THE MECHANISM OF PERMANGANATE OXIDATIONS:
PIVALALDEHYDE, BENZALDEHYDE AND
p-NITROPHENYLTRIFLUOROMETHYLCARBINOL

by

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We accept this thesis as conforming to the
required standard

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A study has been made of the potassium permanganate oxidation of three organic compounds: pivalaldehyde, p-nitrobenzaldehyde and p-nitrophenyltrifluoromethylcarbinol.

The permanganate-pivalaldehyde reaction has been investigated in the pH range 1 to 13. The results show that the reaction is first order in permanganate and aldehyde, that the oxidation by manganate is slower than that of permanganate by a factor of twenty five, and that the oxidation is general acid-catalyzed. The results in alkaline solution show some increase in rate but are not reproducible, which is most likely due to radical decomposition of the pivalaldehyde. Three mechanisms are discussed: Firstly, a typical general acid-catalysis scheme, secondly, one involving a tetragonal transition state and thirdly, one based on a hydride transfer. Of these, only the first two are able to accommodate the experimental evidence found earlier in the permanganate oxidation of benzaldehyde by Wiberg and Stewart (1).

The autocatalysis exhibited by the permanganate benzaldehyde reaction has been studied at low pH. The autocatalysis has also been investigated with
p-nitrobenzaldehyde in order to see if there is any substituent effect. Results show that the p-nitro aldehyde has a longer induction period. Moreover, it has been shown that overoxidation of the benzene ring rather than true autocatalysis has occurred. A radical chain mechanism has been put forward in an attempt to explain this observation.

The permanganate oxidation of p-nitrophenyltrifluoromethylcarbinol has been studied in 0.1 M sodium hydroxide in order to determine the mechanism of the reaction. A large enhancement in rate observed compared to rates found by Stewart and Van der Linden (2) in the permanganate oxidation of other substituted phenyltrifluoromethylcarbinols is good evidence for a reaction path involving hydrogen atom abstraction from the alkoxide to the permanganate ion. Such a mechanism is consequently favoured.
Sincere thanks are extended to my research director, Professor Ross Stewart, for his invaluable help and suggestions during the course of this investigation.
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INTRODUCTION

Oxidations of organic compounds by potassium permanganate are usually multi-stage processes. The degradation of organic molecules proceeds via the breakage of discreet covalent bonds while manganese undergoes reduction to lower valency states via a number of electron transitions. With certain reductants, in strongly acidic solutions, an overall five electron change may occur which is represented by:

$$\text{MnO}_4^- + 8 \overset{+}{\text{H}} + 5 \overset{\text{e}}{=} \text{Mn}^{2+} + 4 \text{H}_2\text{O}$$

In weakly acidic, neutral, and weakly alkaline solutions, the permanganate can undergo a three electron change as shown by:

$$\text{MnO}_4^- + 4 \overset{+}{\text{H}} + 3 \overset{\text{e}}{=} \text{MnO}_2 + \text{H}_2\text{O}$$

and in alkaline solutions (pH 12-14), permanganate reduction may be arrested at the manganate stage without any further noticeable reduction of the manganate:

$$\text{MnO}_4^- + \overset{\text{e}}{=} \text{MnO}_4^-$$

Generally, inorganic substrates appear to reduce acid permanganate to its lowest valency state (Mn$^{2+}$), whereas organic substrates containing oxidizable hydrogen stop
the reduction at the manganese dioxide stage. In fact, Mocek (3) found manganese dioxide precipitating in the oxidation of fluoral in sixty percent sulphuric acid, which is clearly indicative of arrest at this stage.

The stability of the oxy-anions of manganese is of major importance, as many reaction mechanisms have been formulated with reactive species formed from the decomposition of permanganate. Potassium permanganate itself is stable for months in neutral solution when kept in the dark (4), but decomposition is noticeable in acid (5) or in alkaline solutions (6).

The purple, tetrahedral permanganate ion is known to decompose in alkaline solution according to the equation:

\[
4 \text{MnO}_4^- + 4 \text{OH} \rightarrow 4 \text{MnO}_4^2- + 2 \text{H}_2\text{O} + \text{O}_2
\]

The rate of this reaction was first studied by Fergusson and co-workers, (6), under various conditions of temperature and concentration of alkali, but no mechanistic interpretations were made. Later, Stamm (7) suggested that the equilibrium,

\[
\text{MnO}_4^- + \text{OH} \rightleftharpoons ^\cdot\text{OH} + \text{MnO}_4^{2-}
\]

occurs in alkaline solution, with oxidation of a substrate taking place by free hydroxy-radicals.
Kinetic studies on the alkaline decomposition of permanganate have been made by Symons (8) who followed the rate of evolution of oxygen. He presented the following mechanism involving a series of electron and proton transfers.

\[
\begin{align*}
\text{MnO}_4^- + \cdot\text{OH} & \rightarrow \text{OH} + \text{MnO}_4^- \\
\cdot\text{OH} + \cdot\text{OH} & \rightarrow \cdot\text{O} + \text{H}_2\text{O} \\
\text{MnO}_4^- + \cdot\text{OH} + \cdot\text{O} & \rightarrow \text{MnO}_4^- + \text{HO}_2^- \\
\text{MnO}_4^- + \text{HO}_2^- & \rightarrow \text{MnO}_4^- + \text{HO}_2 \\
\text{HO}_2^- + \cdot\text{OH} & \rightarrow \text{O}_2^- + \text{H}_2\text{O} \\
\text{MnO}_4^- + \text{O}_2^- & \rightarrow \text{MnO}_4^- + \text{O}_2
\end{align*}
\]

Symons states that the usual mode of oxidation of alkaline permanganate solutions is by attack on the substrate by hydroxyl radicals or hydroxy-radical ions. He gives good evidence for this by initiating polymerizations of acrylonitrile and styrene in alkaline solutions of permanganate greater than three molar, whereas in less basic solution, only oxidation was found to occur. This conclusion is doubted by Drummond and Waters (9), who showed that diethyl ether and dioxane, which are rapidly oxidized by free hydroxy-
radicals (10), are not attacked by alkaline permanganate. They further showed that tertiary butanol, propionic, succinic and adipic acids are attacked by hydroxyl radicals but not by alkaline permanganate; while conversely, acetone, malonic acid and fumaric acid are rapidly attacked by alkaline permanganate but not by free hydroxyl radicals. However, they point out that in some of these cases inherent differences in acidity may account for differences in reactivity.

It is worthwhile mentioning some of the reactions of the lower oxidation states of manganese which are often helpful in elucidating the mechanisms of permanganate oxidation. Undoubtedly, the transfer of more than two electrons simultaneously would be considered energetically unlikely and thus it seems reasonable that permanganate should pass through some intermediate stage before being reduced to its final state.

The behaviour, stability, and oxidizing power of manganate were investigated extensively by Waters and co-workers (11,9). Manganate is stable only in strong alkali and solutions which are less than one molar in base slowly disproportionate into potassium permanganate and manganese dioxide (4,12).

\[
2 \text{H}_2\text{O} + 3 \text{MnO}_4^- \rightarrow \text{MnO}_2 + 2 \text{MnO}_4^- + 4 \text{OH}^- 
\]
However, the pH at which this occurs has never been precisely defined or investigated.

The blue hypomanganate ion, MnO$_4^{2-}$, was first prepared by Lux (13) and its oxidizing properties and stability have been investigated by Pode and Waters (11). This ion disproportionates into manganate and manganese dioxide, in solutions less than eight molar in sodium hydroxide, as shown by:

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

It is interesting to note that a very fast reaction occurs between hypomanganate and permanganate ions when the two are mixed (4) and this is the reason for the inability to observe any intermediates involving Mn V in permanganate oxidations in alkaline solution (11):

$$\text{MnO}_4^- + \text{MnO}_4^{2-} \rightleftharpoons 2 \text{MnO}_4^{-}$$

The oxidizing power of manganese oxy-anions of the type MnO$_4^x$ decreases in the order MnO$_4^5 >$ MnO$_4^3 >$ MnO$_4^2$. This is explained on the basis that the oxidation process involves acceptance of electrons by the anion, whereby the movement of electrons is contrary to the charge on the anion (12). Moreover, the characteristic green colour of the manganate ion can be seen to accumulate in many oxidation mixtures of alkaline
permanganate and is a further indication of its weaker oxidizing power. Wiberg and Stewart (1) however, found that both manganate and permanganate oxidize substituted benzaldehydes at the same rate. Since the formation of hydroxyl radicals is postulated in the oxidation process, it may well be that induced oxidation is occurring which would account for the same rate for both manganese species.

Decomposition by manganous salts is known as Guyards reaction (14) and occurs in neutral and alkaline solution.

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

The mechanism of this reaction is far from established (15). The main difficulty appears to be the fact that one deals with a heterogeneous reaction involving solid manganese dioxide and also that other manganese species of intermediate valency are formed in this reaction.

The cation \( \text{Mn}^+^3 \) is involved in the rate determining step of many reactions in acid solution, but is stable only in concentrated sulphuric acid (16), with fast disproportionation occurring at lower acidities:

\[
2 \text{Mn}^+^3 \rightarrow \text{Mn}^+^4 + \text{Mn}^+^2
\]
It is possible, however, to stabilize solutions of \( \text{Mn}^{3+} \) with complexing agents such as pyrophosphates, which makes them more suitable as oxidizing agents in the pH region. In fact, Waters and his collaborators (17,18) have extensively investigated the Mn III oxidations of a number of organic substrates using this technique.

Manganese dioxide has long been used as an oxidizing agent. These reactions are usually carried out in the presence of sulphuric acid or in aprotic solvents and are of heterogeneous nature. No homogeneous oxidations involving Mn IV are as yet known (13). It was pointed out from analogy with other transition metal hydroxides that \( \text{Mn(OH)}_4 \) would be too weak an acid to exist in the ionized form in solution and therefore dehydrates to the more thermodynamically stable manganese dioxide (12).

**Examples of Potassium Permanganate Oxidations:**

1. The oxidation of aliphatic aldehydes has received some study. Tronov (19) in 1927 determined the rate of reaction between potassium permanganate and a number of alcohols and aldehydes under a limited range of conditions, but he did not attempt any
mechanistic interpretations. Holluta and Mutschin (20) oxidized formaldehyde with permanganate and found the reaction to be base-catalyzed.

2. Drummond and Waters (9) have investigated the permanganate oxidation of a variety of aliphatic alcohols, aldehydes, ketones and acids; but they have presented little discussion in terms of mechanism. They found that saturated carboxylic acids were inert to permanganate, a result they state as consistent with the stability of C—H and C—C links in paraffin chains. Wiberg and Fox (21) have very recently oxidized a number of branched chain carboxylic acids using alkaline permanganate. In every case they postulate radical abstraction by hydroxyl radicals of a tertiary hydrogen atom as an initiation step in the reaction. Earlier work in this field was done by Kenyon and Symons (22) who found almost quantitative conversion of a number of branched chain carboxylic acids to their corresponding hydroxy acids. The latter workers also postulated a mechanism involving radical abstraction of a tertiary hydrogen atom by hydroxyl radicals.

The majority of alcohols, aldehydes and ketones studied in alkaline media by Drummond and Waters (9)
were oxidized beyond the stage of their corresponding carboxylic acids even though, as stated above, the acid was stable to permanganate. Extensive degradation was found in base and the authors suggest that such oxidations proceed, in part, by way of the enols, which like olefins, could be attacked at the double bond and so be oxidized beyond the original carbonyl site.

3. **Fluoral Hydrate** - The mechanism of the oxidation of this alcohol and its deuterium analogue has recently been studied extensively by Mocek (3) throughout the pH region. Compared with 2,2,2-trifluoroethanol and other substituted alcohols which ionize in the pH region, fluoral hydrate is unique in that it has two acidic hydrogens, both of which can ionize. The pK of the first ionization process was found to be 10.1.

Deuterium isotope effects were found to change with the nature of the substrate, being a maximum of ten for the monoanion. Furthermore, activation parameters and a positive salt effect show that the transition state is formed from species of like charge. These results are indicative of hydride ion transfer to the permanganate ion in the rate determining step. The following mechanism is proposed:
In the strongly alkaline region, (pH 12-14), the rate determining step would be:

$$\text{CF}_3\text{C}-\text{H} + \text{OH} \rightleftharpoons \text{CF}_3\text{C}-\text{H} + \text{H}_2\text{O}$$

$$\text{CF}_3\text{C}-\text{H} + \text{MnO}_4^- \rightleftharpoons \text{CF}_3\text{C}-\text{H} + \text{H MnO}_4^-$$

$$\text{H MnO}_4^- + \text{MnO}_4^- \xrightarrow{\text{fast}} 2 \text{MnO}_4^- + \text{H}$$

The evidence presented by Mocek does not allow an unequivocal interpretation of the kinetic data. It is kinetically impossible (23) to distinguish between a mechanism involving the aldehydrol anion as a discreet intermediate and a concerted mechanism involving hydroxyl ion and aldehyde hydrate. Hence, termolecular mechanisms are also considered, an example of which is:
4. Benzaldehyde - The permanganate oxidation of this aldehyde was first examined by Tompkins (24) who reported a linear increase in rate with hydroxide ion concentration over a very limited range, although in basic solution the rate in a given run was found to drop with time. He attributed the increase in rate to the formation of the "aldehydate ion" -

\[
-C_6H_5-C^{\text{O}}_\text{OH}^{\circ}
\]

The drop in rate with time was attributed to the Cannizzaro reaction, which is known to be catalyzed by oxidizing agents (25). However, this catalysis has since been shown to apply to heterogeneous reactions only. He postulated the following mechanisms:

\[
\text{C}_6\text{H}_5\text{CHO} + \text{MnO}_4^{-} \overset{\text{fast}}{\longrightarrow} \text{C}_6\text{H}_5\text{C}^{\circ} \text{O MnO}_3
\]

\[
\text{C}_6\text{H}_5\text{C}^{\circ} \text{O MnO}_3 \overset{k}{\longrightarrow} \text{C}_6\text{H}_5\text{CO}_2\text{H} + \text{MnO}_3
\]
A more detailed study was undertaken by Wiberg and Stewart (1) using deuterium and oxygen-18 labelling techniques. A substantial isotope effect was found in weakly acidic regions; this effect decreased with increasing pH as did the oxygen-18 transfer from permanganate to substrate. The reaction was also found to be general acid-catalyzed. The following mechanism was proposed:

\[ \text{fast} \quad 2 \text{MnO}_3^- + \text{H}_2\text{O} \rightarrow \text{H MnO}_4^- + \text{OH} + \text{MnO}_2 \]

\[ \text{fast} \quad \text{H MnO}_4^- + \text{C}_6\text{H}_5\text{CHO} \rightarrow \text{C}_6\text{H}_5\text{CO}_2\text{H} + \text{OH} + \text{MnO}_2 \]

A Hammett plot for the reaction in this region showed a good linear relation with a small negative
\( \ell \) value. One would expect the rate determining step to have a positive \( \ell \) since an electron withdrawing group would facilitate the abstraction of a proton in this step. Hence, the equilibrium forming the intermediate ester is proposed as having a negative \( \ell \) which is larger in magnitude than that for the rate determining step. A similar situation is known to exist in the chromic acid oxidation of alcohols (26).

In alkaline solutions the rate was found to depend on the square root of the hydroxyl concentration and most, if not all, of the oxygen introduced into the aldehyde was derived from the solvent. The deuterium isotope effect was small and was found to decrease with increasing pH. This suggested that the reaction may no longer involve cleavage of the aldehyde carbon-hydrogen bond in the rate determining step. Furthermore, the reaction has a large positive \( \ell \) value (+1.83) in contrast to the small negative value found in neutral solution.

The original proposal of Tompkins that the "aldehydate ion" is formed fits some of the facts. This ion could react with the permanganate ion by a hydride shift and the effect of substituents on the rate would be in agreement with the stability of the
ion. However, in order to explain the dependence of the rate on the square root of the hydroxyl concentration, a free radical chain mechanism involving hydroxyl radicals was suggested. Furthermore, manganate and permanganate were found to react with benzaldehyde with rates of the same order of magnitude. This supports a radical mechanism, as one would expect a hydride shift to be much slower for manganate in view of the double negative charge on the ion. A typical mechanism considered is shown below:

Initiation: \[ \text{MnO}_4^- + \text{OH} \xrightarrow{k_1} \text{MnO}_4^- + \text{HO}^- \]

Propagation: \[ \text{HO}^- + \text{C}_6\text{H}_5\text{CHO} \xrightarrow{k_2} \text{C}_6\text{H}_5\text{COH} \]

Termination: \[ 2 \text{HO}^- \xrightarrow{k_4} \text{H}_2\text{O}_2 \xrightarrow{\text{fast}} \text{O}_2 + \text{H MN0}_4^- \]

5. Benzhydrol - This substrate on oxidation yields a product stable to further reaction and was examined thoroughly by Stewart (27). The use of deuterium substitution and oxygen-18 exchange enabled
him to show that the carbon-hydrogen bond is broken in the rate determining step and that none of the oxygen is introduced into the substrate by the permanganate. The rate showed a dependence on the hydroxyl ion concentration and a positive salt effect. On the basis of these observations, a mechanism involving a hydride ion transfer from the benzhydrylate anion to the permanganate ion was postulated:

\[
\begin{align*}
\text{Ph}_2\text{CHOH} + \text{OH} & \rightarrow \text{Ph}_2\text{CHO} + \text{H}_2\text{O} \quad \text{fast} \\
\text{Ph}_2\text{CHO}^- + \text{MnO}_4^- & \rightarrow \text{Ph}_2\text{C}=\text{O} + \text{H} \text{MnO}_4^- \quad \text{slow} \\
\text{H MnO}_4^- + \text{MnO}_4^- + \text{OH} & \rightarrow 2 \text{MnO}_4^- + \text{H}_2\text{O} \quad \text{fast}
\end{align*}
\]

6. **Phenyltrifluoromethylcarbinols** - As a further study on the oxidation of alcohols, a series of aryl trifluoromethylcarbinols proved to be satisfactory since they are highly ionized in tenth normal base and are oxidized cleanly to the corresponding ketones by potassium permanganate.

\[
\text{ArCHOHCF}_3 + 2 \text{MnO}_4^- + 2 \text{OH} \rightarrow \text{ArCOCF}_3 + 2 \text{MnO}_4^- + 2 \text{H}_2\text{O}
\]

Stewart's work on benzhydrol given above has indicated that the alcoholate anion is the reactive species in the oxidation. If this is so, then it should be
possible to observe a levelling-off of the rate in the region where the alcohol is almost fully ionized and moreover, the rate should be determined by the alcoholate ion present. This has in fact been confirmed (2,28). Further, the observation of a positive salt effect, a large negative entropy of activation and a large deuterium isotope effect ($k_H/k_D = 16$) are indicative of a mechanism which involves a hydride ion transfer.

$$\text{ArCHOHCF}_3 + \cdot \text{OH} \rightleftharpoons \text{ArCHOHCF}_3 + \text{H}_2\text{O}$$

$$\text{Ar} - \text{O} - \text{H} + \text{MnO}_4^- \rightarrow \left[ \begin{array}{c} \text{O} \\ \text{CF}_3 \end{array} \right] \rightarrow \text{Ar} - \text{C} - \text{H} - \cdot \text{OMnO}_3^- \rightarrow \text{ArCCF}_3 + \text{H MnO}_4^-$$

Normal deuterium isotope effects, which result from a loss of carbon-hydrogen stretching modes in the transition state, are less than half this size at the same temperature (8). The large effect observed here is postulated as due to the loss of bending as well as stretching modes in the transition states. However, the possibility of quantum mechanical tunnelling is not excluded. The effect of nuclear substitution was found to be slight and this is not in accord with the above mechanism. A hydride transfer from the alkoxide ion to permanganate should result in a negative
value, i.e. a p-methoxy substituent should accelerate and a p-nitro group retard the process. However, the reaction rate was found to be only slightly affected by nuclear substitution and furthermore, the small variations in rate which did occur were not related linearly to the Hammett substituent constant $\rho$. The following explanations have been presented. Firstly, a simple hydride transfer may in fact be occurring with the electronic effect of a distant group in the molecule being unimportant. Secondly, two different processes with different electronic requirements may be occurring, one with a positive and the other with a negative $\rho$ value. Thirdly, one of several termolecular mechanisms may be taking place, an example of which is shown below:

$$\text{H}_2\text{O}^+ + \text{Ar} + \text{H}^+ + \text{MnO}_4^- \rightarrow \text{H}_3^+\text{O} + \text{Ar}-\text{C}-\text{CF}_3 + \text{MnO}_4^-$$

$$\text{Ar}-\text{C}-\text{CF}_3 + \text{MnO}_4^- \rightarrow \text{products}$$
OBJECT OF RESEARCH

This project was undertaken with a view to strengthening some previously reported mechanisms for permanganate oxidations determined in this and other laboratories. Stewart and Wiberg (1) have studied extensively the permanganate oxidation of benzaldehyde and substituted benzaldehydes in the pH range 5 to 13. In order to see if the mechanism they proposed is applicable to other aldehydes of similar nature, the aliphatic analog of benzaldehyde, pivalaldehyde, was oxidized with permanganate. Since neither substrate contains an α-hydrogen, it was of interest to determine if both reacted via similar paths.

Furthermore, Wiberg and Stewart (1) also reported that an auto catalytic effect in the oxidation of benzaldehyde by permanganate occurred when the pH was lowered much below five. As a further extension of their research, it was decided to study this effect in the pH region 1 to 4, in an attempt to elucidate the nature of the auto catalysis. Benzaldehyde itself was studied in this connection, as well as p-nitrobenzaldehyde, in order to see if there was any substituent effect.
Stewart and Van der Linden (2) have postulated three possible mechanisms for the permanganate oxidation of phenyltrifluoromethylcarbinols. However, more recently, Stewart (29) has postulated a mechanism for the oxidation of fluoroalcohols which involves hydrogen atom abstraction from the anion to the permanganate ion. In order to check the possibility of such a mechanism in the oxidation of substituted phenyltrifluoromethylcarbinols, a study of the permanganate oxidation of p-nitrophenyltrifluoromethyl carbinol in tenth normal sodium hydroxide was undertaken. It can be immediately seen that if such a mechanism is operative, then the greatest stabilization of a radical intermediate would be afforded by a p-nitro substituent, as the following resonance structures indicate:

\[
\begin{align*}
\text{O} & \quad \text{O}^- \\
\text{O} & \quad \text{O}^- \\
\text{N} & \quad \text{O}^- \\
- & \quad - \\
\end{align*}
\]
EXPERIMENTAL

A. Preparation, Purification, and Identification of Substrates

1. Pivalaldehyde

Pivalaldehyde was obtained from Columbia Organic Chemicals Ltd. It was purified before use by vapour phase chromatography using a ten foot "Carbowax" column at a temperature of about 30°. Stock solutions of 0.02 molar were prepared by pipetting an accurate volume of the purified aldehyde (pipettes were used) into a volumetric flask and making up to the mark with warm distilled water. The water had been previously boiled in order to remove dissolved oxygen, but had to be cooled to about 45° in order to minimize vaporization losses, since pivalaldehyde boils in the range 71-4° (30). The concentration of the aldehyde could be accurately determined since the density was known (.793 g. per ml.). However, it was found that pivalaldehyde undergoes both autoxidation and decomposition upon standing, and other means had to be employed to determine its concentration.

The decomposition of pivalaldehyde to iso-butane and carbon monoxide and its autoxidation to
pivalic acid have both been shown to be catalyzed by light and/or peroxides (31). However, when stored in a cool dark place, both these effects have been reported as being markedly reduced (30). Stock solutions of pivalaldehyde were then prepared in blackened volumetries and stored in the refrigerator. Solutions prepared and kept in this way were checked periodically for autooxidation by titration with 0.02 N sodium hydroxide. It was found that under such conditions, oxidation is negligible. This is to be contrasted with samples stored at room temperature, where as much as twenty-five percent oxidation was encountered over a two month period.

Qualitative evidence for the decomposition can be gained by simply loosening the cap of a sample bottle stored at room temperature and noticing the relatively large release of pressure due to the isobutane and carbon monoxide. Furthermore, it is worth noting that a sample cell left on the bench overnight showed no absorption the following morning. This result is presumably due to the light catalyzed decomposition. Also, stock solutions made up by the addition of warm water could likely cause some volatilation of the pivalaldehyde due to its high vapour pressure. These troublesome characteristics made a spectroscopic
determination of the concentration mandatory, in that stoichiometric ratios in the oxidation by potassium permanganate be assured. The following procedure was adopted.

One hundred microlitre samples of freshly purified pivalaldehyde were added to 50 ml. blackened volumetrics and immediately dissolved in hexane, methanol, dioxane and water. Using a CARY-14 recording spectrophotometer, the maximum wave length for absorption was found for each of these and using the Beckman D.U. Spectrophotometer, their optical densities were accurately determined. A value for the optical density of pivalaldehyde in aqueous solution was found to be much less than in hexane and dioxane, as shown in Table I. This difference was interpreted as a loss due to vaporization in preparing the solution, rather than to formation of the hydrate. Furthermore, virtually no absorption occurred in methanol, presumably due to the formation of the hemiacetal.

The average optical density of pivalaldehyde in hexane and dioxane was taken and the extinction coefficient was found to be 17.0. Using this value to determine the concentration of the aldehyde in aqueous solution, as much as thirty-five percent deviation
<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{max}}$ (m$\mu$)</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methanol</td>
<td>295</td>
<td>0.06</td>
</tr>
<tr>
<td>Hexane</td>
<td>295</td>
<td>0.290</td>
</tr>
<tr>
<td>Dioxane</td>
<td>290</td>
<td>0.262</td>
</tr>
<tr>
<td>Water</td>
<td>285</td>
<td>0.209</td>
</tr>
</tbody>
</table>

**Table I**

Absorption of Pivalaldehyde in Solution
from that expected by weight calculation was found. As a further check on the value of the extinction coefficient, a reaction was done in which potassium permanganate was added in fifty percent excess of pivalaldehyde and let stand overnight. Upon titration, this yielded a concentration of pivalaldehyde which should have resulted from an extinction coefficient of 16.3. An average value of 16.7 was then decided upon as the extinction coefficient of pivalaldehyde in order to determine its concentration accurately. This gives good agreement with a value of 16.5 obtained in hexane by other workers (32).

The concentration of the aldehyde was determined each day from the optical density found on the Beckman D.U. Spectrophotometer, before any kinetic runs were started. The optical density was found to be constant over a period of about three weeks but then began to decrease. At this point the stock solution was discarded and a fresh one prepared. No kinetic runs were done when the solution gave evidence of decay as the prospect of free radicals interfering with the oxidation was not desirable. A typical decay scheme is shown in Table II.
Table II

Decomposition of a Typical Solution of Pivalaldehyde

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Optical Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.198</td>
</tr>
<tr>
<td>2</td>
<td>.204</td>
</tr>
<tr>
<td>4</td>
<td>.201</td>
</tr>
<tr>
<td>9</td>
<td>.203</td>
</tr>
<tr>
<td>17</td>
<td>.204</td>
</tr>
<tr>
<td>23</td>
<td>.179</td>
</tr>
<tr>
<td>25</td>
<td>.173</td>
</tr>
<tr>
<td>32</td>
<td>.163</td>
</tr>
<tr>
<td>40</td>
<td>.156</td>
</tr>
<tr>
<td>58</td>
<td>.146</td>
</tr>
<tr>
<td>73</td>
<td>.154</td>
</tr>
<tr>
<td>75</td>
<td>.162</td>
</tr>
<tr>
<td>78</td>
<td>.152</td>
</tr>
<tr>
<td>97</td>
<td>.156</td>
</tr>
<tr>
<td>141</td>
<td>.134</td>
</tr>
</tbody>
</table>
2. Benzaldehyde and p-Nitrobenzaldehyde.

Benzaldehyde was distilled over nitrogen immediately before use. A 0.01 molar solution was prepared by pipetting an accurate volume into a volumetric flask and dissolving immediately in boiling distilled water. Stewart and Wiberg (1) have mentioned the stability of aqueous solutions of benzaldehyde to autoxidation and no check for the presence of benzoic acid was undertaken.

p-Nitrobenzaldehyde, obtained from Eastman Kodak Company, was recrystallized from a six to one water to methanol mixture to a constant melting point, m.p. 107° (Lit., 106.5°). A sample was weighed out and dissolved in boiling distilled water in a volumetric flask to give a 0.002 molar solution. The water solubility of this aldehyde is not expected to be much more.

3. Phenyltrifluoromethylcarbinol and p-Nitrophenyltrifluoromethylcarbinol.

A sample of phenyltrifluoromethylcarbinol obtained from Columbia Organic Chemicals Ltd., was purified before use by vapour phase chromatography using a ten foot "Uycon polar" column at a temperature of about 135°.
As before, aqueous solutions were prepared by pipetting accurate volumes and dissolving in boiling distilled water in a volumetric flask. Solutions of the order of 0.006 molar were prepared in this way. The density of this alcohol could not be found in the literature. It was determined both by pipetting \( \lambda \) volumes accurately and weighing by difference, on two occasions, and weighing a pippetted volume from a micro-litre syringe into a small container on one other occasion. All determinations of the density gave good agreement and yielded an average value of \( 1.307 \text{ g. ml}^{-1} \). It is worth noting that the gravimetric balance showed an increase in weight with time for this alcohol, indicating that it may be hygroscopic.

\p-Nitrophenyltrifluoromethylcarbinol was prepared in good yield by Mr. L. J. Muenster. The following is a brief outline of his experimental procedure:
The acetate was first prepared by adding the carbinol dropwise to acetic anhydride. Fuming nitric acid was added to the acetylation mixture. The reaction mixture was then poured onto ice water and left standing overnight. The p-nitroacetate was separated and hydrolyzed with ethanol and hydrochloric acid and after solvent evaporation, a residual brown liquid
solidified to a crystalline mass. This was recrystallized to a constant melting point from a six to one water to methanol mixture. Colorless crystals of p-nitrophenyltrifluoromethylcarbinol were obtained, m.p. 133-134°. Analysis gave excellent agreement with calculated values:

Calcd. for C₈H₆NO₃F₃: C, 43.45; H, 2.74; N, 6.34

Found for C₈H₆NO₃F₃: C, 43.50; H, 2.63; N, 6.40

Infrared spectrum showed the expected absorption bands. Oxidation with potassium permanganate resulted in p-nitrobenzoic acid which was confirmed by mixed melting point determination and infrared spectrum.

Aqueous solutions of the p-nitrophenyltrifluoromethylcarbinol were prepared by weighing and dissolving in boiling distilled water. Even though boiling water must aid in its solubility, this alcohol was found to be very insoluble as solutions could not be made up much in excess of 0.001 molar. Alkaline solutions can be made much more concentrated as p-nitrophenyltrifluoromethylcarbinol has been shown by Stewart and Van der Linden (33) to have a pKₐ of 11.1. However, good kinetics are not obtained when the alcohol is first dissolved in alkaline solution.
B. Kinetic Method

An iodometric method for following the rate of disappearance of the permanganate ion was found suitable for following the oxidation of pivalaldehyde. Wiberg and Stewart (1) and Stewart and Van der Linden (28) had previously found the same method satisfactory for studying the permanganate oxidation of substituted benzaldehydes and phenyl trifluoromethylcarbinols respectively, and it was again employed in these further studies. The method is essentially that described by Tompkins (24); namely, the course of the reaction was followed by quenching aliquots in acidified potassium iodide solution and titrating the liberated iodine with sodium thiosulphate.

In most cases the permanganate-substrate reaction was found to be quite fast and it was not possible to titrate each aliquot immediately after quenching. Instead, aliquots were removed continuously and quenched one after another and the flasks set aside in a darkened place to be later titrated. After the last aliquot had been quenched, the previously set aside flasks were titrated in a random order and all titrations were completed within fifteen minutes after the initial liberation of iodine.
Due to the decomposition of pivalaldehyde by light (an effect which has been previously discussed), all reactions were carried out in darkened flasks. The same procedure was used for all other oxidations. A typical kinetic run was carried out as follows: 0.2 M sodium hydroxide (21.8 ml.), distilled water (20.1 ml.) and pivalaldehyde (3.30 ml.) were added to a 125 ml. darkened erlenmeyer flask. This reaction mixture was allowed to equilibrate in a constant temperature bath of 25.2 ± 0.05°C. The oxidation was then initiated by the addition of 4.78 ml. of potassium permanganate (standardized against sodium oxalate) at the same temperature from a fast delivery pipette (tip removed) and a timer immediately started. All reactions were based on a 50 ml. total volume. Before the addition of potassium permanganate, 50 ml. erlenmeyer flasks were made ready with dilute sulphuric acid to which was added a mixture of solid potassium iodide and sodium bicarbonate. The latter reagent was added to eliminate possible air oxidation of the iodide. After the evolution of carbon dioxide had ceased, potassium permanganate was added to the reaction mixture, the vessel swirled, and aliquots removed one after another and quenched in the acidified iodide. These were set aside and later titrated with
sodium thiosulphate from a 5 ml. capacity burette using thyodene as indicator. Overall concentrations used here were: sodium hydroxide 0.1 M, substrate 0.000555 M, permanganate 0.00111 M. Here the ratio of permanganate to substrate is two to one since the permanganate is reduced to manganate in alkaline solutions.

For reactions in weakly basic and acidic solutions, a two to three ratio of permanganate to substrate was used as the permanganate is reduced to manganese dioxide at pH's less than 11.5. Dipotassium hydrogen phosphate was used as a buffer with addition of sulphuric acid or sodium hydroxide to vary the pH. Potassium sulphate was used to maintain the ionic strength. It was found that kinetic plots were most accurate in this region and rates were reproducible to within five percent.
RESULTS

Although three different substrates were employed in this work, all were two equivalent reductants and as such consumed equal amounts of permanganate. Molar ratios were consequently the same for all three substrates. A brief outline of the kinetic expressions and the stoichiometries used is in order here.

In the pH range 1 to about 10.5 the Mn VII is reduced to Mn IV. Hence, a three equivalent electron change occurs. Since the oxidation involves a two equivalent change, this sets the ratio of the substrate to permanganate at 3:2 as the following equation indicates:

\[ 2 \text{MnO}_4^- + 3 \text{RCHO} + 2 \text{H}^+ \rightarrow 2 \text{MnO}_2 + 3 \text{RCOOH} + 4 \text{H}_2\text{O} \]

In more strongly alkaline solutions, above pH 12, the permanganate is reduced to manganate which accumulates and reacts with the substrate at a slower rate compared to that of oxidation by permanganate. Since here, a one equivalent change occurs, the ratio of substrate to permanganate now becomes 1:2, as shown:

\[ 2 \text{MnO}_4^- + \text{RCHO} + 2 \text{OH}^{-} \rightarrow 2 \text{MnO}_4^{2-} + \text{RCOOH} + 2 \text{H}_2\text{O} \]
In the region between pH 10.5 and 12, some intermediate ratio applies. Manganate is stable above pH 12 and completely unstable below pH 10.5; however, in the intermediate range the disproportionation of manganate appears to be both time and pH dependent and therefore precise information about the oxidation rate cannot be obtained. Mocek gives a good account of this in his thesis (3). Stoichiometric ratios of the substrate to permanganate of 3:2 and 1:2 below pH 11 and above pH 12 respectively were used throughout this investigation.

Integrated rate expressions for a second order reaction were derived by Stewart (1,27) for permanganate oxidations in aqueous solution where thiosulphate is used in an iodometric titration and the stoichiometric concentration of the reactants is present throughout the oxidation. In alkaline solutions, the rate expression is given by:

$$k_2 = \frac{1}{\text{substrate}_o} \times \frac{V_o - V_t}{V_t - 4/5 V_o}$$

where $V_o = \text{initial volume of thiosulphate at} \ t=0$

$V_t = \text{volume of thiosulphate used at time} \ t$

$V_\infty = 4/5 \ V_o = \text{final volume at} \ t$
\[ t = \text{time in seconds} \]
\[ \left[ \text{substrate} \right]_o = \text{initial concentration of substrate at } t=0 \]
\[ k_2 = \text{second order rate constant in } 1 \text{ mole}^{-1} \text{sec.}^{-1} \]

A similar expression is found for the ratio 3:2 and is given by:

\[ k_2 = \frac{1}{\left[ \text{substrate} \right]_o} \times \frac{V_o - V_t}{V_t - 2/5 V_o} \]

A plot of \((V_o - V_t)/(V_t - 4/5 V_o)\) and \((V_o - V_t)/(V_t - 2/5 V_o)\) vs. time gave good straight lines passing through the origin.

A. The Permanganate Oxidation of Pivalaldehyde

1. Nature of the Substrate

It is well established that trichloroacetaldehyde exists in aqueous solution in the hydrated form. Similarly, trifluoroacetaldehyde takes up water to form the hydrate (3). In the experimental part of this thesis the difficulty encountered in determining the concentration of pivalaldehyde in aqueous solution is discussed. In that study, the optical density of
solutions prepared in hexane, water and methanol (Table I) decreased in the order hexane \succ water \succ methanol. The decrease in optical density in water was attributed to volatilization of the pivalaldehyde upon preparation of the solution rather than to formation of the hydrate. This assumption is supported by the data given in Table II, which shows a constant optical density for about three weeks before decomposition occurs. Such a result would not be consistent with formation of a hydrate. Furthermore, hydrate formation would be inconsistent with the electronic nature of the methyl groups when one considers the mechanism of hydrate formation which involves a proton transfer (34) (35).

It is worthwhile to comment upon the optical density of a solution prepared in methanol which shows virtually no absorption (Table I). This could only be due to the formation of the hemiacetal, which is consistent with the well known hemiacetal formation of acetaldehyde in methanol (36).

2. Oxidation of Pivalaldehyde in the Region pH 1-12.5

Constant ionic strength conditions (\( \mu = 0.6 \)) were used for all runs throughout this region. At constant
pH and ionic strength the rate of oxidation of pivalaldehyde is given by the expression:

\[ \frac{d[\text{MnO}_4^-]}{dt} = k_2 [\text{MnO}_4^-] [\text{Pivalaldehyde}] \]

Good second order rate plots have been obtained for all experiments in this region. No kinetic runs were done in the region pH 10.5 to 12.0. The results for a typical run are given in Table III, with the corresponding straight line plot shown in Figure 1.

A dependence on pH is observed, with the rate rising below a pH of 4.5 and beyond 10.5 and pH independent between these two values, as shown in Figure 2. By inspection, the changes in rate are shown as linear, although such may not be the case, especially in the basic region. This plot is not unlike that found by Wiberg and Stewart (1) in the pH region 5 to 13 for the permanganate oxidation of benzaldehyde, although the rate of oxidation of pivalaldehyde is observed to be ten times faster. The results corresponding to Figure 2 are given in Table IV.
Table III

The Permanganate Oxidation of Pivalaldehyde

A Typical Kinetic Run

<table>
<thead>
<tr>
<th>$V_t$ (ml.)</th>
<th>$V_o - V_t$ (ml.)</th>
<th>$V_t - 2/5V_o$ (ml.)</th>
<th>$\frac{V_o - V_t}{V_t - 2/5V_o}$</th>
<th>time (secs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.812</td>
<td>0.417</td>
<td>2.121</td>
<td>0.196</td>
<td>33</td>
</tr>
<tr>
<td>3.620</td>
<td>0.609</td>
<td>1.929</td>
<td>0.316</td>
<td>55</td>
</tr>
<tr>
<td>3.470</td>
<td>0.759</td>
<td>1.779</td>
<td>0.427</td>
<td>73</td>
</tr>
<tr>
<td>3.278</td>
<td>0.951</td>
<td>1.587</td>
<td>0.650</td>
<td>98</td>
</tr>
<tr>
<td>3.200</td>
<td>1.029</td>
<td>1.509</td>
<td>0.682</td>
<td>117</td>
</tr>
<tr>
<td>3.105</td>
<td>1.124</td>
<td>1.414</td>
<td>0.795</td>
<td>134</td>
</tr>
<tr>
<td>3.011</td>
<td>1.218</td>
<td>1.320</td>
<td>0.921</td>
<td>157</td>
</tr>
<tr>
<td>2.885</td>
<td>1.344</td>
<td>1.194</td>
<td>1.125</td>
<td>196</td>
</tr>
</tbody>
</table>

$$\left[\text{Pivalaldehyde}\right]_0 = 1.512 \times 10^{-3} \text{ Mole l.}^{-1}$$

$$\left[\text{MnO}_4^-\right]_0 = 1.008 \times 10^{-3} \text{ Mole l.}^{-1}$$

$V_o = 4.229 \text{ ml.}$

$2/5 \ V_o = 1.691 \text{ ml.}$
FIGURE 1

A typical rate plot
Oxidation of Pivalaldehyde

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

pH = 10.37
\( \mu = 0.6 \)
FIGURE 2

Oxidation of Pivalaldehyde
Dependence of rate on pH

$k_z$ (l. mole$^{-1}$ sec$^{-1}$)

pH
Table IV

Permanganate Oxidation of Pivalaldehyde

Variation of Rate Constant with pH

<table>
<thead>
<tr>
<th>pH</th>
<th>rate (l. mole$^{-1}$ sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.65</td>
<td>9.2</td>
</tr>
<tr>
<td>2.70</td>
<td>8.6</td>
</tr>
<tr>
<td>3.45</td>
<td>7.6</td>
</tr>
<tr>
<td>4.60</td>
<td>5.7</td>
</tr>
<tr>
<td>5.50</td>
<td>4.6</td>
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<tr>
<td>6.65</td>
<td>5.1</td>
</tr>
<tr>
<td>7.18</td>
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<td>8.05</td>
<td>5.1</td>
</tr>
<tr>
<td>9.13</td>
<td>4.8</td>
</tr>
<tr>
<td>10.38</td>
<td>4.6</td>
</tr>
<tr>
<td>12.50</td>
<td>21.4</td>
</tr>
</tbody>
</table>

Temperature $= 25.00 \pm 0.05^\circ$

Ionic Strength $= 0.6$ mole l.$^{-1}$
3. General Acid-catalysis

To demonstrate that general acid-catalysis does occur, rates were determined in solutions containing varying amounts of buffer at constant ionic strength and pH and hence containing varying amounts of undissociated acid. A catalytic effect is apparent as shown in Figure 3, although rates are only about twenty percent enhanced at pH's studied for a tenfold change in phosphate concentration. The results for Figure 3 are given in Table V. This is to be compared with a similar plot of Stewart's (1) in the permanganate oxidation of benzaldehyde which also shows a twenty percent increase in rate over the same buffer concentration range.

In addition, several runs were done at constant buffer concentration while varying the pH by the addition of concentrated sulphuric acid. Again, this resulted in varying amounts of undissociated acid. Results for these runs are given in Table VI. A general acid-catalysis effect is evident again in Figure 4.

In order to give further evidence for general acid-catalysis, several runs were done with sodium
FIGURE 3
Oxidation of Pivalaldehyde
Dependence of rate on Orthophosphate concentration, constant pH

$\frac{k_2}{(l. \text{ mole}^{-1} \text{ sec}^{-1})}$

$pH = 1.4$
$pH = 2.9$
$pH = 5.0$

$[\text{HPO}_4^{2-}] \text{ M.}$
### Table V

Oxidation of Pivalaldehyde at Constant pH

Variation of the Rate Constant with Buffer Concentration

<table>
<thead>
<tr>
<th>pH</th>
<th>$[\text{HPO}_4^{2-}]$ (mole 1.⁻¹)</th>
<th>$k_2$ (l. mole⁻¹ sec⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.04</td>
<td>4.98</td>
</tr>
<tr>
<td>5.0</td>
<td>0.20</td>
<td>5.45</td>
</tr>
<tr>
<td>5.0</td>
<td>0.40</td>
<td>5.98</td>
</tr>
<tr>
<td>2.90</td>
<td>0.08</td>
<td>6.48</td>
</tr>
<tr>
<td>2.90</td>
<td>0.20</td>
<td>6.65</td>
</tr>
<tr>
<td>2.90</td>
<td>0.28</td>
<td>6.90</td>
</tr>
<tr>
<td>2.90</td>
<td>0.34</td>
<td>7.02</td>
</tr>
<tr>
<td>2.90</td>
<td>0.40</td>
<td>7.18</td>
</tr>
<tr>
<td>1.40</td>
<td>0.04</td>
<td>7.31</td>
</tr>
<tr>
<td>1.40</td>
<td>0.20</td>
<td>7.75</td>
</tr>
<tr>
<td>1.40</td>
<td>0.40</td>
<td>8.05</td>
</tr>
</tbody>
</table>
Table VI

Oxidation of Pivalaldehyde at Constant Buffer Concentration

Variation of the Rate Constant with pH

<table>
<thead>
<tr>
<th>$[\text{HPO}_4^{2-}]$ (mole 1.$^{-1}$)</th>
<th>pH</th>
<th>$k_2$ (1. mole$^{-1}$ sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>1.65</td>
<td>9.10</td>
</tr>
<tr>
<td>0.2</td>
<td>2.70</td>
<td>8.10</td>
</tr>
<tr>
<td>0.2</td>
<td>3.25</td>
<td>7.30</td>
</tr>
<tr>
<td>0.2</td>
<td>4.60</td>
<td>5.60</td>
</tr>
<tr>
<td>0.2</td>
<td>5.50</td>
<td>4.50</td>
</tr>
<tr>
<td>0.6</td>
<td>1.65</td>
<td>10.6</td>
</tr>
<tr>
<td>0.6</td>
<td>2.90</td>
<td>9.40</td>
</tr>
<tr>
<td>0.6</td>
<td>3.00</td>
<td>9.00</td>
</tr>
<tr>
<td>0.6</td>
<td>6.00</td>
<td>6.00</td>
</tr>
<tr>
<td>0.6</td>
<td>6.73</td>
<td>5.25</td>
</tr>
</tbody>
</table>
FIGURE 4
Oxidation of Pivalaldehyde
Dependence of rate on pH, constant orthophosphate concentration

\[ k_x (\text{1. mole}^{-1} \text{sec}^{-1}) \]

\[ \begin{align*}
\text{pH} & \quad k_x \\
2 & \quad 11 \\
4 & \quad 9 \\
6 & \quad 7 \\
8 & \quad 5 \\
\end{align*} \]

\[ \left[ \text{HPO}_4^{2-} \right] = 0.6 \text{ M} \]

\[ \left[ \text{HPO}_4^{2-} \right] = 0.2 \text{ M} \]
pyrophosphate buffers. Results for these runs are given below in Table VII and are shown in Figure 5, along with a representative plot for orthophosphate catalysis at the same pH.

Table VII

Oxidation of Pivalaldehyde by Permanganate at Constant pH

Variation of the Rate Constant with Pyrophosphate Concentration

<table>
<thead>
<tr>
<th>pH</th>
<th>$[P_2O_7^{4-}]$ (mole$^{-1}$)</th>
<th>$k_2$ (l. mole$^{-1}$sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.0</td>
<td>0.02</td>
<td>6.1</td>
</tr>
<tr>
<td>5.0</td>
<td>0.08</td>
<td>8.0</td>
</tr>
<tr>
<td>5.0</td>
<td>0.14</td>
<td>9.4</td>
</tr>
</tbody>
</table>

The lower solubility of the sodium pyrophosphate did not allow solutions of the same molarity as available for orthophosphate to be prepared. The pyrophosphate shows a marked catalytic effect over the poorer catalytic species orthophosphate; this was also observed in the permanganate oxidation of benzaldehyde by Wiberg and Stewart (1). Both the ortho- and pyrophosphate plots shown in Figure 5 appear to approach the same
FIGURE 5

Oxidation of Pivalaldehyde

Dependence of rate on buffer concentration, pH = 5.0

$\text{Buffer Conc. (M.)}$

$\text{$k_2$, (1. mole$^{-1}$ sec$^{-1}$)}$

- Pyrophosphate
- Orthophosphate
rate at zero concentration of phosphate. This is to be expected in view of the 'uncatalyzed' rate operative in the permanganate oxidation of pivalaldehyde, as shown in Figure 2.

4. Oxidation in alkaline solution.

As can be seen from Figure 2, the rate appears to show a marked dependence on the hydroxyl ion concentration. Consequently, several oxidations of pivalaldehyde by permanganate were carried out in the range 0.02 M to 0.20 M sodium hydroxide. The manganate formed in this region, as a result of permanganate reduction, is stable and reacts with the pivalaldehyde slowly. A typical rate plot for these reactions is shown in Figure 6. Unfortunately, large differences in rate were often observed for the same concentration of base. As a result, not too much can be said of the oxidation in this region as rates were very erratic and far from reproducible. This could perhaps be due to some radical decomposition of the pivalaldehyde, as Symons (8) has pointed out that alkaline permanganate undergoes decomposition to manganate via a radical path and it has already been shown in the experimental section of this thesis that pivalaldehyde is susceptible to radical decomposition.
FIGURE 6

Oxidation of Pivalaldehyde
Typical rate plot in alkaline solution

\[
\frac{V_0 - V_t}{V_t - \frac{3}{4}V_0}
\]

\[ [\text{OH}^-] = 0.02 \]
\[ \mu = 0.20 \]

time in sec.
5. **Effect of ionic strength.**

The effect of ionic strength on the reaction rate was found to be negligible, as the results shown in Table VIII indicates.

**Table VIII**

The Permanganate Oxidation of Pivalaldehyde

Influence on the Rate of Ionic Strength

<table>
<thead>
<tr>
<th>[HPO₄²⁻] (mole l.⁻¹)</th>
<th>pH</th>
<th>µ (mole l.⁻¹)</th>
<th>k₂ (l. mole⁻¹sec.⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>10.37</td>
<td>1.04</td>
<td>4.60</td>
</tr>
<tr>
<td>0.2</td>
<td>10.37</td>
<td>0.60</td>
<td>4.60</td>
</tr>
<tr>
<td>0.2</td>
<td>5.50</td>
<td>0.60</td>
<td>5.41</td>
</tr>
<tr>
<td>0.2</td>
<td>5.00</td>
<td>1.20</td>
<td>5.44</td>
</tr>
</tbody>
</table>

Although there is a slight difference in pH for one of these values, the rate has already been shown to be pH independent in this region (Figure 2). The two values for the rate shown for each ionic strength were obtained with different solutions of pivalaldehyde and some indication of an ionic strength effect is apparent from the results shown in the last column above. However, difficulty was experienced throughout
this work in determining exactly the concentration of the pivalaldehyde. As a consequence, rates found with different solutions at the same pH were often as much as twenty percent different. Nevertheless, rates determined on the same solution were reproducible to within five percent at the same pH. Furthermore, experimental trends were not appreciably changed even when different solutions were used. For this reason it is felt that there is a negligible ionic strength effect in the permanganate oxidation of pivalaldehyde.

6. Oxidation by Manganate.

Even though manganate is seen to accumulate during the permanganate oxidation in alkaline solution, it was advisable to determine the magnitude of the rate constant for the manganate reaction. Some potassium manganate had been previously prepared in this laboratory and this was used in these determinations. The concentration of the manganate was determined on the Beckman D.U. spectrophotometer, since the extinction coefficient and the maximum wave length for absorption are accurately known (37). The rate was followed by the iodometric method in the same manner used for the permanganate oxidations. Linear second order rate
plots were obtained and rate constants were determined from the expression:

\[ k_2 = \frac{1}{[\text{Pivalaldehyde}]_0} \times \frac{V_0 - V_t}{V_t - \frac{1}{2}V_o} \]

Kinetic data for the runs done are shown below in Table IX and a typical rate plot is given in Figure 7. The results show that the oxidation of pivalaldehyde by permanganate occurs twenty four times slower than the permanganate oxidation at the same alkalinity.

Table IX

Manganese Oxidation of Pivalaldehyde in Alkaline Solution

<table>
<thead>
<tr>
<th>[OH(^{-})] (mole (1^{-1}))</th>
<th>(k_2) (1. mole(^{-1})sec(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>.890</td>
</tr>
<tr>
<td>0.1</td>
<td>.870</td>
</tr>
</tbody>
</table>

\([\text{Pivalaldehyde}]_0 = 9.56 \times 10^{-4}\) M.

\([\text{Manganate}]_0 = 9.56 \times 10^{-4}\) M.

Temperature = 25.0 ± 0.05°.

Ionic Strength = 0.10 mole \(1^{-1}\).
FIGURE 7

Oxidation of Pivalaldehyde by Manganate

\[
\frac{V_0 - V_t}{V_t - \frac{1}{2}V_0}
\]

[OH] = 0.1 M
\[\mu = 0.1\]

time in sec.
B. The Permanganate Oxidation of Benzaldehyde and p-Nitrobenzaldehyde.

1. Effect of pH

The autocatalytic effect in the permanganate oxidation of benzaldehyde was found to be markedly dependent on the pH, with very fast rates at low pH. In addition, the initial rate in the permanganate oxidation of benzaldehyde was found to be dependent in the same way on the pH, being faster at low pH. The effect of pH on the autocatalysis is shown in Figure 8. The effect of pH on the initial rate of oxidation is shown in Table X. The first three rates in this table were found in this work and are representative of initial rates at low pH. These gave excellent straight line plots, an example of which is shown in Figure 9. This is to be compared with the upper curve of Figure 8 in order to appreciate the effect of time on the oxidation. The remaining data shown in Table X is taken from the work of Wiberg and Stewart (1), whose rates have been corrected for differences in buffer concentration. The overall effect of pH on the permanganate oxidation of benzaldehyde is shown in Figure 10.
FIGURE 8

Oxidation of Benzaldehyde
Effect of pH on autocatalysis

\[ \frac{V_0 - V_t}{V_t - \frac{2}{3}V_0} \]

- \( \bullet \) pH = 1.40
- \( \circ \) pH = 2.90

time in sec.
FIGURE 9

Oxidation of Benzaldehyde
Initial rate at pH = 1.40

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

time in sec.
Table X

The Permanganate Oxidation of Benzaldehyde

Dependence of Rate on the pH

<table>
<thead>
<tr>
<th>pH</th>
<th>$k_2$ (1. mole$^{-1}$ sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>1.64</td>
</tr>
<tr>
<td>2.90</td>
<td>0.890</td>
</tr>
<tr>
<td>5.00</td>
<td>0.586</td>
</tr>
<tr>
<td>5.85*</td>
<td>0.477</td>
</tr>
<tr>
<td>6.80*</td>
<td>0.448</td>
</tr>
<tr>
<td>7.22*</td>
<td>0.448</td>
</tr>
<tr>
<td>9.35*</td>
<td>0.444</td>
</tr>
<tr>
<td>11.06*</td>
<td>0.480</td>
</tr>
<tr>
<td>12.43*</td>
<td>0.733</td>
</tr>
<tr>
<td>13.00*</td>
<td>0.865</td>
</tr>
</tbody>
</table>

* These rates were those found by Wiberg and Stewart (1) and have been corrected for ionic strength effect.

$[\text{Benzaldehyde}]_o = 1.622 \times 10^{-3}$ mole l.$^{-1}$

$[\text{MnO}_4^-]_o = 1.082 \times 10^{-3}$ mole l.$^{-1}$

Ionic Strength = 1.20 mole l.$^{-1}$
FIGURE 10

Oxidation of Benzaldehyde
Effect of pH on initial rate

$k_2$ (l. mole$^{-1}$ sec$^{-1}$)

pH
p-Nitrobenzaldehyde was found to oxidize at a slower rate than benzaldehyde. It also exhibited autocatalysis and both the autocatalytic and the initial rates were reduced by a factor of about four compared to benzaldehyde. The p-nitroaldehyde was studied only at a pH of 1.40. The differences in initial rates of benzaldehyde and p-nitrobenzaldehyde are given in Table XI while the differences in rates of autocatalysis of these two aldehydes are shown in Figure 11.

Marked over oxidation was observed for both benzaldehyde and p-nitrobenzaldehyde as evidenced by the experimental values of \( V_\infty \) given in Table XII.

**Table XII**

**Over Oxidation of Benzaldehyde and p-Nitrobenzaldehyde**

**Experimental Differences Found in Final Volumes**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Calculated ( V_\infty = 2/5 V_0 \text{ (ml.)} )</th>
<th>Experimental ( V_\infty \text{ (ml.)} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_6\text{H}_5\text{CHO} )</td>
<td>1.818</td>
<td>1.165</td>
</tr>
<tr>
<td>( \text{pNO}_2\text{C}_6\text{H}_4\text{CHO} )</td>
<td>1.847</td>
<td>1.551</td>
</tr>
</tbody>
</table>
Table XI

The Permanganate Oxidation of p-Nitrobenzaldehyde

Differences in Initial Rate From Benzaldehyde

<table>
<thead>
<tr>
<th>pH</th>
<th>Substrate</th>
<th>$k_2$ (1.mole$^{-1}$sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.40</td>
<td>C$_6$H$_5$CHO</td>
<td>1.64</td>
</tr>
<tr>
<td>1.40</td>
<td>pNO$_2$C$_6$H$_4$CHO</td>
<td>0.470</td>
</tr>
</tbody>
</table>
FIGURE 11

Autocatalysis in the oxidation of Benzaldehyde and p-Nitrobenzaldehyde
Differences shown between experimental and calculated are far too great to be accounted for by any decomposition of manganese dioxide into oxygen and lower oxidation states of manganese, which could account for small changes in titre volume. Over oxidation was also observed in kinetic runs carried out with the permanganate present in excess of aldehyde. The large differences found are interpreted as over oxidation and are suggested as being due to decomposition of the benzene ring. This has been previously postulated by Cullis and Ladbury (39) in the oxidation of toluene, which they say exhibits over oxidation at the benzaldehyde stage.

In order to see if the 'autocatalytic' effect observed at low pH in the permanganate oxidation of benzaldehyde was completely a result of over oxidation or if in fact some true autocatalysis was operative, the experimental value of \( V_\infty \) was used in determining the rate plot at a pH of 1.40. This result is shown in Figure 12 along with the original plot shown in Figure 8. It seems to be apparent that in spite of over oxidation, some true autocatalysis is occurring, but such an effect is difficult to separate.
FIGURE 12

Oxidation of Benzaldehyde

Autocatalysis corrected for overoxidation

(lower curve)

\[ \frac{V_o - V_c}{V_c - \frac{3}{5}V_o} \]

time in sec.
2. The Effect of Added Manganous Salt.

The addition of manganous sulphate was found to reduce both the initial and autocatalysis rates for the permanganate oxidation of benzaldehyde. This suggests that the active oxidant in the reaction is permanganate and not some intermediate manganese species. That this is true can be realized from the reductions in rate observed above which are attributed to immediate decomposition of the permanganate to manganese dioxide. This reduces the concentration of permanganate and hence reduces the rate. Such an occurrence can be readily understood from the reaction shown below:

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

Rate differences are shown in Table XIII. It was found that percent reductions in rate were of the same order as predicted from a consideration of the stoichiometries of the above reaction.
Table XIII

The Permanganate Oxidation of Benzaldehyde

Effect of MnSO₄ on the Reaction Rate at pH = 1.40

<table>
<thead>
<tr>
<th>[Mn²⁺] (mole 1⁻¹)</th>
<th>k₂ (1. mol⁻¹ sec⁻¹)</th>
<th>% reduction in rate found</th>
<th>% reduction predicted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.64</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>1.62 x 10⁻⁴</td>
<td>1.48</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>4.40 x 10⁻⁴</td>
<td>1.35</td>
<td>20</td>
<td>27</td>
</tr>
</tbody>
</table>

3. Permanganate Oxidation of Benzoic Acid.

In order to further determine the nature of the observed over oxidation of benzaldehyde, it was of interest to see if benzoic acid underwent any oxidation by permanganate. After reaction times ten fold in excess of that required for autocatalysis, the amount of oxidation of benzoic acid was found to be negligible. The degree of oxidation of benzoic acid was determined only qualitatively by observing changes in the initial volume of permanganate. Furthermore, the effect of added manganous sulphate on the permanganate oxidation of benzoic acid was studied and this also was found to be negligible. Results are shown in Table XIV.
Table XIV

The Permanganate Oxidation of Benzoic Acid

Change in Initial Volume of Permanganate With Time

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>$V_t$(without MnSO$_4$) (ml.)</th>
<th>$V_t$(with MnSO$_4$) (ml.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>4.585</td>
<td>4.545</td>
</tr>
<tr>
<td>55</td>
<td>4.400</td>
<td>4.558</td>
</tr>
<tr>
<td>70</td>
<td>4.495</td>
<td>4.518</td>
</tr>
<tr>
<td>110</td>
<td>4.362</td>
<td>4.475</td>
</tr>
<tr>
<td>120</td>
<td>4.362</td>
<td>4.522</td>
</tr>
<tr>
<td>130</td>
<td>4.368</td>
<td>4.490</td>
</tr>
<tr>
<td>140</td>
<td>4.408</td>
<td>4.370</td>
</tr>
<tr>
<td>150</td>
<td>4.410</td>
<td>4.460</td>
</tr>
</tbody>
</table>

$V_0$ = 4.618 ml.

$[\text{Benzoic acid}]_0 = 1.665 \times 10^{-3}$ mole l.$^{-1}$

$[\text{MnO}_4]_0 = 1.110 \times 10^{-3}$ mole l.$^{-1}$

pH = 1.40

Ionic Strength = 1.20 mole l.$^{-1}$
C. The Permanganate Oxidation of p-Nitrophenyltrifluoromethylcarbinol.

1. Oxidation in 0.1 M Sodium Hydroxide.

The permanganate oxidation of the unsubstituted alcohol was first studied in order to have a basis for comparison in the oxidation of p-nitrophenyltrifluoromethylcarbinol. Excellent straight line plots were obtained as shown in Figure 13 and rates were found to give very good agreement with those obtained earlier by Stewart and Van der Linden (2). The rate of oxidation of the p-nitro alcohol was found to be almost three times as fast as that of the unsubstituted alcohol. A typical rate plot is shown in Figure 14. When compared to the plot shown in Figure 13, the scatter of points is hardly satisfactory but understandable when one considers the small volume changes encountered in the titration.

It is interesting to note the kinetics found when the p-nitrophenyltrifluoromethylcarbinol was dissolved in 0.2 M sodium hydroxide (in order to enhance its solubility) and allowed to stand in this solution before being oxidized. Experiments performed
FIGURE 13

Oxidation of Phenyltrifluoromethylcarbinol

\[ \frac{V_0 - V_t}{V_t - \frac{4}{3}V_0} \]

\[ [\text{OH}] = 0.1 \text{ M} \]

\[ \mu = 0.1 \]

time in sec.
FIGURE 14

Oxidation of p-Nitrophenyltrifluoroacetate
methylcarbinol

A typical rate plot

\[ \frac{V_o - V_e}{V_e - \frac{4}{3}V_o} \]

\[ [\text{OH}^-] = 0.1 \text{ M} \]
\[ \mu = 0.1 \]

time in sec.
with these solutions gave very erratic results and sigmoid rate curves, from which a true rate constant could not be determined. An example of such kinetics is shown in Figure 15. These sigmoid curves are suggested as due to hydrolysis occurring in alkaline solution, leaving p-nitrobenzaldehyde which then undergoes the Cannizzaro reaction. The benzyl alcohol produced would then undergo a two stage oxidation to benzoic acid and this could account for the sigmoid rate plot.

Stewart and Van der Linden (2) have studied the permanganate oxidation of a number of substituted phenyl trifluoromethylcarbinols in 0.1 M sodium hydroxide. Their rates are shown in Table XV along with the results found in this work. It is felt that a valid comparison exists between the corrected rates for one hundred percent ionization for the p-nitro alcohol and others since the rates found for the unsubstituted alcohol were the same in both Van der Linden's (28) and this work. It can be seen then from Table XV that the effect of substituents is negligible on the rate, save for the p-nitro group which shows a large increase in rate.
FIGURE 15

Oxidation of p-Nitrophényltri-fluoromethylcarbinol

A sigmoid rate plot

\[
\frac{V_0 - V_t}{V_t - \frac{4}{5}V_0}
\]

OH = 0.1 M
\[\mu = 0.1\]

time in sec.
### Table XV

**The Permanganate Oxidation of Phenyltrifluoromethylcarbinols**

Oxidations in 0.1 M NaOH

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$k_2$ (1. mole$^{-1}$sec$^{-1}$)</th>
<th>$k_2$ corrected to 100% ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-NO$_2$*</td>
<td>8.7</td>
<td>8.9</td>
</tr>
<tr>
<td>M-Br*</td>
<td>7.4</td>
<td>7.6</td>
</tr>
<tr>
<td>P-CH$_3$*</td>
<td>7.1</td>
<td>7.9</td>
</tr>
<tr>
<td>H</td>
<td>7.7</td>
<td>8.3</td>
</tr>
<tr>
<td>P-NO$_2$</td>
<td>21.2</td>
<td>21.4</td>
</tr>
</tbody>
</table>

* These rates were found by Stewart and Van der Linden (2). The rate of oxidation of the unsubstituted alcohol was found to be 7.6 1. mole$^{-1}$sec$^{-1}$ by Van der Linden (28).
2. **Oxidation in Weakly Alkaline Solution.**

In order to see if the p-nitro alcohol reacted faster at lower pH, the oxidation of the unsubstituted and the p-nitrophenyl trifluoromethylcarbinol was studied at a pH of 9.17. The reaction is expected to be much slower here since Stewart and Van der Linden (2) have shown that the rate determining step involves the anion. The results are shown in Table XVI along with values found for other substituents at a pH of 9.10 by Van der Linden (28). As in Table XV, the rates have been corrected for one hundred percent ionization and again it is felt that a valid comparison can be made between the corrected rate for the p-nitro alcohol and others since the rate of oxidation of the unsubstituted alcohol in this work was found to be identical with that found by Van der Linden (28).

The rates of oxidation of the m-bromo and m-nitro alcohols were studied by Van der Linden (28) at a pH of 9.10 and one might expect a slight increase in rate for a pH of 9.17, as was used in this work. However, any increase would not bring the oxidation rate up to that found for the p-nitro alcohol. That the difference
Table XVI

The Permanganate Oxidation of Phenyltrifluoromethylcarbinols

Oxidations at pH = 9.17

<table>
<thead>
<tr>
<th>Substituent</th>
<th>$k_2 \text{ (1. mole}^{-1} \text{ sec}^{-1})$</th>
<th>$k_2$ corrected to 100% ionization</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-NO$_2^*$</td>
<td>0.019</td>
<td>2.58</td>
</tr>
<tr>
<td>M-Br*</td>
<td>0.0061</td>
<td>1.54</td>
</tr>
<tr>
<td>H</td>
<td>0.0051</td>
<td>2.76</td>
</tr>
<tr>
<td>P-NO$_2$</td>
<td>0.039</td>
<td>3.41</td>
</tr>
</tbody>
</table>

* Results obtained by Van der Linden (28) at pH=9.10.

The rate of oxidation of the unsubstituted alcohol was found to be 0.0053 at a pH=9.10 by Van der Linden.

\[
\begin{align*}
[HNO_2]_o &= 5.57 \times 10^{-4} \text{ Mole l}^{-1} \\
[PNO_2C_6H_4CHOHCF_3]_o &= 8.35 \times 10^{-4} \text{ Mole l}^{-1} \\
[MnO_4^-]_o &= 1.11 \times 10^{-3} \text{ Mole l}^{-1} \\
[C_6H_5CHOHCF_3]_o &= 1.665 \times 10^{-3} \text{ Mole l}^{-1} \\
\text{Ionic Strength} &= 0.35 \text{ mole l}^{-1}
\end{align*}
\]
in ionic strength in the two studies (0.35 vs. 0.20) might account for increases in rate can be refuted by the fact that the unsubstituted alcohol gives identical rates in both cases.

The rate of oxidation of p-nitrophenyltrifluoromethylcarbinol at a pH of 9.17 is not nearly as enhanced as was found at a pH of 13, but nevertheless is still faster than the m-nitro alcohol which has comparable acidity. It is suggested that a much better basis for comparison is in the rates of oxidation in 0.1 M sodium hydroxide, where the alcohols are all appreciably ionized. At low alkalinities, the rate is markedly dependent on the pH. In fact, the pH was found to change over the course of reaction in the oxidation p-nitrophenyltrifluoromethylcarbinol and this is shown in Table XVII, along with corresponding changes in rate that one would expect. It should be noted that the reaction involving the unsubstituted alcohol underwent no change in pH during the course of the reaction.

That the rates of oxidation of these alcohols should yield different rate constants for one hundred percent ionization seems rather puzzling. The
Table XVII

Permanganate Oxidation of p-Nitrophenyltrifluoromethylcarbinol

Rate Changes with pH During Course of Reaction

<table>
<thead>
<tr>
<th>time (min.)</th>
<th>pH</th>
<th>$k_2$ corrected to 100% ionization (1. mole$^{-1}$sec.$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>9.17</td>
<td>3.41</td>
</tr>
<tr>
<td>107</td>
<td>9.13</td>
<td>3.77</td>
</tr>
<tr>
<td>229</td>
<td>9.10</td>
<td>4.03</td>
</tr>
<tr>
<td>334</td>
<td>9.09</td>
<td>4.12</td>
</tr>
<tr>
<td>478</td>
<td>9.05</td>
<td>4.51</td>
</tr>
<tr>
<td>570</td>
<td>9.01</td>
<td>4.94</td>
</tr>
<tr>
<td>715</td>
<td>8.99</td>
<td>5.17</td>
</tr>
<tr>
<td>826</td>
<td>8.99</td>
<td>5.17</td>
</tr>
</tbody>
</table>
disparity is likely the result of a combination of effects due to different reaction conditions at low and high pH and to departure from ideality in the measurement of hydroxyl ion concentration by the glass electrode. Stewart and Van der Linden (33) measured the $pK_a$ values of their substituted phenyltrifluoromethylcarbinols in the strongly basic region and the pH was obtained directly from the concentration of hydroxide present. It was not measured on a pH meter. Furthermore, the stoichiometries are different at low and high pH and consequently different concentrations of alcohol were used, since the permanganate concentration was kept constant. The concentration of alcohol varied by about thirty percent over the two ratios and this could contribute to changes in the rate constant since effects of this order are commonly observed in kinetics.

3. The Hammett Plot

Stewart and Van der Linden (2) have previously shown the Hammett plot in the oxidation of substituted phenyltrifluoromethylcarbinols in 0.2 M sodium hydroxide to be a shallow curve. Table XVIII gives the data for the Hammett plot which is shown in Figure 16. The
## Table XVIII

The Permanganate Oxidation of Phenyltrifluoromethylcarbinols

The Hammett Plot at 0.1 M NaOH

<table>
<thead>
<tr>
<th>substituent</th>
<th>σ value</th>
<th>$k_2$ corrected for 100% ionization (1. mole$^{-1}$ sec.$^{-1}$)</th>
<th>log $k_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-NO$_2^*$</td>
<td>0.71</td>
<td>8.9</td>
<td>0.949</td>
</tr>
<tr>
<td>M-Br$^*$</td>
<td>0.39</td>
<td>7.6</td>
<td>0.881</td>
</tr>
<tr>
<td>p-CH$_3^*$</td>
<td>-0.17</td>
<td>7.9</td>
<td>0.898</td>
</tr>
<tr>
<td>H</td>
<td>0</td>
<td>8.3</td>
<td>0.919</td>
</tr>
<tr>
<td>p-NO$_2$</td>
<td>-0.78</td>
<td>21.4</td>
<td>1.33</td>
</tr>
</tbody>
</table>

*These rates were found by Van der Linden (28).*
FIGURE 16

Oxidation of Phenyltrifluoromethyl-carbinols

The Hammett plot

log $k_2$

$\sigma$
points shown are for one hundred percent ionization in 0.1 M sodium hydroxide and it can be clearly seen that the p-nitro group shows an enhanced effect. Generally, a plot of log k versus $\sigma$ gives a straight line, the slope of which gives the reaction constant $\rho$. The slight curve shown in Figure 16 as a dotted line has been interpreted by Stewart and Van der Linden (2) as due to two different processes occurring in the reaction with different electronic requirements, one with a positive and the other with a negative value. However, this will not be pursued, since the degree of curvature is small and should be interpreted as a straight line, as indicated in the diagram. This straight line is then representative of a normal Hammett plot, having $\rho$ approximately equal to zero, which shows that the rate is independent of nuclear substitution. The exception is the p-nitro group, which shows a marked departure from all the other points shown in Figure 16.
DISCUSSION OF RESULTS

A. The Permanganate Oxidation of Pivalaldehyde

From the pH profile shown in Figure 2, it can be seen that the rate is independent of pH in the neutral and weakly alkaline region. It is obvious then that an uncatalyzed or 'neutral' reaction is operative, which is very likely due to the general-acid water. It is apparent from the increases in rate observed at low pH that the reaction follows some dependence on hydrogen ion concentration and indeed general acid catalysis has been shown to occur.

The rate of the reaction was also found to be proportional to the first powers of permanganate and pivalaldehyde concentrations. Furthermore, although no experimental evidence is available, it seems a reasonable assumption that the aldehyde carbon-hydrogen bond is broken in the rate determining step, especially in light of the amount of evidence available on a variety of substrates which supports such a step.

It has been stated that one of the objects of
this work was to see if pivalaldehyde underwent oxidation via a similar path as its aromatic analog benzaldehyde. In that study, Stewart and Wiberg (1) have shown that the oxygen introduced into the aldehyde was derived mainly from the oxidizing agent, indicating that a bond was at some time formed between the aldehyde carbon and an oxygen of the oxidizing agent. Furthermore, these workers were able to show that a normal isotope effect, \( k_H / k_D = 7.0 \), existed and hence the rate determining step must involve cleavage of the aldehyde carbon-hydrogen bond. A reasonable mechanism then for the oxidation of pivalaldehyde by permanganate is the following:

\[
RCHO + H_3O^+ \quad \overset{K_1}{\xrightarrow{\text{OH}}} \quad RCH + H_2O
\]

\[
RCHOH + MnO_4^- \quad \overset{K_2}{\xrightarrow{\text{OH}}} \quad R-C-OMnO_3
\]

\[
R-C-OMnO_3 + A \quad \overset{k_2}{\xrightarrow{\text{fast}}} \quad RCO_2H + HA + MnO_3
\]

\[
2 MnO_3^- + H_2O \quad \overset{\text{fast}}{\xrightarrow{2 MnO_2 + MnO_4 + 2 OH}}
\]
This mechanism accommodates the experimental evidence found in this work as well as incorporating that found by Stewart (1) in the permanganate oxidation of benzaldehyde. The Hammett $\rho$ value in the permanganate oxidation of benzaldehyde is found to be negative (-0.25) and hence electron donating groups will aid the reaction. This was also found at low pH in this work when the oxidation of p-nitrobenzaldehyde was found to be fourfold slower than the oxidation of benzaldehyde. Hence it seems a reasonable extension to expect that electron donating groups on the pivalaldehyde will enhance the reaction rate.

However, other mechanisms should be considered, such as the one shown below:

\[
\begin{align*}
R-C=O + MnO_4^- & \quad \xrightarrow{k_2} \quad \left[ R-C-O-MnO_3 \right] \\
& \quad \xrightarrow{\text{fast}} \quad R-C=O + MnO_3^- \\
2 MnO_3^- + H_2O & \quad \xrightarrow{\text{fast}} \quad 2 MnO_2^- + MnO_4^- + 2 OH^-
\end{align*}
\]

Again, this mechanism would incorporate the facts found by Wiberg and Stewart (1) in the permanganate oxidation of benzaldehyde since both oxygen-18 transfer would
occur and the carbon-hydrogen bond would be weakened in the transition state. Such a reaction path could also accommodate general acid-catalysis found in this work in that complexing could occur with the permanganate and so aid in its reduction to lower valency states. That this should cause an increase in rate can be realized from the fact that permanganic acid is a stronger oxidant than permanganate itself and hence one would expect a hydrogen bond formed with permanganate to also result in a stronger oxidizing agent. One would not predict such an effect to show large catalysis and in fact only a twenty percent increase in rate has been observed for a tenfold change in buffer concentration.

In order to explain the enhancement in rate observed for pivalaldehyde over benzaldehyde in terms of the above mechanism, one can consider that in going from the trigonal aldehyde to a tetra-coordinated transition state, a loss of conjugation must occur. That conjugation effects can be important in aromatic systems is well known, whereas similar effects are negligible in aliphatic saturated systems. Hence, it is reasonable to postulate that benzaldehyde would
undergo a greater loss of conjugation in forming the transition state than pivalaldehyde and correspondingly, one would expect a faster reaction for the pivalaldehyde.

This 'loss of conjugation' concept can moreover be included in the former mechanism postulated, since the abstraction of a proton by the general base in the rate determining step would result in the following transition state:

\[
\begin{array}{c}
\text{OH} \\
\text{R--Q---O---MnO}_3 \\
\text{H} \\
\end{array}
\]

The trigonal aldehyde has now approached a tetra-coordinated transition state with consequent loss in conjugation which would be more pronounced for benzaldehyde than pivalaldehyde. Again, this would result in greater rates of oxidation for the latter aldehyde, in accordance with what has been observed.

On the other hand, there is no assurance that the oxygen introduced into the pivalaldehyde arises from the oxidizing agent and may in fact come from
the solvent. Furthermore, the oxidation of pivalaldehyde by manganate occurs twenty five times slower than that by permanganate, whereas Stewart (1) found the same rates of oxidation for both with benzaldehyde. This could most easily be interpreted in terms of a mechanism involving hydride transfer, which would be slower to manganate than to permanganate in view of the extra negative charge on the manganate. Also, the inductive effect of the tertiary butyl group would serve to weaken the carbon-hydrogen bond and so enhance a hydride transfer to permanganate. In view of the well known electron withdrawing effect of the phenyl group (the Taft $\sigma^*$ (39) values for tertiary butyl and phenyl are -0.300 and +0.600 respectively) this could aid in explaining the enhancement in rate observed for pivalaldehyde over benzaldehyde. The following mechanism then is not unlikely:

$$\begin{align*}
R-C=O + MnO_4^- \xrightarrow{k_2} & R-C=O + H MnO_4^- \\
R-C=O + H_2O \xrightarrow{\text{fast}} & R-C-\overset{O}{\overset{\cdot}{\overset{H}{\cdot}}}
\end{align*}$$
The above mechanism is in no way meant to be conclusive, and in fact suffers from a number of drawbacks. First of all, the Hammett $\rho$ value in the permanganate oxidation of benzaldehyde is known to be small and negative whereas one would expect a large negative $\rho$ if hydride transfer was occurring in the rate determining step. If pivaldehyde and benzaldehyde react via different paths, then the value observed for benzaldehyde would be of no importance in discussing the mechanism of the oxidation of pivalaldehyde, but it seems perfectly plausible that the two should react by the same path. Secondly, conjugation effects in the stabilization of the carbonium ion formed would be very important and phenyl could provide much more in this direction than tertiary butyl, whose resonance effect would be negligible.
It is not proposed that the inductive effect of the tertiary butyl group would be more important than the conjugative effect of the phenyl group.

In summary, then, there is no clear cut single mechanism which explains all the facts in the permanganate oxidation of pivalaldehyde. In order to determine this, more work would have to be done to find whether the oxygen is introduced via the solvent or the permanganate, whether the oxidation by manganese is significant, and if in fact the carbon-hydrogen bond is involved in the rate determining step, although this does not seem unlikely.

B. The Permanganate Oxidation of Benzaldehyde and p-Nitrobenzaldehyde

Although this work was undertaken with the view to studying the nature of the autocatalytic effect observed by Wiberg and Stewart (1) below a pH of 5, it was also worthwhile to study the initial rates of oxidation at low pH. As the results show in Figure 10, the oxidation shows some dependence on hydrogen ion concentration, although it certainly does not exhibit specific catalysis. This is not surprising
in view of the general acid-catalysis which the system exhibits. Furthermore, the initial rate of oxidation of p-nitrobenzaldehyde is reduced by almost four fold compared to benzaldehyde at the same pH. This is in accord with the negative $\ell$ value found by Wiberg and Stewart (1) in the permanganate oxidation of substituted benzaldehydes. It seems obvious that the experimental results gained at low pH in this work serve to strengthen the mechanism already proposed by Wiberg and Stewart (1) at high pH. That mechanism is as follows:

$$\begin{align*}
C_6H_5CHO + H_3O^+ & \rightleftharpoons K_1 C_6H_5CH(OH) + H_2O \\
C_6H_5CH(OH)^+ + MnO_4^- & \rightleftharpoons K_2 C_6H_5C(OH) - MnO_3^-
\end{align*}$$

$$\begin{align*}
C_6H_5C(OH) - MnO_3^- + HA & \rightarrow C_6H_5CO_2H + HA + MnO_3^-
\end{align*}$$

$$3 MnO_3^- + H_2O \xrightarrow{\text{fast}} 2 MnO_2^- + MnO_4^- + 2 OH^-$$

However, in view of the enhancement in rate observed with pivalaldehyde, an analogous mechanism can be proposed for the permanganate oxidation of
benzaldehyde. The following mechanism then also accommodates the experimental facts found by Wiberg and Stewart (1) although the of the reaction would be difficult to predict.

\[
C_6H_5CHO + MnO_4^– \overset{k}{\longrightarrow} C_6H_5CO_2H + MnO_3 + 2 \text{OH}^{-}
\]

\[
3 MnO_3 + H_2O \overset{\text{fast}}{\longrightarrow} 2 MnO_2 + MnO_4^– + 2 \text{OH}^{-}
\]

The autocatalytic effect was also found to be reduced by almost four fold for the permanganate oxidation of p-nitrobenzaldehyde compared to benzaldehyde. For both cases, since experimental evidence has shown that the system exhibits overoxidation, it is postulated that the benzene ring is undergoing decomposition at later stages in the reaction. The mechanism of this is far from certain, but it seems reasonable to suggest a radical reaction path. It seems likely that the permanganate oxidation of benzaldehyde, and also p-nitrobenzaldehyde, goes by two paths; i.e. a major one which is responsible for the normal oxidation, giving good second order kinetics and a minor path which involves a very small
percent of a radical species formed from hydrogen atom abstraction by the permanganate ion. This radical then initiates rupture of the benzene ring, likely via a chain mechanism.

\[
\text{C}_6\text{H}_5\text{CHO} + \text{MnO}_4^- \xrightarrow{k_r} \text{products}
\]

The observed reduction in the overoxidation of p-nitrobenzaldehyde is difficult to explain. Gullis and Ladbury (38) have observed a similar effect in the oxidation of p-nitrotoluene compared to toluene itself. That the electron withdrawing effect of the p-nitro group should retard formation of a radical species does not seem plausible. Perhaps once the radical is formed there is sufficient stabilization due to the p-nitro group to retard the chain reaction which results in ring degradation. Such stabilization would result from the following resonance structures:

\[
\text{etc.}
\]
However, in view of the short lifetime of most radical species (approximately $10^{-6}$ sec.), this also does not seem likely.

Further inexplicable experimental evidence is presented by the marked dependence on pH for the overoxidation of both benzaldehyde and p-nitrobenzaldehyde, as shown in Figure 8. It might be suggested that some radical reaction involving the conjugate of the aldehyde initiates ring rupture but this seems extremely unlikely as this species would be present to about one part in a billion. Intermediate species of manganese are known to be stable in acidic solutions (16) and it may be that such a species is complexing with the benzaldehyde in some way which enhances the radical induced overoxidation. However, again this seems unlikely, since no increase in overoxidation was observed upon the addition of manganous ions.

All that can be said then with any degree of certainty is that the overoxidation with permanganate exhibited by benzaldehyde at low pH is a result of ring rupture. As to the mechanism of this occurrence, not enough experimental evidence has been gathered
to allow the presentation of any concrete proposals. It would be interesting, for example, to study the effect of other substituents on the overoxidation and also to see if oxidation by other oxidants results in ring rupture.

C. The Permanganate Oxidation of p-Nitrophenyltrifluoromethylcarbinol

It has been conclusively shown in the results of this thesis that p-nitrophenyltrifluoromethylcarbinol shows an enhanced rate of oxidation by potassium permanganate over all other substituted phenyltrifluoromethylcarbinols studied by Stewart and Van der Linden (2).

Stewart and Van der Linden (2) have shown that although the prospect of a hydride transfer occurring in the rate determining step seemed likely, they found no substituent effect; i.e. p-methoxy gave essentially the same rate as m-nitro. Moreover, the enhancement in rate observed for the p-nitro alcohol is further evidence against a hydride transfer occurring. Stewart and Van der Linden (2) also listed three termolecular mechanisms as possible
paths for the reaction, but only one of these seems likely since the other two require termolecular solute collisions and will therefore not be considered. The following mechanism they proposed does not require a termolecular solute collisions:

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

What is involved here is a simultaneous process, electron abstraction by the permanganate and proton abstraction by the solvent.

It seems energetically more favourable however, to have a one stage process in the transfer of a hydrogen atom from the alkoxide ion to the permanganate ion. This is more likely than the earlier mechanism shown above and in addition accommodates all the experimental evidence gathered by Stewart and Van der Linden (2), including the negligible substituent effect. Moreover, the enhancement in rate observed
for the p-nitro alcohol fits very well into this mechanism in that the p-nitro group would afford enhanced radical stabilization. It has been found in the past that p-nitro substituents enhance radical reactions (40) as evidenced by the large dissociation constant of p-nitrohexaphenylethane over all other substituents.

A mechanism involving hydrogen atom abstraction by permanganate from the alkoxide ion is thus favoured in view of the results found in this work on the permanganate oxidation of p-nitrophenyltrifluoromethylcarbinol. In fact, it seems reasonable to postulate the same mechanism as occurring in the potassium permanganate oxidation of all substituted phenyltrifluoromethylcarbinols and indeed alcohols in general. That the p-nitro group should be expected to give an enhancement in rate can be realized from the resonance structures shown with the mechanism for the oxidation below:

\[
\begin{align*}
\text{pNO}_2\text{ArCHOHCF}_3 + \text{OH} & \rightarrow \text{pNO}_2\text{ArCH-CH-CH-F} + \text{H}_2\text{O} \\
\text{pNO}_2\text{Ar-C-H} + \text{MnO}_4 & \rightarrow \text{pNO}_2\text{Ar-C-F} + \text{HMnO}_4
\end{align*}
\]
\[
pNO_2Ar-\text{C}-\text{CF}_3 + \text{MnO}_4^- \rightarrow pNO_2Ar\text{CCF}_3
\]
LIST OF REFERENCES


