>
<td>-0.918</td>
<td>306.30</td>
<td>237.20</td>
</tr>
<tr>
<td>4-F</td>
<td>0.062</td>
<td>-0.073</td>
<td>59.88</td>
<td>41.21</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.226</td>
<td>0.112</td>
<td>46.98</td>
<td>32.21</td>
</tr>
<tr>
<td>4,4'-diCl</td>
<td>0.452</td>
<td>0.224</td>
<td>39.84</td>
<td>-0.3997</td>
</tr>
<tr>
<td>4,4';4''-triCl</td>
<td>0.678</td>
<td>0.336</td>
<td>28.56</td>
<td>20.73</td>
</tr>
<tr>
<td>3,3';3''-triCl</td>
<td>1.119</td>
<td>1.119</td>
<td>5.34</td>
<td>3.52</td>
</tr>
<tr>
<td>4-NO$_2$</td>
<td>0.777</td>
<td>0.777</td>
<td>11.08</td>
<td>8.02</td>
</tr>
<tr>
<td>3-CF$_3$,4'-Me</td>
<td>0.245</td>
<td>0.109</td>
<td>50.44</td>
<td>32.93</td>
</tr>
</tbody>
</table>

* $3.045 \times 10^{-4}$ M manganous acetate added.
Fig. 32. Chromic Acid Oxidation of Triarylcarnbinols.

HAMMETT PLOT.
1 : Mn$^{2+}$ absent.
2 : Mn$^{2+}$ present.

T = 25°

$H_R = -3.95$
Fig. 33. Chronic Acid Oxidation of Triarylcarbinols.

HAMMETT PLOT

1: Mn⁺⁺ absent.
2: Mn⁺⁺ present.

$H_R = -3.95$

$T = 25^\circ$

$\rho = -0.879$

$\rho = -0.906$
The two plots show that the better correlation between rate constant and substituent constant is obtained when \( \sigma^+ \) is used. From the two lines in Fig. 33 the values of \( \rho^+ \) for the oxidation reaction with and without added manganous ion are obtained; the former gives a value of \(-0.906\) and the latter \(-0.879\).

(ii) Permanganate Oxidation: The effects of different ring substituents on the reaction centre were studied. The rate constants of the substituted triphenylcarbinols are listed in Table XIX. Fig. 34 shows the Hammett plot when the substituent constant \( \sigma \) is used and Fig. 35 when the substituent constant \( \sigma^+ \) is used.

**TABLE XIX**

Permanganate Oxidation of Triphenylcarbinol.

Effects of Substituents.

\( H_o = -0.65, T = 25^o \)

<table>
<thead>
<tr>
<th>Substituent</th>
<th>( \sigma ) (124)</th>
<th>( \sigma^+ ) (124)</th>
<th>( 10^4 k ) sec(^{-1} )</th>
<th>( \log k )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>0</td>
<td>0</td>
<td>20.70</td>
<td>-2.684</td>
</tr>
<tr>
<td>4-Me</td>
<td>-0.17</td>
<td>-0.306</td>
<td>58.10</td>
<td>-2.237</td>
</tr>
<tr>
<td>4,4'-diMe</td>
<td>-0.34</td>
<td>-0.612</td>
<td>120.00</td>
<td>-1.921</td>
</tr>
<tr>
<td>4,4',4''-triMe</td>
<td>-0.51</td>
<td>-0.918</td>
<td>448.00</td>
<td>-1.348</td>
</tr>
<tr>
<td>4-F</td>
<td>0.062</td>
<td>-0.073</td>
<td>26.90</td>
<td>-2.570</td>
</tr>
<tr>
<td>4-Cl</td>
<td>0.226</td>
<td>0.112</td>
<td>12.90</td>
<td>-2.886</td>
</tr>
<tr>
<td>4,4'-diCl</td>
<td>0.452</td>
<td>0.224</td>
<td>8.11</td>
<td>-3.091</td>
</tr>
</tbody>
</table>
Fig. 34. Permanganate Oxidation of Triarylcarbinols.

HAMMETT PLOT.

$\rho = -1.56$

$T = 25^\circ$

Coeff. of Correlation = 0.976
Fig. 35. Permanganate Oxidation of Triarylcarbinols.

HARTMANN PLOT.

\[ H_0 = -0.65 \]
\[ T = 25^\circ \]

\[ \rho = -1.39 \]

Coeff. of Correlation = 0.998
From a comparison of Figs. 34 and 35, it appears that a better linear relationship is obtained when substituent constant $\sigma^+$ is used. The slope of the line gives the value of $\rho^+$, which is -1.39.

**Activation Parameters:**

The temperature effect on the rates of chromic acid and permanganate oxidation of triphenylcarbinol was studied. The plot of $\log(k/T)$ against $1/T$ for the chromic acid oxidation is given in Fig. 36 and the same for the permanganate oxidation is given in Fig. 37. The results are given in the following Table.

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$\sigma$(124)</th>
<th>$\sigma^+$(124)</th>
<th>$10^4k$ sec$^{-1}$</th>
<th>$\log k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$4,4',4''$-triCl</td>
<td>0.678</td>
<td>0.336</td>
<td>5.87</td>
<td>-3.231</td>
</tr>
<tr>
<td>$3,3',3''$-triCl</td>
<td>1.119</td>
<td>1.119</td>
<td>0.66</td>
<td>-4.181</td>
</tr>
<tr>
<td>$3$-$CF_3,4'$-Me</td>
<td>0.245</td>
<td>0.109</td>
<td>10.90</td>
<td>-2.963</td>
</tr>
</tbody>
</table>
Fig. 36. Chronic Acid Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Temperature.

\[ H_R = -3.95 \]

\[ \Delta H = 11.8 \text{ kcal/mole} \]

\[ \Delta S = -25.1 \text{ e.u.} \]
Fig. 37. Permanganate Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Temperature.

\[ H_0 = -1.00 \]

\[ \Delta H = 17.2 \text{ kcal/mole} \]

\[ \Delta S = -11.7 \text{ e.u.} \]
TABLE XX

Activation Parameters for Oxidation of Triphenylcarbinol.

<table>
<thead>
<tr>
<th>Oxidant</th>
<th>Acidity of the Medium</th>
<th>Reaction Order</th>
<th>$\Delta H^\ddagger$ (kcal/mole)</th>
<th>$\Delta S^\ddagger$ (e.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromic Acid</td>
<td>$H_R$ -3.95</td>
<td>Second</td>
<td>11.8</td>
<td>-25.1</td>
</tr>
<tr>
<td>Permanganate</td>
<td>$H_O$ -1.00</td>
<td>First</td>
<td>17.2</td>
<td>-11.7</td>
</tr>
</tbody>
</table>

As in the case of benzhydryl the permanganate oxidation reaction is of first order in carbinol and the rate-determining step is the ionization of the carbinol, as discussed later. Thus in this case also the activation parameters calculated are those for the ionization reaction.

The rate constants of the two reactions at different temperatures are given in Tables XX(a) and XX(b) respectively.

TABLE XX(a)

Chromic Acid Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$k_2$ (1.mole$^{-1}$sec$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>0.24</td>
</tr>
<tr>
<td>25</td>
<td>0.55</td>
</tr>
<tr>
<td>43</td>
<td>1.44</td>
</tr>
<tr>
<td>50</td>
<td>2.10</td>
</tr>
</tbody>
</table>
### TABLE XX(b)

Permanganate Oxidation of Triphenylcarbinol.

Variation of Rate Constant with Temperature.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$10^3 k$ sec$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>1.12</td>
</tr>
<tr>
<td>25</td>
<td>4.14</td>
</tr>
<tr>
<td>35</td>
<td>11.4</td>
</tr>
<tr>
<td>40</td>
<td>17.8</td>
</tr>
</tbody>
</table>
DISCUSSION

The analysis of the products of permanganate oxidation of triarylcarbinols showed that almost quantitative yields of diaryl ketones were obtained, although no phenol was detected. The formation of phenols during the reactions was inferred from the evolution of carbon dioxide from the reaction mixtures, quantitative estimation of the gas showing the formation of one mole of phenol from every mole of carbinol. Since no other product was detected the following stoichiometry can be suggested for the reaction:

$$3\text{Ar}_2\text{COH} + 2\text{MnO}_4^- + 2\text{H}^+ \rightarrow 3\text{Ar}_2\text{C}=\text{O} + 3\text{ArOH} + \text{H}_2\text{O} + 2\text{MnO}_2$$

As in the case of the diarylcarbinols the permanganate oxidation of triphenylcarbinol was found to be acid-catalyzed and to be directly proportional to the substrate concentration but independent of the concentration of the oxidant. As in the case of the diarylcarbinols, discussed in p.85, the increase in rate is believed to be due to the ionization of the carbinol, this being the rate-determining step in the oxidation reaction. Recently, a direct observation of the ionization of a triarylcarbinol has been reported (139). The same rate law that was used in the case of diarylcarbinols was found to be suitable for the triarylcarbinols.
The negative value of $\rho$ that is observed, $(\rho^+ = -1.39)$ also supports the formation of a positive reaction centre in the rate-determining step.

The $pK_R^+$ of triphenylcarbinol is -6.63 (121). Therefore at $H_R = -3.75$, the maximum acidity used in the present investigation, the ionization of the carbinol to the corresponding carbonium ion is only 0.1%. This means that most of the substrate is not present in carbonium ion form in the range of acidity employed. Furthermore, the operative acidity function within this range of acidity was found to be $H_2O$ and not $H_R$.

Following the same arguments as in the case of the diarylcarbinols, it can be suggested that the permanganate oxidation of triarylcarbinols between 1.7M and 4.2M aqueous sulfuric acid proceeds through protonation and incipient ionization of the substrate; the steps can be represented as:

\[
\begin{align*}
\text{Ar}_3\text{COH} + H_3O^+ & \rightleftharpoons \text{Ar}_3\text{COH}_2 + H_2O \\
\text{Ar}_3\text{COH}_2 & \xrightarrow{\text{slow}} [\text{Ar}_3\text{C} \ldots \ldots \text{OH}] \longrightarrow \text{Ar}_3\text{C}^+ + H_2O \\
\text{Ar}_3\text{C}^+ + \text{MnO}_4^- & \longrightarrow \text{ArC} \quad \text{δ+} \quad \text{O-MnO}_3 \\
\text{Ar}_2\text{C} ==\text{OH} + \text{ArOH} + \text{MnO}_3^- \\
\text{Ar}_2\text{C} ==\text{OH} & \longrightarrow \text{Ar}_2\text{C} ==\text{O} + H^+
\end{align*}
\]
As mentioned in the case of the diarylcarbinols, it is not possible to distinguish between the two possible modes of aryl migration, namely 1,2- and 1,4-shifts, from the rate studies. However, as discussed in Section I, there are many evidences of 1,2-shifts, whereas no example of a 1,4-shift is available.

From the above mechanism it appears that the aromatic ring that migrates becomes the phenol. It has been observed in the cases of similar reactions, like pinacol rearrangement (140), acid-catalyzed rearrangement of arylmethyl hydroperoxides (141, 142) etc., that the preferential migration of the ring containing the stronger electron releasing group occurs. A similar effect can also be expected in this case. This is supported by the product analysis which showed that the major fraction of the diaryl ketone formed contained the least electron-releasing group, indicating the migration of the ring containing the strongest electron-releasing group. A quantitative estimate of the relative proportions of the ketones formed, as done in the case of chromic acid oxidation which is discussed later, was not possible, since the ketones were found to react with acidic permanganate to a significant extent.

On increasing the acidity of the medium the order of reaction changes. This has been shown by the experiments with tri-(p-tolyl)carbinol. At higher acidity free carbonium ions are formed faster than their reaction with permanganate and thus, under such
conditions, the latter becomes the rate-determining step. The reaction then becomes one of second order, first order in each of the carbinol and the oxidant. The $pK_r^+$ of tri(p-tolyl)carbinol is $-3.56$ (21). The rate of oxidation was found to increase steadily up to $H_R = -3.50$, which is very close to the acidity required for the half-ionization of the carbinol. Beyond this acidity the rate increases slowly and then remains fairly constant up to $H_R = -7.2$, above which the rate again rises sharply as the acidity becomes sufficiently high to form permanganic acid, which is believed to be a stronger oxidising agent than permanganate (24). This variation in the rate of oxidation with acidity clearly shows that the reaction proceeds through the formation of carbonium ions at acidities near and beyond the $pK_r^+$ of the triarylcarbinol, the rate-determining step being the decomposition of the manganate ester formed between the carbonium ion and manganate ion of the oxidant.

The activation parameters for permanganate oxidation of triphenylcarbinol, listed in Table XX, are similar to those for the permanganate oxidation of benzhydrol. This indicates that both the reactions proceed through similar mechanism.

From the analysis of the products of chromic acid oxidation of triarylcarbinols the stoichiometry of the reaction was found to be:

$$3\text{Ar}_3\text{COH} + 2\text{H}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow 3\text{Ar}_2\text{C}=\text{O} + 3\text{ArOH} + \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O}^+$$
The chronic acid oxidation of triphenylcarbinol was also found to be acid-catalyzed and the operative acidity function in the range of 8.3% to 39.6% sulfuric acid in 80 wt% aqueous acetic acid to be $H_R$. The reactions were found to be of second order, first order in each of the reactants. There is evidence that the chronic acid oxidation of alcohols involves the formation of a chromate ester intermediate with the rate-determining step being the unimolecular decomposition of this intermediate (44, 89–91, 128). Accordingly, the mechanism of the chronic acid oxidation of triphenylcarbinol can be represented as:

\[
\begin{align*}
\text{Ar}_3\text{COH} + \text{HCrO}_4^- & \rightarrow 2\text{H}^+ \rightarrow \text{Ar} \quad \text{O} \quad \text{CrO}_3\text{H}_2 \\
\delta^+ & \quad \text{O} \quad \delta^+ & \quad \text{H}^+ & \rightarrow \text{Ar}_2\text{C} = \text{OAr} + \text{H}_3\text{CrO}_3^{-} \\
\text{Ar}_2\text{C} = \text{OAr} & \quad \text{H}_2\text{O} & \rightarrow \text{Ar}_2\text{C} \rightarrow \text{O} + \text{ArOH} + \text{H}^+ 
\end{align*}
\]
1,2-shifts of aryl groups occur in the pinacol rearrangement of triphenylethylene glycol (140) and acid-catalyzed rearrangements of benzhydryl hydroperoxide (141) and triarylmethyl hydroperoxides (142). In the first case, the shift is from one carbon atom to another, the reaction may take either path (a) or (b), depending on the reaction conditions; this is discussed in a later section. In the latter two, the shift is from carbon to oxygen:

(i) \[
\begin{align*}
\text{Ph}_2\text{C} -&- \text{CHPh} \\
\text{OH} & \quad \text{OH}
\end{align*}
\]

\[
\begin{align*}
\text{Ph}_2\text{C} - \rightarrow & \text{Ph}_2\text{C}
\end{align*}
\]

(a)

OR

(b)

(ii) \[
\begin{align*}
\text{Ph}_2\text{C} - &- \text{OH} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H}^+ & \rightarrow \quad \text{Ph}
\end{align*}
\]

(iii) \[
\begin{align*}
\text{Ph}_3\text{C} - &- \text{OH} \\
\text{H} & \quad \text{H}
\end{align*}
\]

\[
\begin{align*}
\text{H}^+ & \rightarrow \quad \text{Ph}_2\text{C}
\end{align*}
\]
Baeyer-Villiger reactions are also examples of 1,2-shifts, as mentioned in Section I. A 1,4-shift leading to a five-membered ring in the transition state is not possible in any of these cases. Moreover, in all these cases, as in the present investigation, a preferential migration of the aryl group containing the stronger electron-donating substituent was observed.

Further support for the 1,2-shift can be obtained from a comparison of the rates of chromic acid oxidation of benzhydrol and triphenylcarbinol under identical conditions. It has been found that at the same acidity, the rate is higher for benzhydrol than for triphenylcarbinol; for example, at $H_0 = -1.12$, the rate of oxidation of benzhydrol is $3.93 \text{ l.mole}^{-1}\text{sec}^{-1}$, whereas that for triphenylcarbinol at the same acidity is $0.31 \text{ l.mole}^{-1}\text{sec}^{-1}$. This indicates that the 1,2-hydride shift is much faster than 1,2-phenyl shift, assuming for purposes of discussion that secondary alcohols are oxidized by chromic acid by such a mechanism. Collins has observed that in the pinacol rearrangement of triphenylethylene glycol a wide variation in the ratio of phenyl to hydrogen migration occurs, and this depends upon the acidity of the medium (140). In highly acidic medium preferential phenyl migration takes place, the ratio of phenyl to hydrogen migration being 7.33. In weak acid, such as in dilute sulfuric acid, hydrogen migration becomes predominant and the ratio changes to 0.435. In strong acid, it is
believed that carbonium ion (A) formation takes place. In this case the reaction proceeds through the path (ia), causing the preferred migration of phenyl over hydrogen, since the positive charge on carbon will attract the π-electron cloud of the ring more strongly than the hydrogen and consequently this effect overrides the steric effect, discussed below.

![Diagram](A)

However, in less acidic medium, carbonium ion formation is negligible and it is possible that a steric resistance to phenyl migration might take place at the migration terminus and the smaller size of the hydrogen then permits its migration in preference to phenyl. The reaction then takes the path (ib).

From the chromic acid oxidation of diarylcarbinols in the present investigation, discussed in Section I, it has been found that the hydride-shift is faster than the phenyl-shift, assuming that the oxidation of secondary alcohols takes place through hydride-
shifts, which is in agreement with the observation of the Baeyer-Villiger oxidation of aldehydes (128a, 128b) (p.93). The Baeyer-Villiger oxidation reactions are believed to take place through 1,2-hydride shifts, and hydride-shifts are more favored than aryl-shifts in these reactions as well as in the reactions under the present investigation.

The migratory aptitudes of aryl groups were calculated from the relative amounts of different products obtained. From the analysis of the products it is apparent that a preferential migration of the electron-donating group occurs. However, the migratory aptitudes were found to be lower for electron-donating groups and higher for electron-attracting groups than those reported by other workers for the acid-catalyzed rearrangements of di- and triarylmethyl hydroperoxides (141, 142), which also proceed through aryl migration from carbon to an adjacent electron-deficient oxygen atom. The value of \( \rho \) for migration in the first case is -3.78 and in both cases the relative migratory aptitudes are very close to each other (141). The value of the reaction constant for migration was found to be -1.44 in the present investigation. This is much lower than the value of the migration reaction constant in the hydroperoxide cases mentioned above. This indicates the absence of extensive aryl participation. In the acid-catalyzed rearrangements of arylmethyl hydroperoxides, a
considerable amount of aryl participation takes place, as shown in the mechanisms (ii) and (iii), and the reactions proceed mainly through phenonium ions. The lower value of reaction constant $\rho$ in the present investigation indicates that the amount of positive charge on the central carbon atom in the chromate ester (I) is less than that in the carbon atom of the intermediate (IV) of hydroperoxide rearrangement reaction. The possible path of the two mechanisms are shown below:

Chromic acid oxidation of triarylcarnbinol:

\[ \begin{align*}
\text{Ar} & \quad \text{Ar} \quad \text{Ar} \quad \text{C} \quad \text{O} \quad \text{CrO}_3\text{H}_2 \\
\text{Ar} & \quad \text{Ar} \quad \text{Ar} \quad \text{C} \quad \text{O} \quad \text{Ar} + \text{H}_2\text{CrO}_3
\end{align*} \]
Rearrangement of triarylmethyl hydroperoxide (142):

The main difference between the hydroperoxide rearrangement reactions and the chromic acid reaction is the nature of the leaving groups. It is probable that the O—Cr bond of II will be stronger than the O—O bond of V, and that bond rupture in the transition state will be less advanced in II than in V. This will result in less positive charge accumulating on the central oxygen atom and the ring carbon atoms of II than of V. Thus the aryl participation in II is not as great as that in V, and the driving force due to aryl participation is less. This might be the cause of the more modest value of $\rho$ found in the present study than in the rearrangement reactions of hydroperoxide where extensive aryl participation takes place.
Curtin and Crew (143) also found lower migration ratios in the rearrangement reactions of a variety of 2-amino-1, 1-diaryl-ethanols than in other cases of migration from carbon to nitrogen. These workers also explained the lower values by postulating a transition state with little aryl participation. They believed that the rearrangement of the compound VI proceeds mainly through the structure VII, and not VIII, to the product IX.
However, this example is not parallel to the reaction under the present investigation.

The reaction constant $p^+$ for chromic acid oxidation of triarylcarbinols was found to be -0.879. A negative $p$ (usually near -1) is commonly found for chromic acid oxidation and this supports the idea that the central carbon becomes electron-deficient. The moderate size of the reaction constant shows that the amount of positive charge developed at this site is not great. This is also in agreement with the proposed mechanism that does not contain carbonium ion character to a great extent and consequently extensive aryl participation, as pointed out by Collins (140).

The value of $p^+$ for the overall reaction is less than that for aryl migration. In the first case, the observed value is the composite value, which includes the effect of electron withdrawing phenyl rings on the formation of the chromate ester, and thus it reduces the overall value of $p^+$.

The higher acidity of the medium increases the ionization of the carbinol and consequently the concentration of the chromate ester, and thus accelerates the reaction.

On addition of manganous ion a decrease in the rate of chromic acid oxidation of triarylcarbinols was observed. This is believed to be due to the oxidation of manganous ion to manganese dioxide by the intermediate chromium(IV) and chromium(V), induced
by the reacting carbinol. Similar reduction in rates in the presence of manganous ions have also been reported by other workers (53, 75). According to Wiberg and Richardson (75) an organic substrate $\text{ZH}_2$ can be oxidized by chromium(VI) following the possible paths (a), (b) or (c):

(a) $\text{ZH}_2 + \text{Cr}^{VI} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{IV}$

$\text{Cr}^{IV} + \text{Cr}^{VI} \rightarrow 2\text{Cr}^{V}$

$\text{ZH}_2 + \text{Cr}^{V} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{III}$

(b) $\text{ZH}_2 + \text{Cr}^{VI} \rightarrow \text{ZH}^* + \text{H}^+ + \text{Cr}^{V}$

$\text{ZH}^* + \text{Cr}^{VI} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{V}$

$\text{ZH}_2 + \text{Cr}^{V} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{III}$

(c) $\text{ZH}_2 + \text{Cr}^{VI} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{IV}$

$\text{ZH}_2 + \text{Cr}^{IV} \rightarrow \text{ZH}^* + \text{H}^+ + \text{Cr}^{III}$

$\text{ZH}^* + \text{Cr}^{VI} \rightarrow \text{Z} + \text{H}^+ + \text{Cr}^{V}$

$\text{ZH}_2 + \text{Cr}^{V} \rightarrow \text{Z} + 2\text{H}^+ + \text{Cr}^{III}$
In a recent communication Rošek et al. have ruled out the path (a) for the oxidative cleavage of cyclobutanol by chromic acid in presence of vanadium(IV) (144). This may be applicable to the chromic acid oxidation of other alcohols also even in the absence of vanadium. These workers have proposed another possible path (d), showing a rapid reaction between chromium(IV) and an organic substrate. This new mechanism has been based on Espenson's work (145), shown in (e):

(d)  \[
\begin{align*}
\text{Cr}^{VI} + \text{V}^{IV} & \xrightarrow{\text{fast}} \text{Cr}^{V} + \text{V}^{V} \\
\text{Cr}^{V} + \text{V}^{IV} & \xrightarrow{\text{slow}} \text{Cr}^{IV} + \text{V}^{V} \\
\text{Cr}^{IV} + n-C_4H_7\text{OH} & \rightarrow \text{Cr}^{III} + R^* \\
R^* + \text{V}^{V} & \rightarrow \text{HOCH}_2\text{CH}_2\text{CH}_2\text{CHO} + \text{V}^{IV}
\end{align*}
\]
where \( R^* \) represents a free radical.

(e)  \[
\begin{align*}
\text{Cr}^{VI} + \text{V}^{IV} & \xrightarrow{\text{fast}} \text{Cr}^{V} + \text{V}^{V} \\
\text{Cr}^{V} + \text{V}^{IV} & \xrightarrow{\text{slow}} \text{Cr}^{IV} + \text{V}^{V} \\
\text{Cr}^{IV} + \text{V}^{IV} & \rightarrow \text{Cr}^{III} + \text{V}^{V}
\end{align*}
\]
The added manganous ion, being a strong reducing agent, reduces chromium(V) and chromium(IV) thus eliminating the later steps in all the above possible sequences of the oxidation reaction. This effectively decreases the rate of oxidation of the carbinol since the intermediate chromium(IV) acts as a strong reducing agent and reacts with a second chromium(VI) species to form two of chromium(V), which then oxidize two more molecules of carbinol.

The product analysis showed that there is no appreciable change in the relative amounts of different products when manganous ions are added to the reaction mixture containing carbinol and chromic acid. This, together with the fact that the $p^+$ values in the absence and presence of manganous ion are very close to each other (Fig. 33), indicates that the mechanism of oxidation of triphenylcarbinol by chromium(V) or chromium(VI) is essentially the same.

The activation parameters calculated for the chromic acid oxidation of triphenylcarbinol, listed in Table XX, are somewhat similar to those reported by D.G. Lee for chromic acid oxidation of secondary alcohols (129).
A COMPARISON BETWEEN THE REACTIONS OF

PERMANGANATE AND CHROMIC ACID

Both permanganate and chromic acid oxidation of di- and triarylcarnbinols were found to be acid-catalyzed. This, together with the observed negative values of the respective reaction constants, indicates that in all the cases the reaction proceeds through electron-deficient transition states which are stabilized by electron-donating ring substituents. In both the oxidation reactions the diarylcarbinols give only diaryl ketones whereas the triarylcarnbinols produce the corresponding ketones along with phenols. Although the reactions of both chromic acid and acid permanganate are believed to proceed through an ester mechanism, the permanganate oxidation reactions are of first order in carbinol and of zero order in the oxidant, (except at very high acidities, as discussed later) whereas in chromic acid oxidations the reactions are of first order in each of the two reactants, i.e., of overall second order.

The oxidation of triarylcarnbinols in acid is believed to involve the formation and decomposition of manganate and chromate esters. The decomposition of manganate ester is much more rapid than that of chromate ester. This can be shown from a comparison
of the rates of oxidation of tri(p-tolyl)carbinol with the two oxidants at the same acidity. Although the permanganate oxidation reactions of triarylcarbinols are of first order in carbinol and zero order in permanganate, they change to second order at higher acidities, and thus the rate can be compared at these acidities. Although the two sets of reactions were carried out in different systems, the rates can be compared in systems where the apparent acidity functions are the same. The comparison is shown below:

<table>
<thead>
<tr>
<th>Acidity</th>
<th>Rate of Chromic Acid Oxidation (Table XVIII)</th>
<th>Rate of Permanganate Oxidation (Calculated from Fig.31)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_R$</td>
<td>$3.06 \text{ l.mole}^{-1}\text{sec}^{-1}$</td>
<td>$75.86 \text{ l.mole}^{-1}\text{sec}^{-1}$</td>
</tr>
</tbody>
</table>

The rapid decomposition of manganate ester compared to chromate ester causes the step preceding the reaction of carbinol and permanganate ion to be slower than the decomposition, and thus in this case the scission of protonated carbinols is the slow step. On the other hand the decomposition of chromate ester, being slower than the ionization of carbinols, becomes the rate-determining step. At higher acidities, where the ionization of
carbinols is faster, as shown in the case of tri(p-tolyl)carbinol, the permangante reactions become second order, as in the case of chronic acid oxidation.
PERMANGANATE OXIDATION OF BENZHYDROL

IN FROZEN SYSTEMS

During recent years it has been found that many reactions proceed much more rapidly in frozen systems than in the corresponding liquid systems (146-150). According to these workers an increase in concentration of reactants in ice crystals causes the acceleration. The permanganate oxidation of benzylamine has been studied and a similar acceleration of rate was found in the frozen systems (148). In order to study the oxidation of alcohols in such systems, benzhydrol was chosen as the substrate, since its reaction with permanganate in liquid systems has been studied by Stewart (4), and a comparison of rates in the two systems was convenient.

EXPERIMENTAL

For a typical run a solution was made up with 10 ml of a standard solution of benzhydrol in water, 20 ml of 1M KH₂PO₄ buffer, and 68 ml distilled water which was boiled previously to expel dissolved gases, in a 125 ml red Erlenmeyer flask. For reactions at pH higher than 12, the required quantity of 0.1M carbonate-free potassium hydroxide was added instead of buffer to maintain the desired pH. The total volume of mixture was kept
the same as before by adding water. To the mixture thus prepared, 2 ml of standard potassium permanganate solution was added and immediately after the addition 5 ml of the mixture was delivered into a screw-capped bottle, which was then immersed into a Dry Ice-acetone bath. This sample was used as the blank.

Eight more samples were prepared in the same way and were frozen in Dry Ice-acetone bath. After 5 minutes all the samples, except the blank, were taken out of the bath and immersed in an ice-water bath for a minute and then transferred to an ethylene-glycol bath maintained at \(-10 \pm 0.02^\circ\) with the aid of a cooling-unit. The baths were prepared in covered Dewar flasks in order to maintain a constant temperature. The initial time was reckoned from the time the samples were placed in the \(-10^\circ\) bath.

The blank was next warmed under tap water and was transferred quantitatively to a quenching mixture containing an excess of potassium iodide and sulfuric acid. The liberated iodine was titrated with sodium thiosulphate using Thyodene as indicator. The other samples were also analyzed in the same way after definite intervals of time.

For the reactions at pH less than 12, the ratio of substrate to permanganate taken was 3:2, according to the three
equivalent change of the oxidant to the two equivalent change of the substrate. A 1:4 molar ratio of benzhydrol to permanganate was taken for reactions at pH above 12.

RESULTS

Order of Reaction: Good second order rate plots were obtained by using the rate expression

$$k_2 = \frac{1}{[\text{alcohol}]_0 t} \times \frac{V_o - V_t}{V_o - 2V_o/5}$$

for the 3:2 ratio of substrate to permanganate and the rate expression

$$k_2 = \frac{-2.30}{[\text{alcohol}]_0 t} \times \log \frac{V_t - 9V_o/10}{V_t - 4V_o/5}$$

for the 1:4 ratio of the reactants (4). A typical rate plot is shown in Fig. 1.

Dependence of Rate on pH: The rates of reaction of benzhydrol and permanganate at -10° were studied between pH 1.50 and 12.40. The results are given in Table I. Fig. 2 shows a comparison of the oxidation rates at 25° (4) and -10°.
Fig. 1. Permanganate Oxidation of Benzhydrol in Frozen Systems.

\[ T = -10^\circ \]

\[ \text{pH} = 11.3 \]

\[ \frac{V_0 - V_t}{V_t - \frac{2}{5}V_0} \]

\[ k_2 = 26.2 \text{ l.mole}^{-1}\text{min}^{-1} \]
TABLE I

Permanganate Oxidation of
Benzhydrol in Frozen System.

Variation of Rate Constant with pH at $-10^\circ$.

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_2 \text{l.mole}^{-1}\text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.50</td>
<td>34.50</td>
</tr>
<tr>
<td>3.48</td>
<td>23.01</td>
</tr>
<tr>
<td>7.00</td>
<td>15.00</td>
</tr>
<tr>
<td>8.30</td>
<td>13.90</td>
</tr>
<tr>
<td>9.40</td>
<td>20.00</td>
</tr>
<tr>
<td>11.30</td>
<td>26.20</td>
</tr>
<tr>
<td>11.80</td>
<td>65.80</td>
</tr>
<tr>
<td>12.20</td>
<td>95.50</td>
</tr>
<tr>
<td>12.40</td>
<td>164.00</td>
</tr>
</tbody>
</table>

Activation Parameters and Isotope Effect:

The oxidation of benzhydrol at pH 7.00 was studied at temperatures ranging from $-20^\circ$ to $30^\circ$, and that of benzhydrol-$\alpha$-d was studied between the temperatures $-14^\circ$ to $25^\circ$ under the same experimental conditions. The variation of rate constant of
Fig. 2. Permanganate Oxidation of Benzhydrol. Variation of Rate Constant with pH.

- O - At -10° (frozen)
- O - At 25° (4)
the oxidation of benzhydrol with temperature is shown in Table II. The deuterium isotope effects at different temperatures are listed in Table III. Fig. 3 shows the change in rate constants with temperature for the two substrates.

**TABLE II**

Permanganate Oxidation of Benzhydrol in Frozen and Liquid Systems.

Variation of Rate Constant with Temperature at pH 7.00.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$k_2 \text{l.mole}^{-1} \text{min}^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>8.05</td>
</tr>
<tr>
<td>25</td>
<td>7.00</td>
</tr>
<tr>
<td>20</td>
<td>5.80</td>
</tr>
<tr>
<td>10</td>
<td>3.95</td>
</tr>
<tr>
<td>0</td>
<td>2.80</td>
</tr>
<tr>
<td>-2</td>
<td>3.33</td>
</tr>
<tr>
<td>-3</td>
<td>11.50</td>
</tr>
<tr>
<td>-4</td>
<td>18.00</td>
</tr>
<tr>
<td>-5</td>
<td>22.89</td>
</tr>
<tr>
<td>-10</td>
<td>15.00</td>
</tr>
<tr>
<td>-15</td>
<td>8.20</td>
</tr>
<tr>
<td>-20</td>
<td>4.56</td>
</tr>
</tbody>
</table>
Fig. 3. Permanganate Oxidation of Benzhydrol and Benzhydrolα-d.

Variation of Rate Constant with Temperature.

pH = 7.00

- Benzhydrol
- Benzhydrolα-d.
TABLE III

Permanganate Oxidation of Benzhydrolα-d in Frozen and Liquid Systems.

Variation of Rate Constant with Temperature at pH 7.00.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>$k_2$ l.mole$^{-1}$min$^{-1}$</th>
<th>$k_H/k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.95</td>
<td>7.3</td>
</tr>
<tr>
<td>10</td>
<td>0.57</td>
<td>7.7</td>
</tr>
<tr>
<td>0</td>
<td>0.37</td>
<td>7.7</td>
</tr>
<tr>
<td>-3</td>
<td>1.42</td>
<td>7.6</td>
</tr>
<tr>
<td>-5</td>
<td>3.01</td>
<td>7.4</td>
</tr>
<tr>
<td>-10</td>
<td>2.08</td>
<td>7.2</td>
</tr>
<tr>
<td>-14</td>
<td>1.20</td>
<td>7.5</td>
</tr>
</tbody>
</table>

From Fig. 3 it can be found that the maximum rate is obtained at $-5^\circ$ in both the cases. The rate decreases on lowering as well as on raising the temperature. On one side, a steady decrease in rate is found up to $-20^\circ$, this part shows the rates in the frozen system. On the other side the rate reaches a minimum at $0^\circ$ and then it again rises steadily up to $30^\circ$, this part represents the rates in the liquid system.
Fig. 4 shows the plot of $\log(k_2/T)$ against $1/T$ for the reactions of benzhydrol and benzhydrol-$d$. As in Fig. 3, in this case also, linear parts, representing the reactions in liquid and frozen systems can be distinguished. From these portions the activation parameters for the reaction in the two systems were calculated. Table IV lists the results.

**TABLE IV**

Permanganate Oxidation of Benzhydrol and Benzhydrol-$d$ in Frozen and Liquid Systems.

**pH 7.00**

Activation Parameters.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\Delta H$ kcal.mole$^{-1}$ (frozen)</th>
<th>$\Delta H$ kcal.mole$^{-1}$ (liquid)</th>
<th>$\Delta S$ e.u. (frozen)</th>
<th>$\Delta S$ e.u. (liquid)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzhydrol</td>
<td>18.4</td>
<td>5.68</td>
<td>17.2</td>
<td>-44.0</td>
</tr>
<tr>
<td>Benzhydrol-$d$</td>
<td>18.3</td>
<td>5.80</td>
<td>4.6</td>
<td>-47.7</td>
</tr>
</tbody>
</table>
Fig. 4. Permanganate Oxidation of Benzhydrol and Benzhydrol-d

Arrhenius Plot.

pH = 7.00

- Benzhydrol
- Benzhydrol-d
DISCUSSION

The order of reaction in the frozen systems was found to be the same as in the liquid systems between pH 1.5 and 12.4, with the same stoichiometry:

$$3(C_6H_5)_2CHOH + 2MnO_4^- = 3(C_6H_5)_2CO + 2MnO_2 + 2H_2O + 2OH^-$$

In the frozen systems a large acceleration in rate compared to that in the liquid system at same pH was observed. At pH 7.0 the rate constant in liquid systems at 25°C was found to be 7.0 l.mole\(^{-1}\)min\(^{-1}\) (4), whereas the same in the frozen system at -10°C is 15.0 l.mole\(^{-1}\)min\(^{-1}\). Apart from this and the activation parameters, the dependency of rate on other variables is quite similar to that for the liquid system. The rates are found to increase with pH in the same fashion as in the case of the liquid system, as shown in Fig. 2. The deuterium isotope effects are almost same for reactions in both the systems. These show that the reaction mechanism in the frozen system is the same as that in the liquid system. The higher rate of reaction in the frozen system is thus due to the higher \(\Delta S^+\).
It has been found in some earlier work (146-150) that the rates of several types of bimolecular reactions in frozen systems are higher than the corresponding rates of identical reaction at 25°. This acceleration is believed to be due to the crystallization of water which results in a higher concentration of solutes in the remaining liquid phase. This increase in concentration causes a higher rate of reaction in frozen systems. The variation of rate constant with temperature in frozen systems depends on two factors. In general, the second order rate constant for a bimolecular reaction in solution decreases with decrease in temperature. On the other hand in frozen systems the concentrations of the reactants in the liquid region increase, causing an increase in rate. Thus the temperature dependence of rates in frozen systems is the result of the competition between the two factors. It has been observed (149) that the maximum rate is obtained at a temperature below the freezing point of the solution. In the case of reaction between permanganate and benzhydrol, the same effect was found, the maximum rate was found at -5°, below which the rate decreases steadily due to the normal temperature effect, as in the liquid system, following the Arrhenius Law. The minimum rate was obtained at 0°. Between 0° and -5° the concentration effect was stronger than the temperature effect and thus a gradual increase in rate was observed in this temperature range.
Suggestion for Further Work

The rate-determining steps in the permanganate oxidation of benzhydrol and triphenylcarbinol have been found to be the ionization of the carbinol. Further support for this mechanism can be obtained by studying the racemization of unsymmetrically substituted carbinols in acidic media.

The kinetics of the permanganate oxidation of benzhydrol in weakly acidic regions, between pH 7.00 and 1.50 requires further elucidation. The reaction has been found to be of second order in this region in both liquid (4) and frozen systems. The rate increases with acidity but the increase does not follow the pattern expected for simple acid catalysis. The slow increase in rate requires further investigation.

The migratory aptitudes of different aryl groups during the chromic acid oxidation of triarylcarbinols have been determined by a quantitative estimation of the products. The values have been found to be somewhat different than those found by other workers for migrations in analogous systems. This can be checked by labelling one of the rings with tritium and determining the quantity of tritium in the two products, benzophenone and phenol. For the chromic acid oxidation of benzhydrol no migration of phenyl rings has been detected; that is, no benzaldehyde appears to have been formed. This can be checked by the method of isotope dilution.
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