THE OXIDATION OF OLEFINS BY PERMANGANATE AND RELATED REACTIONS

a Thesis by

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Submitted to the
Faculty of Pure and Applied Sciences,
in partial fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY
in the
DEPARTMENT OF CHEMISTRY
UNIVERSITY OF OTTAWA

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OCTOBER 1957

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PREFACE

As a result of recent publications by Lemieux and co-workers concerning the periodate-permanganate reagent, we have become interested in the mechanisms of the various reactions which take place during the periodate-permanganate oxidation of an olefin. The present study deals with the initial stages of this reaction, which involve a permanganate oxidation of the olefin. The mechanism of this oxidation has been examined in a number of ways, and considerable information has been gained concerning the chemistry of the various intermediate species which are formed during the reaction, both in the presence and in the absence of periodate.

I have been aided in many ways during the course of this research by the staff of the National Research Council and the staff and students of the Department of Chemistry of the University of Ottawa, and I wish to acknowledge this assistance. Grateful acknowledgement is also made to the National Research Council for the award of two Studentships.

It has been written,

"..... wherefore I say that your chief aim in the building up of Man is not to give him learning, which serves no end if he be but a walking book, but to lift his eyes and point him to those higher levels on which there are no more things-in-themselves, but only aspects of that divine bond which binds things together."

... Antoine de Saint-Exupéry

I thank Dr. Raymond U. Lemieux for turning me in the proper direction.

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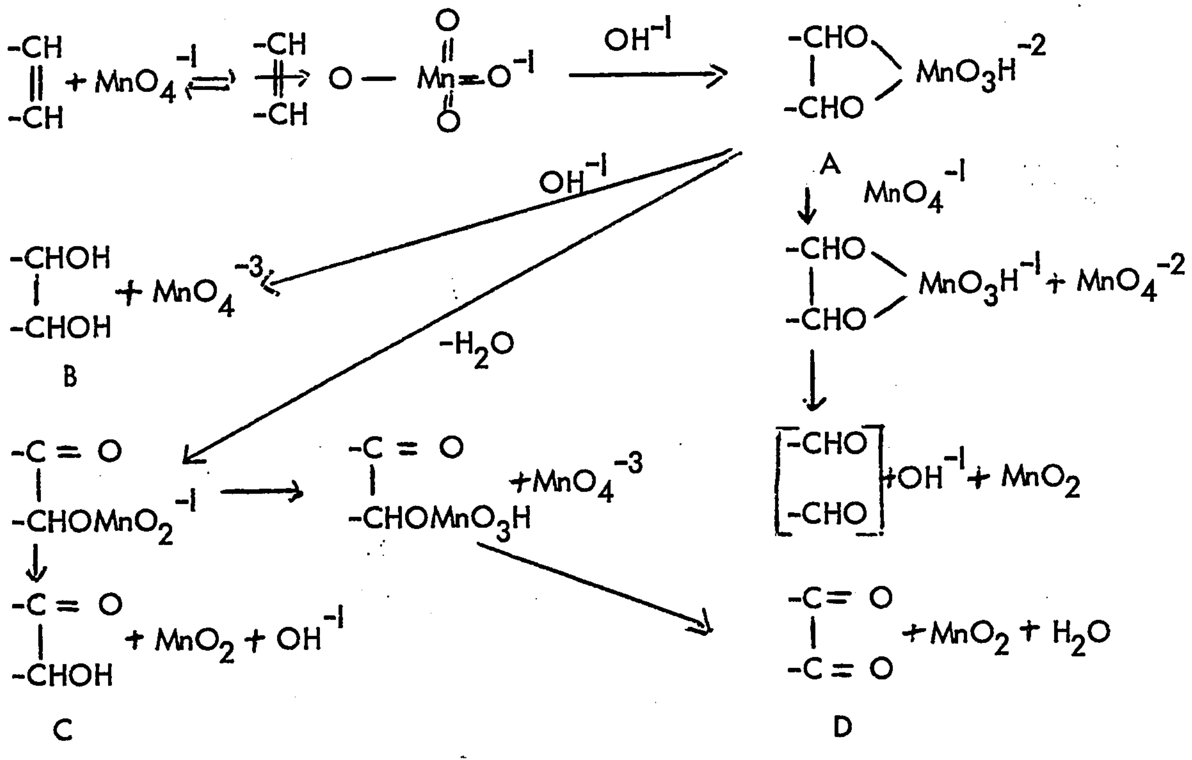
ABSTRACT

A study was made of the various reactions which take place during the oxidation of an olefin by potassium permanganate. Though the experimental work reported here refers mainly to reactions conducted in aqueous media above pH 7, the conclusions arrived at can be satisfactorily extended to explain the results obtained by other workers, under other reaction conditions.

The oxidation was found to proceed under all reaction conditions by way of a cyclic ester intermediate (A). The route of the reaction is governed by the way in which the reaction conditions affect the decomposition of this intermediate. The following scheme demonstrates the kinds of reactions which have been shown to be involved.



A. - Obtained in 50-100% at 0-10° in aqueous media above pH 12, and in 0-60% yield in mixed solvents.

B. - Obtained in 80-90% yield using a 1-5 molar exesss of permanganate and a olefin concentration of 0.1%; obtained in 25% yield using a 30-fold excess of permanganate.

C. - Obtained in 20% yield using an olefin concentration of 0.5% and a 30-fold excess of permanganate.

D. - Obtained in 10-20% yield in aqueous media in the pH region 7-10, using an olefin concentration of 0.5% and a 30-fold excess of permanganate; obtained in 0-50% yield in mixed solvents; obtained in 50-100% yield in non-aqueous media.

The formation of the intermediate π-complex and the hydroxyl ion-catalyzed rearrangement of this complex to the cyclic intermediate (A) were demonstrated by the results of a kinetic study of the reaction of permanganate with oleate ion. The order with respect to the permanganate and olefin concentrations was unity, whereas a complex order with respect to the hydroxyl ion concentration was observed. A number of different kinds of oxyanions, such as borate, tellurate and periodate, also appear to form π-complexes with an olefin, since the addition of one of these oxyanions to the permanganate-olefin reaction mixture resulted in a kinetic competition for the olefin between permanganate and the added oxyanion. It was possible to calculate the equilibrium constant of an olefin-oxyanion complex by a suitable interpretation of the effect of the added oxyanion on the olefin-permanganate reaction. Thus a novel procedure can be developed for the study of certain kinds of π-complexes.

The formation of cyclic intermediate requires a transfer of two electrons to the manganese and the valence state of the manganese should, therefore, be reduced, initially, from seven to five. Evidence for this two-electron exchange was obtained by a demonstration that, in the pH region 12-13, the variation in the concentrations of Mn(VII), Mn(VI) and Mn(IV) during the hydroxylation reaction was that which would have been expected if hypomanganate were the initial reduced stage in the reaction. A study was made of the chemistry of this valence state, and it was shown that, under the conditions of the hydroxylation reaction, a hypomanganate intermediate would undergo two rapid reactions,

$$\mathrm{Mn(V)} + \mathrm{Mn(VII)} \longrightarrow 2\,\mathrm{Mn(VI)}$$

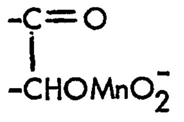
$$2\,\mathrm{Mn(V)} \longrightarrow \mathrm{Mn(IV)} + \mathrm{Mn(VI)}.$$

The rate of the first of these reactions should be increased by an increase in the initial concentration of permanganate ion; the rate of the second reaction was increased by a decrease in the concentration of hydroxyl ions. The relative yields of Mn(VI) and Mn(IV) corresponding to a given set of reaction conditions could then be predicted if the two-electron exchange to form hypomanganate were taking place.

An analytical procedure was developed for the estimation of the yields of Mn(VI) and Mn(IV) during a run; the relative yields of these valence states were in agreement with expectation, assuming the two-electron exchange.

The mechanism of ketol formation (B) was established by the results of a study of the oxidation of 1,1-dideuteroethylene by solutions containing periodate and permanganate. It was shown that glycolaldehyde was a product of this reaction, formed by further oxidation of the initially-formed cyclic ester intermediate, and that the extent of a deuterium isotope effect would be indicative of the mechanism of the oxidation of the cyclic intermediate to ketol. The extent of the isotope effect was determined from the amount of deuterium in the formaldehyde product of the reaction. A quantitative infrared procedure was developed for the analysis of the amount of deuterium in the formaldehyde. A mass effect of 1.6-2.0 was observed in the oxidation.

The mechanism of diketone formation (C) could be deduced once the mechanism of ketol formation had been established. Since the diketone was not formed by further oxidation of the glycol or ketol, it must have resulted from oxidation of an intermediate manganese ester, and presumably from oxidation of an ester,



$$\begin{array}{l} -\mathrm{C{=}O} \\ \;\;| \\ -\mathrm{CHOMnO_2^-} \end{array}$$

which was shown to be an intermediate during the ketol formation.

The central carbon-carbon linkage of a glycol, ketol or diketone was found to undergo oxidation by permanganate much less readily than an olefin (to yield products of type D). Hence, it is concluded that the cyclic ester also can decompose with fission of the carbon-carbon bond. This conclusion is supported by the fact that this route of reaction was found to be promoted by the use of non-aqueous media.

I. INTRODUCTION

1. Scope of the Work

A. General Introduction

Although potassium permanganate is one of the most versatile oxidizing agents, and is effective in acid, neutral, alkaline and non-aqueous media, few satisfactory studies have been made on the mechanisms of permanganate oxidations. The major advances toward the elucidation of the mode of action of permanganate in organic oxidations have been made only in recent years by application, especially, of a variety of labelling techniques.

The author feels that a keen awareness of the great complexity of permanganate oxidations is of prime importance for any fruitful investigation in this field. For this reason, the information which has accumulated on the mechanisms of a variety of organic oxidations by permanganate will be reviewed in this thesis, with special emphasis on those observations which may have a bearing on the present study.

Probably the major complicating factor in the study of permanganate oxidations is the fact that the element manganese can exist, under varying conditions, and in varying degrees of stability, in each of the valence states from zero to seven, and a large variety of reactions can take place among these various valence states. Since permanganate can undergo reduction to the tetravalent stage in neutral and alkaline media,

$$MnO_4^- + 3e + 4H^+ \longrightarrow MnO_2 + 2H_2O ,$$

and to the divalent stage in acid media,

$$MnO_4^- + 5e + 8H^+ \longrightarrow Mn^{+2} + 4H_2O ,$$

four different valence states can conceivably take part in neutral and alkaline oxidations, while six valence states can conceivably be involved in oxidations in acid medium. Obviously, therefore, the study of any permanganate oxidation, whether organic or inorganic, requires a knowledge of the chemistry of manganese in its various oxidation states.

But this should not obscure the fundamental problem. It is generally recognized that the simplest model in which oxidation-reduction reactions can be discussed is that of electron transfer; thus the important step in any oxidation-reduction reaction is that step in which there is a transfer of electrons between the oxidizing agent, or some active form of it, and the reducing agent. Mechanistic studies of oxidation reactions should ultimately, therefore, be directed towards an elucidation of the configuration of the complex in which the electron transfer takes place, and they should tell us how many electrons are transferred within this complex.

At the present time, the majority of permanganate oxidations can be divided into three distinct groups, distinguished by the apparent active oxidizing species in each case; oxidations by the manganic cation, Mn^{+3} (which is involved in many of the rate-determining processes in acid solution), oxidations by the manganite cation, Mn^{+4}, and oxidations in which the permanganate ion itself is involved in the slow step. Some idea of the versatility of permanganate can be seen in Table I, which shows the apparent active oxidizing species in a number of different kinds of oxidation reactions.

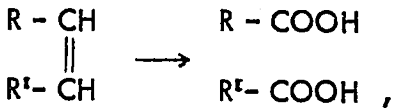
TABLE I

The Oxidation of Organic Compounds by Permanganate

Substrate	Conditions	Products	Oxidant	Reference
olefin	aqueous alkali	cis glycol	MnO_4^-	1,2
olefin	neutral water	α-ketol	MnO_4^-	3
olefin	non-aqueous media	-COOH -COOH	MnO_4^-	4
$R\text{-}CH_2CHOH$ $\vert$ $R'\text{-}CH_2CHOH$	aqueous alkali	RCOOH , R'COOH , $H_2C_2O_4$	MnO_4^-	5
ArCHO	aqueous acid	ArCOOH	MnO_4^-	6,7
ArCHO	aqueous alkali	ArCOOH	•OH ?	7
$C_6H_5CHOHC_6H_5$	aqueous alkali	$C_6H_5COC_6H_5$	MnO_4^-	8
$H_2C_2O_4$	aqueous acid	CO_2	Mn^{+3}	9-11
HCOOH	water	CO_2	MnO_4^-	12-14
$CH_2(COOH)_2$	aqueous acid	HCOOH, CO_2	Mn^{+3}	15
$CH_3CHOHCH_3$	aqueous acid, trace of ferrous ion or peroxide	CH_3COCH_3	Mn^{+4}	16
2,6-dinitrophenol	aqueous acid	CO_2, HNO_3	Mn^{+4}	17,18
naphthalene	acetic acid	α -naphthyl acetic acid	MnO_4^{-3} ?	19
R_3CH	aqueous alkali	R_3COH	•OH	20
$C_2H_5COO^-$	aqueous alkali	CO_3^{-2}, $C_2O_4^{-2}$	•OH, MnO_4^-	21

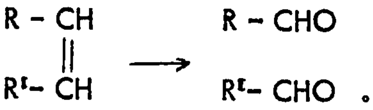
B. Origin and Purpose of this Work

Organic chemists are always interested in acquiring techniques which permit the "smooth" conversion of one substance to another. Since synthetic organic chemistry depends, to a large extent, on reactions involving multiple bonds, many fundamental studies of the chemistry of the carbon-carbon double bond have been made. In view of this extensive chemistry, it is surprising that, until recently, no satisfactory techniques existed for the "smooth" conversion of an olefin to dicarboxylic acid,



$$\begin{matrix} R-CH \\ \| \\ R'-CH \end{matrix} \longrightarrow \begin{matrix} R-COOH \\ R'-COOH \end{matrix} ,$$

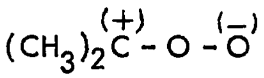
or to dialdehyde,



$$\begin{matrix} R-CH \\ \| \\ R'-CH \end{matrix} \longrightarrow \begin{matrix} R-CHO \\ R'-CHO \end{matrix} .$$

Though it is easy to open the double bond, a one-step scission of the olefinic carbon-carbon linkage is generally rather difficult, owing to the undesirable side reactions which accompany the use of many of the common oxidizing agents. The side reactions result from the fact that these oxidizing agents usually operate by alternative routes, and the exact conditions required to make one route predominant are often difficult to specify.

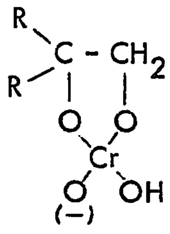
For example, the ozonolysis reaction, which has recently been studied by Criegee and co-workers (22-25), and by P.S. Bailey (26, 27), is often accompanied by peroxide formation. The by-products are inescapable, for the reaction mechanism requires them. Thus, the ozonolysis of isobutylene is thought (27) to yield a zwitter-ion intermediate, I, which can decompose in various ways, depending on the solvent and the reaction conditions.



$$(CH_3)_2\overset{(+)}{C} - O - \overset{(-)}{O}$$

I

The cleavage of the olefinic linkage by chromic acid is often accompanied by oxidation at the α- methylenic position and degradation of the molecule. This reaction, recently studied by Hickinbottom and co-workers (28-30), and by Zeiss and Zwanzig (31), is now postulated (31) to proceed by way of a cyclic ester intermediate (II), which can decompose in two different ways.



II

Most textbooks of organic chemistry describe the reaction of permanganate with olefins by the following equations,

$$3\,RCH=CHR' + 8\,MnO_4^- \longrightarrow$$
$$3\,RCOO^- + 3\,R'COO^- + 8\,MnO_2 + 2\,H_2O + 2\,OH^-,$$

$$3\,R_2C=CR'_2 + 4\,MnO_4^- \longrightarrow$$
$$3\,R_2CO + 3\,R'_2CO + 4\,MnO_2 + 4\,OH^-.$$

However, the reaction seldom corresponds to these equations, and the yields of products are generally poor.

One alternative to the use of these oxidizing agents, which now receives wide application when only small amounts of olefin are available, is to convert the olefin to a glycol with a hydroxylating agent such as peracid or osmium tetroxide, and then to cleave the glycol with a glycol-splitting agent such as periodate, bismuthate or lead tetraacetate. This approach requires two stages and a stoichiometric amount of oxidizing agent in the first stage.

R.U. Lemieux conceived the idea of using a hydroxylating agent which is regenerated by the glycol-splitting agent, and could thus serve as a catalyst for the oxidation of the olefin by the glycol-splitting agent. On the basis of this idea, a periodate-permanganate reagent was developed for the conversion of olefins to dicarboxylic acids (32), and a periodate-osmium tetroxide reagent was developed for the conversion of olefins to dialdehydes (33). Both of these reagents have already received wide application. The success of the periodate-permanganate reagent has been attributed to the fact that, since the ratio of the reactants is permanganate:olefin:periodate = 1:8:64, and the reaction can be conducted near neutrality, the action of the permanganate should be restricted to its more selective oxidations involving the olefin and dialdehyde intermediates. These speculations naturally have led to an interest, in this laboratory, in the mechanism of the permanganate-olefin reaction.

In the present work, a study has been undertaken of the oxidation of olefins by permanganate in neutral, alkaline and non-aqueous media. The direction of the work has been generally guided by the experiences of others in this field, but an attempt has been made, as well, to bring a fresh viewpoint to some of the problems. The results we have obtained from a study of the kinetics, inorganic chemistry, stereochemistry and deuterium isotope effect of the reaction, together with findings reported by others, have provided a much clearer insight into the nature of the intermediate stages of the reaction, and they give some indication of the kinds of problems which still remain.

2. The Mechanisms of Permanganate Oxidations

It is useful to consider some previous studies of permanganate oxidations, so that the factors which govern these reactions and account for the versatility of this oxidizing agent may be set forth at the outset. In this chapter, as they become pertinent to the general discussion, certain aspects of the chemistry of manganese will also be presented. An attempt has been made to assess the data critically, in order to demonstrate the limitations of certain experimental approaches to these reactions, and to introduce the reader to the kind of thinking which has governed the work to be reported in this thesis.

A. Oxidation of Formic Acid and Formate Ion

Skrabal and Preiss carried out an early study of this reaction (34), but most of the early work was done by Holluta and his co-workers, who investigated the mechanism of the reaction in weakly acid (35), neutral (36,37), and alkaline medium (12, 38, 39). Mann and Tompkins (13) studied the reaction in dilute sulphuric acid, while Hill and Tompkins (40) examined the oxidation of sodium formate. More recently, Wiberg and Stewart (14) have reinvestigated the reaction in detail. The authors all agree that the reaction is first order in permanganate and first order in formate ion regardless of the pH, the sulphuric acid merely serving to regulate the concentration of formate ion. The limiting slope of the ionic strength-rate curve (13) was 1.06, indicating that the reaction was between two charged ions of the same sign. Addition of manganous ion had no effect on the reaction, and the addition of fluoride ion served merely to increase the dissociation of formic acid (with a resulting acceleration of the rate); when manganous ion was added in excess to formic acid-permanganate reaction mixtures, there was a reduction in the rate due to the removal of permanganate by the Guyard reaction,

$$3\,Mn^{+2} + 2\,MnO_4^- + 2\,H_2O \rightarrow 5\,MnO_2 + 4\,H^+ .$$

These results thus serve to identify the permanganate and formate ions as the species which react in the slow step. Tompkins and co-workers, therefore, proposed the following mechanism, which should hold regardless of the pH,

$$(1)\ldots \quad MnO_4^- + HCOO^- \xrightarrow{\text{slow}} MnO_3^- + CO_2 + OH^-$$

$$(2)\ldots \quad 2\,MnO_3^- + H_2O \xrightarrow{\text{fast}} MnO_2 + HMnO_4^- + OH^-$$

$$(3)\ldots \quad HMnO_4^- + HCOO^- \xrightarrow{\text{fast}} MnO_2 + CO_2 + 2\,OH^- .$$

Holluta's earlier work had led to a proposed mechanism for which the initial steps were those shown in equations 4-6 .

$$(4)\ldots \quad MnO_4^- + HCOO^- \xrightarrow{\text{slow}} MnO_4^{-3} + H^+ + CO_2$$

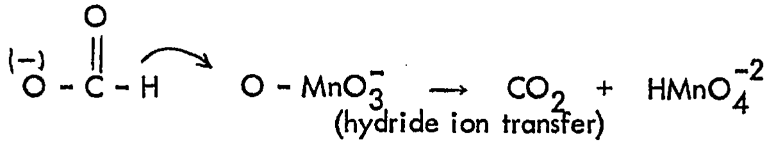
$$(5)\ldots \quad 2\,MnO_4^{-3} + H^+ + 5\,HCOO^- \xrightarrow{\text{fast}} MnO_4^- + Mn(HCOO)_5^{-2}$$

$$(6)\ldots \quad Mn(HCOO)_5^{-2} \rightarrow Mn^{+3} + 5\,HCOO^- .$$

Tompkins, however, found no evidence for manganese(III)-formate complexes, and hence equations 5 and 6 may be eliminated.

The importance of Holluta's work lies in his recognition (38) of the fact that he had not proved the nature of the products of the initial bimolecular reaction. At the time of this work (1923), there was considerable indirect evidence for the existence of a "mangani-manganate", containing pentavalent manganese, and stable in strongly alkaline medium. Although the fact that this blue material was indeed pentavalent manganese was not satisfactorily proved until much later (see page53), Holluta was able to reduce permanganate with sodium formate in strongly alkaline media to solutions which had the same absorption spectrum as this mangani-manganate. The absorption maxima of these solutions differed sufficiently from that of manganate (λ max. = 600 mμ), that Holluta was able to conclude that an appreciable part of the permanganate had been reduced to pentavalent manganese.

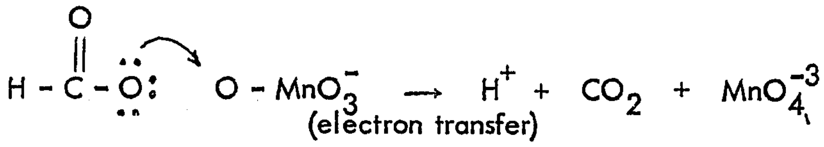
In their recent study of this reaction (14), Wiberg and Stewart, using DCOOH, have observed a deuterium isotope effect of 7.4; using permanganate -O^{18}, they find that over one-third of the oxygen introduced into the product comes from the oxidizing agent. (For a discussion of the deuterium isotope effect, see page 220). These results place important limitations on the possible mechanisms for the rate-determining step. The large deuterium isotope effect shows that the breaking of the carbon-hydrogen bond is involved in the rate-determining step. Possible mechanisms for this step, therefore, include



$$\overset{(-)}{O}-\overset{\overset{O}{\|}}{C}-H \quad O-MnO_3^- \longrightarrow CO_2 + HMnO_4^{-2}$$

(hydride ion transfer)

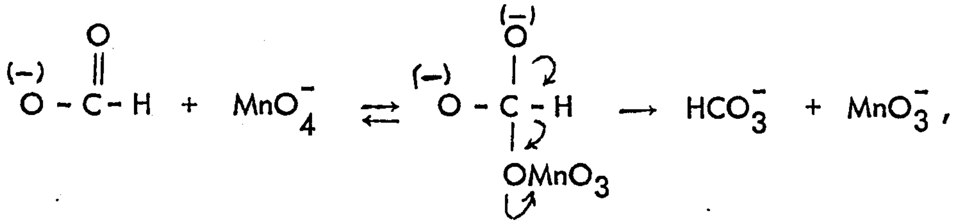
or



$$H-\overset{\overset{O}{\|}}{C}-\ddot{\underset{\cdot\cdot}{O}}: \quad O-MnO_3^- \longrightarrow H^+ + CO_2 + MnO_4^{-3}$$

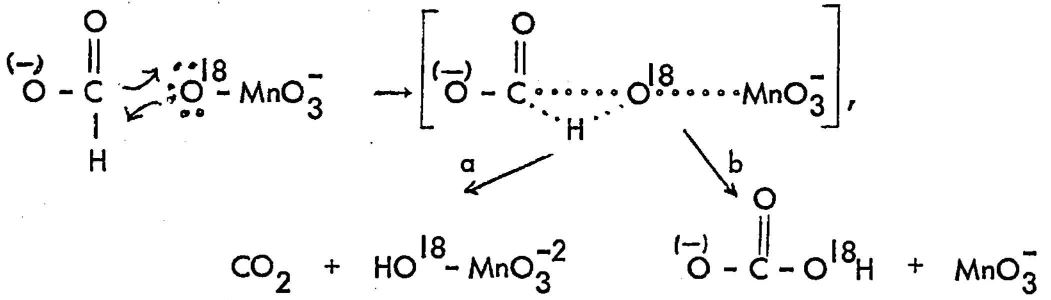
(electron transfer)

However, in view of the oxygen transfer data, these reactions cannot in themselves explain the nature of the reaction. Wiberg and Stewart rule out a mechanism,



$$\overset{(-)}{O}-\overset{\overset{O}{\|}}{C}-H + MnO_4^- \rightleftarrows \overset{(-)}{O}-\underset{\underset{OMnO_3}{|}}{\overset{\overset{\overset{(-)}{O}}{|}}{C}}-H \longrightarrow HCO_3^- + MnO_3^-,$$

on grounds that the free acid should react more readily with the negatively-charged permanganate than the ion, a fact which does not agree with experiment. They prefer, instead, a mechanism of the sort,



$$\overset{(-)}{O}-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}\;\ddot{\underset{\cdot\cdot}{O}}{}^{18}-MnO_3^- \longrightarrow \left[\overset{(-)}{O}-\overset{\overset{O}{\|}}{C}\cdots\cdots O^{18}\cdots\cdots MnO_3^-\right],$$

$$\xrightarrow{a} CO_2 + HO^{18}-MnO_3^{-2} \qquad \xrightarrow{b} \overset{(-)}{O}-\overset{\overset{O}{\|}}{C}-O^{18}H + MnO_3^-.$$

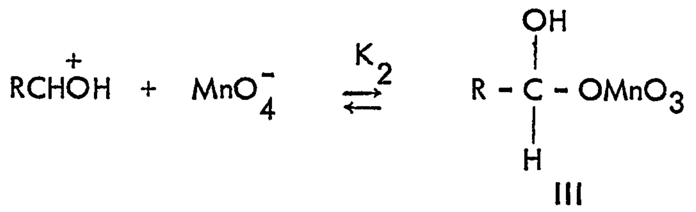
which can lead to both labelled and unlabelled carbonate, depending on which bonds are broken. It is suggested, therefore, that Mn(V) exists, and may be the first reduced state of permanganate.

B. Oxidation of Aromatic Aldehydes. Ester Intermediates in Oxidation Reactions

The oxidation of benzaldehyde has been studied by Tompkins (6) in neutral and alkaline medium, and by Wiberg and Stewart (7) in the pH region 5 - 13. Wiberg and Stewart also report studies of the oxidation of a number of other aromatic aldehydes. At constant pH, the reaction is first order in permanganate and in aldehyde. Wiberg and Stewart were also able to demonstrate general acid catalysis in neutral and acid medium; under these conditions, the rate-controlling step involved the cleavage of the aldehyde carbon-hydrogen bond, as indicated by a large deuterium isotope effect. Using $KMnO_4 - O^{18}$, it was found 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. In alkaline medium, on the other hand, the deuterium isotope effect was negligible, and the oxygen introduced into the aldehyde was derived mainly from the solvent. Also a one-half power dependence on hydroxyl ion was observed.

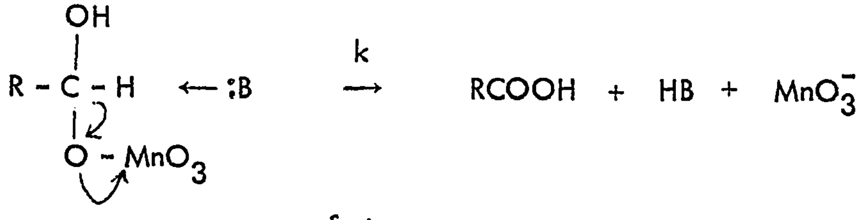
The oxidation, therefore, proceeds by different mechanisms, depending on the pH. In acid medium, the experimental results are satisfactorily accommodated by the mechanism,

(7)... $$RCHO + H_3O^+ \underset{}{\overset{K_1}{\rightleftarrows}} RCH\overset{+}{O}H + H_2O$$

(8)...


$$\overset{+}{\mathrm{RCHOH}} + \mathrm{MnO_4^-} \underset{\longleftarrow}{\overset{K_2}{\longrightarrow}} \mathrm{R - \underset{H}{\overset{OH}{C}} - OMnO_3}$$

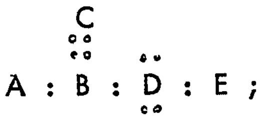
III

(9)...


$$\mathrm{R - \underset{O - MnO_3}{\overset{OH}{C}} - H} \longleftarrow :\mathrm{B} \xrightarrow{k} \mathrm{RCOOH} + \mathrm{HB} + \mathrm{MnO_3^-}$$

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

The fact that this mechanism is in complete agreement with experiment is in itself strong evidence for the kind of intermediates which have been proposed. It is entirely reasonable to anticipitate that an ester intermediate, III, is formed (equation 8), and decomposes by a two-electron transfer to yield the product (equation 9). These points are particularly stressed because, as mentioned on page 2, the common feature of most oxidation-reduction reactions is the formation of an intermediate or a complex in which an electron transfer can take place. The question of whether one-electron transfer or two-electron transfer takes place in a given system, or, indeed, whether it is possible to conceive of a general mechanism for oxidation reactions involving one or the other of these possibilities, is a very controversial one and has been discussed by many workers in the field. In spite of the controversy over this point, there can be no question concerning the existence of "ester intermediates" in many of the common organic oxidation reactions. By ester intermediate in this general sense, we mean any substance which can be written,



$$A : \overset{\overset{C}{\vdots}}{B} : \underset{..}{\overset{..}{D}} : E \;;$$

here B will usually be an atom of the oxidizing element, and A, C and D will usually be oxygens.

The hydroxylation of olefins with osmium tetroxide, (41), the cleavage of α-glycols with periodate (42-44) or lead tetraacetate (45,46), and the oxidation of isopropyl alcohol with chromic acid (47-49) are all common reactions which are known to proceed <u>via</u> ester intermediates. Westheimer's brilliant studies (47-49) of the chromic acid oxidation of isopropyl alcohol merit further consideration here, since the mechanism arrived at is analogous to that proposed by Wiberg and Stewart (7) for the oxidation of aromatic aldehydes:

$$H^+ + CH_3CHOHCH_3 + HCrO_4^- \overset{\text{fast}}{\rightleftarrows} (CH_3)_2CHOCrO_3H + H_2O$$

$$B + (CH_3)_2CHOCrO_3H \xrightarrow{\text{slow}} BH + (CH_3)_2CO + HCrO_3^-$$

This mechanism agrees with the observed kinetics and with an observed deuterium isotope effect. In addition, the acid chromate ion ($HCrO_4^-$) has been proved to be the active oxidizing species, and a tetravalent chromium compound ($HCrO_3^-$) has been proved to be the first chromium product of the reaction. Finally, chromic acid esters of the required formula can be isolated from the reaction mixture and, as expected, are extremely base-labile.

Thus there is no fundamental difference between the kind of intermediate proposed by Wiberg and Stewart, and that found in other oxidation reactions. Although the ester postulated in the oxidation of benzaldehyde could not be isolated owing to the lability of the carbon-hydrogen bond, there is some evidence that stable manganese-containing esters can be formed; for example, Sidgwick (50) describes a compound $CH_3COOMnO_3$. According to Sidgwick, the green manganese heptoxide, prepared by the addition of permanganate to concentrated sulphuric acid, dissolves without decomposition in acetic anhydride, forming a purple solution of the mixed anhydride,

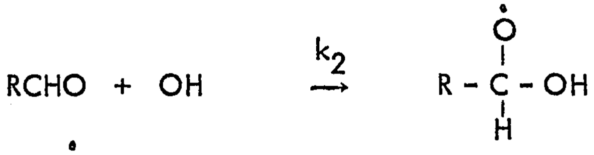
$$CH_3COOCOCH_3 \ + \ MnO_3OMnO_3 \ \longrightarrow 2\ CH_3COOMnO_3 .$$

The mechanism of the oxidation of benzaldehyde in alkaline medium is not clear. The absence of an isotope effect, the half power dependence on hydroxyl ion concentration, and the fact that most of the oxygen introduced into the aldehydes is derived from the solvent, all suggest a free-radical chain mechanism. Wiberg and Stewart (7) consider that the hydroxyl radical, formed by the reaction,

$$(10)\ldots \quad MnO_4^- \ + \ OH^- \ \xrightarrow{k_1} \ MnO_4^{-2} \ + \ OH,$$

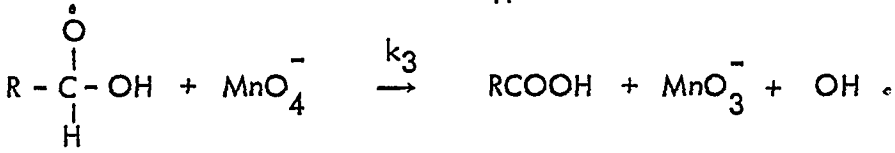
may carry out the initial attack on the aldehyde, (equation 11) and this stage is followed by the reaction shown in equation 12.

(11)...



$$RCHO + OH \xrightarrow{k_2} R-\overset{\dot{O}}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH$$

(12)...



$$R-\overset{\dot{O}}{\underset{H}{\overset{|}{\underset{|}{C}}}}-OH + MnO_4^- \xrightarrow{k_3} RCOOH + MnO_3^- + OH.$$

The chain reaction can be terminated by combination of two hydroxyl radicals to form hydrogen peroxide,

$$2\,OH \xrightarrow{k_4} H_2O_2$$

$$H_2O_2 + 2\,MnO_4^- \xrightarrow{\text{fast}} O_2 + 2\,HMnO_4^-.$$

Though this mechanism gives a rate equation,

(13)... $$-d[MnO_4^-]/dt = k[RCHO][MnO_4^-]^{\frac{1}{2}}[OH^-]^{\frac{1}{2}},$$

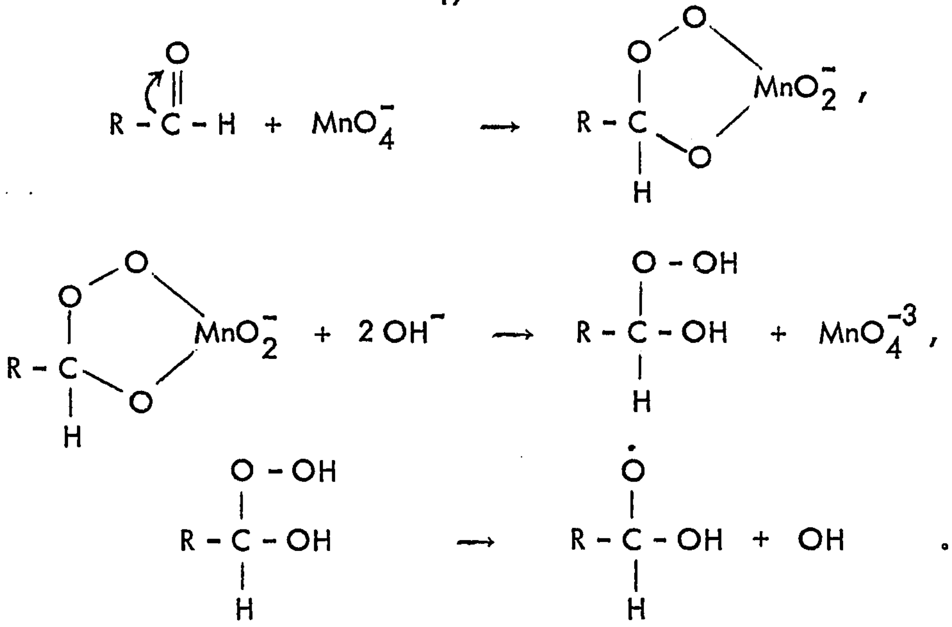
having the correct half order dependence on hydroxyl ion concentration, it gives only half order dependence on permanganate concentration. Hence, the mechanism probably is not correct.

Nevertheless, the postulate that free radicals are involved in this reaction appears to be a reasonable one in view of the isotope effects and the effect of hydroxyl ion concentration. Since it is conceivable that permanganate may operate in alkaline medium via the formation of hydroxyl radicals, it is important to examine the plausibility of this reaction route. In the mechanism suggested by Wiberg and Stewart, the half-power dependence on permanganate concentration arises from the consideration that permanganate is involved in the initiation step (equation 10). This would indicate that such a step is not important, at least under these reaction conditions. At pH 12.6, manganate oxidized eight aromatic aldehydes at essentially the same rate as permanganate, and the results obtained from both oxidizing agents were found to fit the same Hammett plot (7). Thus manganate and permanganate seem to oxidize these aldehydes in the same way. If equation 10 represented the initiation step for oxidation by permanganate, then oxidation by manganate would have to be initiated by the reaction,

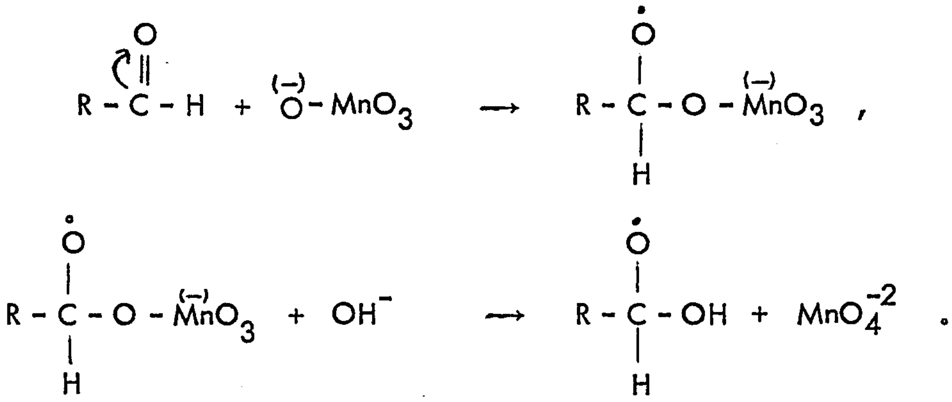
$$MnO_4^{-2} + OH^- \longrightarrow MnO_4^{-3} + OH,$$

and there is no evidence for this reaction, even in 8 M alkali (51), although reduction of permanganate to hypomanganate (MnO_4^{-3}) can take place in hot 12 M alkali (52).

Even though it is unlikely that the hydroxyl radical is present in sufficient concentration to initiate the attack on the aldehyde, this does not preclude the possibility that this species is formed during the reaction. Since the oxidizing agent does not attack the carbon-hydrogen bond, the attack may occur at the carbon-oxygen bond, either by addition to the double bond (two-electron exchange), or by attack at the carbon of the carbonyl (one-electron exchange). Both of these paths could lead to the formation of free radicals. In the first case, the mechanism would be described as follows;



In the case of one-electron exchange, the reaction would be written;



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-H + \overset{(-)}{O}-MnO_3 \longrightarrow R-\overset{\overset{\displaystyle \dot{O}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-\overset{(-)}{Mn}O_3 ,$$

$$R-\overset{\overset{\displaystyle \dot{O}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-O-\overset{(-)}{Mn}O_3 + OH^- \longrightarrow R-\overset{\overset{\displaystyle \dot{O}}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}-OH + MnO_4^{-2} .$$

It was not possible, however, to demonstrate that either of these mechanisms was compatible with the kinetic results of Wiberg and Stewart (7).

C. The Oxidation of Benzhydrol

This reaction has recently been investigated by Stewart (8) in alkaline medium. Kinetic studies showed that the reaction was first order in the permanganate, benzhydrol and hydroxyl ion concentrations. The salt effect was difficult to interpret but indicated that the slow step involved a reaction between two ions of like, single charge. A mechanism consistent with these kinetic results is the following;

(14)... $(C_6H_5)_2CHOH + OH^- \overset{K}{\rightleftharpoons} (C_6H_5)_2CHO^- + H_2O$

(15)... $(C_6H_5)_2CHO^- + MnO_4^- \xrightarrow{k}$ products.

To establish the mechanism of the slow step (equation 15), the deuterium isotope effect and the effect of using permanganate - O^{18} were examined. There was a definite deuterium isotope effect ($k_H/k_D = 6.6$), but no oxygen was transferred from the oxidizing agent to the alcohol. The mechanism shown in equations 16 and 17 satisfies these experimental results.

(16)... $(C_6H_5)_2CHO^- + MnO_4^- \xrightarrow{\text{slow}} (C_6H_5)_2CO + HMnO_4^{-2}$

(17)... $HMnO_4^{-2} + MnO_4^- \xrightarrow{\text{fast}} 2\,MnO_4^{-2} + H^+$.

The reaction, therefore, appears to involve a two-electron transfer in the rate-controlling step, with formation of pentavalent manganese.

D. Oxidation of the Tertiary Carbon-Hydrogen Bond.

Free Radical Intermediates in Permanganate Oxidations

Kenyon and Symons (20) have reported on the oxidation of branched-chain carboxylic acids RR'CH - $(CH_2)_2$ - COOH to the corresponding hydroxyacids RR'COH - $(CH_2)_2$ - COOH, the oxidants being permanganate in concentrated (10 N) alkaline solution and manganate in dilute alkaline solutions. Good yields of hydroxyacids were obtained.

Under the conditions used, the oxidations proceeded rapidly, at room temperature, and the hydroxyacids formed were stable to further oxidation. In dilute alkali, the oxidation by permanganate was slow, even at elevated temperatures, and led to extensive degradation of the acids. When optically active branched-chain acids were subjected to oxidation, the hydroxyacids obtained by permanganate oxidation had no optical activity, while the hydroxyacids obtained by manganate oxidation retained most of their optical activity. However, since the starting materials and the products were not related configurationally, it could not be established whether the manganate oxidations proceeded with retention or inversion of configuration.

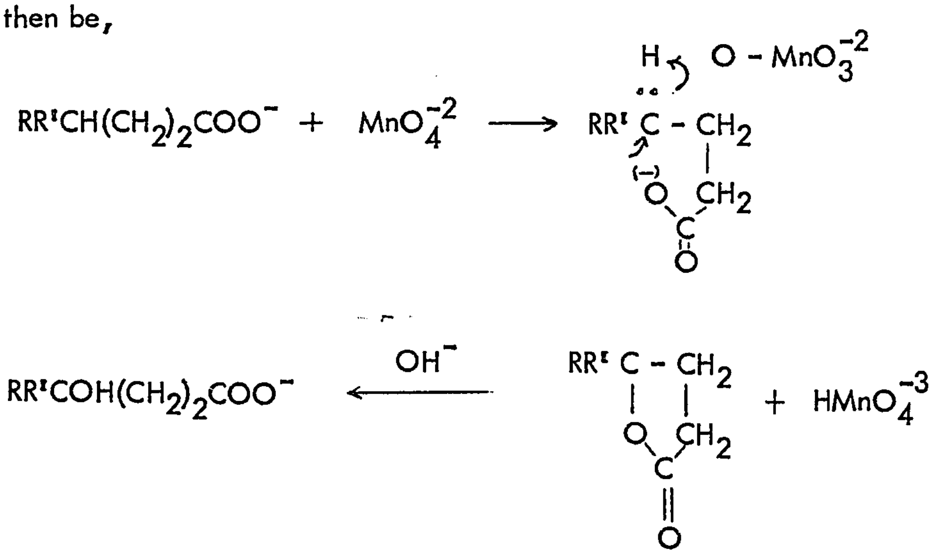
There was no racemization when the optically-active branched-chain carboxylic acids were heated for several hours in concentrated alkaline solution. Hence the permanganate oxidation is not initiated by carbanion formation,

$$RR'CH(CH_2)_2COO^- + OH^- \longrightarrow RR'\overset{(-)}{C}(CH_2)_2COO^- + H_2O.$$

The permanganate reaction likewise cannot occur by removal of a hydride ion to form a zwitter-ion,

$$RR'CH(CH_2)_2COO^- + MnO_4^- \longrightarrow RR'\overset{(+)}{C}(CH_2)_2COO^- + HMnO_4^{-2},$$

since studies with optically-active halogeno-carboxylic acids (53) show that formation of this kind of intermediate results in complete inversion about the positive carbon atom. On the other hand, the reaction with manganate can conceivably proceed via the latter reaction route. This viewpoint is supported by the fact that the γ-branched-chain acids, in which an attack by the carboxylate ion at the back side of the tertiary carbon-hydrogen bond is sterically favourable (54), reacts smoothly, while the α- and β- branched-chain acids, in which such assistance by the carboxylate ion is not favourable, undergo extensive degradation. A satisfactory formulation of the manganate reaction would then be,



The loss of optical activity during the permanganate reaction suggests that the radical-ion $RR' - \dot{C} - (CH_2)_2 - COO^-$ is an intermediate in the reaction, and the fact that the reaction proceeds smoothly only in strong alkali, where permanganate rapidly decomposes to manganate,

$$4\,KMnO_4 + 4\,KOH \longrightarrow 4\,K_2MnO_4 + 2\,H_2O + O_2 ,$$

suggests that the course of the reaction is related to this decomposition.

That the two phenomena are indeed related has been demonstrated by further studies by Symons (51, 55, 56). A kinetic study of the decomposition of permanganate in alkaline medium was undertaken first (51). Although the reaction was extremely complex, Symons was able to formulate a mechanism satisfying his kinetic results, which postulated the formation of a hydroxyl radical in the first step;

(18)... $$MnO_4^- + OH^- \rightleftharpoons MnO_4^{-2} + OH$$

(19)... $$OH + OH^- \rightleftharpoons \cdot O^- + H_2O$$

(20)... $$MnO_4^- + OH^- + \cdot O^- \rightleftharpoons MnO_4^{-2} + HO_2^-$$

(21)... $$MnO_4^- + HO_2^- \rightleftharpoons MnO_4^{-2} + HO_2$$

(22)... $$HO_2 + OH^- \rightleftharpoons O_2^- + H_2O$$

(23)... $$MnO_4^- + O_2^- \longrightarrow MnO_4^{-2} + O_2 .$$

To test this mechanism, experiments were conducted in water enriched in oxygen - 18. In order to minimize the rapid exchange of manganate with the solvent, (55), barium ions were added to the reaction mixture so that the manganate was precipitated as it formed. The oxygen evolved under these conditions had the same percentage isotopic enrichment as the solvent (55). Hence the oxygen came entirely from the solvent, as required by the mechanism shown in equations 18-23. Additional support for the idea that alkaline solutions of permanganate contain a free radical was obtained by adding permanganate to suspensions of acrylonitrile and styrene in 3 M alkali (56). Polymerization was observed. There was no polymerization when potassium manganate was used in place of permanganate, or when permanganate and acrylonitrile were allowed to react in neutral solution. The initiation of polymerization of vinyl monomers is usually considered to be a test for the presence of free radicals, but it is often dangerous to draw specific conclusions from a positive test. In this case, since the result is consistent with other evidence, it is safe to conclude that some radical-promoting species was present in the mixture.

On the basis of Symons' additional experiments, therefore, it seems probable that the oxidation of the branched-chain carboxylic acids by alkaline permanganate proceeds as follows;

$$MnO_4^- + OH^- \rightleftharpoons MnO_4^{-2} + OH$$

$$OH + RR'CH(CH_2)_2COO^- \longrightarrow RR'\dot{C}(CH_2)_2COO^- + H_2O$$

$$RR'\dot{C}(CH_2)_2COO^- + OH \longrightarrow RR'COH(CH_2)_2COO^- .$$

In view of this finding, and of the results described previously for the oxidation of aromatic aldehydes, it could be conjectured that the usual mode of reaction of permanganate in alkaline medium is via attack by hydroxyl radicals. Though it would be attractive to generalize in this way, the weight of evidence does not favour this idea. The oxidations of benzhydrol and formate ion in alkaline medium have already been described, and in both of these reactions, the permanganate ion itself was the active oxidizing agent. Likewise, in the oxidation of olefins, as has been shown in the present work, the permanganate ion attacks the double bond. Drummond and Waters (57) have reported that in 1-2 N alkali, permanganate rapidly attacks acetone, malonic acid and fumaric acid, compounds which are stable to hydroxyl radicals (from the Fenton reagent), while compounds such as ethyl ether, dioxane, t-butyl alcohol and propionic, succinic and adipic acid were attacked by hydroxyl radicals but not by alkaline permanganate. They do not report studies in more strongly alkaline solutions. In the pH region 12-14 at normal temperatures, however, their work shows clearly that the hydroxyl radical plays little part in oxidations by permanganate. It is quite reasonable to conclude, therefore, that hydroxyl radicals are not obtained from a permanganate-hydroxyl ion reaction, unless the hydroxyl ions are in very great excess. It may also be concluded that, while permanganate may undergo a one-electron exchange with hydroxyl ion, in no case yet discussed is there any definite evidence that permanganate can abstract a single electron from an organic compound. These reactions all appear to be two-electron transfers.

E. Oxidation of Propionate Ion

When propionate ion is treated with hot, alkaline permanganate, an oxidation to oxalate and carbonate occurs (58).

(24)... $C_2H_5CO_2^- + 4\,MnO_4^- \longrightarrow C_2O_4^{-2} + CO_3^{-2} + 4\,MnO_2 + OH^- + 2\,H_2O$

Nahinsky and co-workers investigated the route of this reaction using propionate-1-C^{11} (59, 60). Though oxalate is slowly oxidized by alkaline permanganate, in 2 N sodium hydroxide at 100°, the carbonate to oxalate ratio was unity, indicating that only the reaction shown in equation 24 need be considered. Under these reaction conditions, they found 25% activity in the carbonate and 75% of the activity in the oxalate ion. Hence the ratio

$$\frac{\alpha C - \beta C \text{ rupture}}{\alpha C - CO_2^- \text{ rupture}}$$

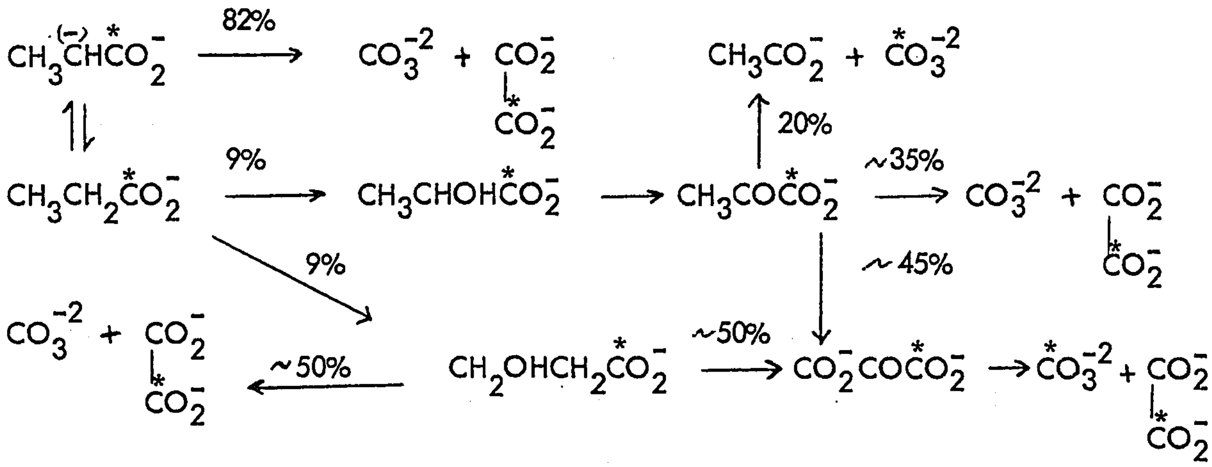
was 3.0.

Since it was reasonable to suppose that hydroxyacids were intermediates in the oxidation, the reactions of α- hydroxypropionate-1-C^{11} and β-hydroxypropionate-1-C^{11} were also studied under the same conditions.

The ratio of carbon-carbon to carbon-carboxylate rupture was 3.0 with these compounds also. This indicated that, in 2 N alkali, the hydroxyacids were probably intermediates in the reaction.

In 10 N alkali, at 100°, the propionate ion underwent a more preferential α-carbon-β-carbon cleavage (87% activity in the oxalate), while the hydroxyacids gave 50% activity in the oxalate and 50% in the carbonate. Therefore, in strong alkali, the major route of the reaction probably did not proceed through hydroxyacid intermediates.

Mahler and Roberts (21) reinvestigated the reaction in strong alkali, using propionate-1-C^{14}. They found 90% of the activity in the oxalate, and 10% in the carbonate, or a preferential α-carbon-β-carbon cleavage of 9.0. The oxidation of pyruvate-2-C^{14} was also studied to determine whether this acid could be an intermediate in the reaction. This compound gave 0.2 mole of acetate and 0.8 mole of oxalate per mole of carbonate; all of the acetate was formed by decarboxylation, and none of the carbonate originated in the carbonyl carbon. It was calculated from these results that less than 10% of the propionate ion passed through a pyruvate intermediate, and that 20% of the pyruvate molecules decarboxylated before being oxidized. The route of the propionate oxidation in 10 N alkali was, therefore, formulated as follows.



The mechanism of the oxidation seems to be dependent on the hydroxyl ion concentration. Since the route of the reaction appears to change in the pH region where the oxidation can be due to hydroxyl radicals, it is suggested that this factor may well govern the course of the reaction.

3. The Oxidation of Olefins by Permanganate

Pean de Saint Gilles (61), working around the middle of the nineteenth century, was among the first to recognize that the character of the oxidation products of both organic and inorganic substances with permanganate was partially dependent upon whether the reaction took place in acid, neutral or alkaline media. Among the compounds he worked with was ethylene, which he oxidized to carbon dioxide. Other workers obtained analogous results with other olefins, and it was believed that, in general, the route of this reaction involved scission of the olefinic linkage to yield acids or ketones.

In 1879, Tanatar (62), who was studying some of the properties of cis-trans isomerism, began an investigation of maleic and fumaric acids. Working first with fumaric acid, he found that cold aqueous permanganate converted the free acid and the potassium salt to the same product, a dioxysuccinic acid, m.p. 206°. This compound must have been formed, therefore, without scission of the olefinic linkage. Kekulé and Anschütz (63, 64) confirmed this result and found, in addition, that maleic acid also gave a dioxysuccinic acid, m.p. 140°, which differed from that obtained from fumaric acid. Though they did not realize it, this result showed that the reaction was stereospecific.

Just prior to this work, the Russian chemist Butleroff (65) had speculated on the cleavage of olefins by permanganate and suggested that the first product of the reaction was an oxide which, by hydration and dehydration, was converted to an aldehyde or ketone. The effect of these papers was to stimulate a number of workers to study the hydroxylation reaction, and much exploratory work was done by Saytzeff (66-70), Hazura (71) and Wagner (72).

Working with ethylene, isopropylethylene and butadiene, Wagner (72) found that α-glycols were the primary products of the reaction with 1% aqueous permanganate; in no case was an oxide isolated from the reaction, even when the conditions were such that hydration of the corresponding oxide would be slow. Thus the glycols must have been formed directly from the olefins. A direct scission of the double bond by the oxidizing agent was considered improbable, this worker favouring instead a mechanism involving further oxidation of the glycol to explain the formation of cleavage products. However, he did not study the oxidation of glycols under these reaction conditions.

Saytzeff and Hazura (66-71) did much important work on the hydroxylation of unsaturated fatty acids by permanganate, but it was Albitski (73) who first demonstrated the stereospecific nature of the reaction with these olefins. This work may be illustrated using the <u>cis</u> and <u>trans</u> pair, oleic and elaidic acids.

$$\begin{tikzcd}
\text{oleic acid (m.p., } 14^\circ\text{)} \arrow[r, "MnO_4^-"] \arrow[d, "H_2O_2\text{, HOAc}"] & \text{glycol (m.p., } 132.5^\circ\text{)} \\
\text{oxide} \arrow[d, "H_2O\text{, }H^+"] & \text{oxide} \arrow[u, "H_2O\text{, }H^+"'] \\
\text{glycol (m.p., } 99\text{–}100^\circ\text{)} \arrow[r, "MnO_4^-"] & \text{elaidic acid (m.p., } 44\text{–}45^\circ\text{)} \arrow[u, "H_2O_2\text{, HOAc}"']
\end{tikzcd}$$

Thus, one of these reactions involved <u>cis</u> addition and the other involved <u>trans</u> addition to the olefin, but there was as yet no way of establishing which was which. Indeed, the configurational relationships were not rigorously achieved until 1956.

It should be mentioned here that the early workers did not obtain good yields of glycols, the amount of material isolated being usually in the vicinity of 20-25% of theoretical. Indeed, the permanganate method of hydroxylation has never become popular due to these low yields, which are general, and to the occurrence of unavoidable and undesirable side-reactions. It was one of the aims of the present investigation to see whether, by identifying and determining the mechanisms of these side-reactions, conditions could be established for making hydroxylation by permanganate a useful reaction.

That the reaction can lead to a good yield of glycol from at least one olefin has been shown by Lapworth and Mottram (2). These workers established that the conditions for the conversion of oleic acid in 96% yield to dihydroxystearic acid were the following;

(1) a low temperature (0-10°) during the reaction;

(2) a concentration of oleic acid not greater than 0.1% ;

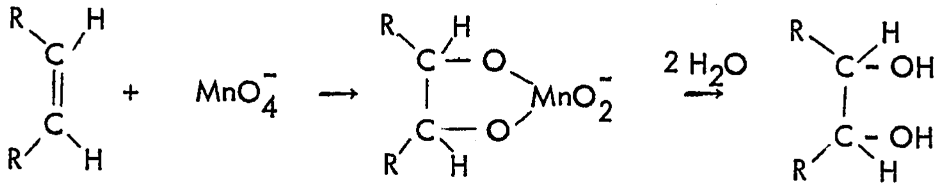
(3) a concentration of the added aqueous permanganate not greater than 1% (15 moles per mole of olefin) ;

(4) a short reaction period (five minutes) ;

(5) a slight excess of alkali should be present from the beginning of the oxidation.

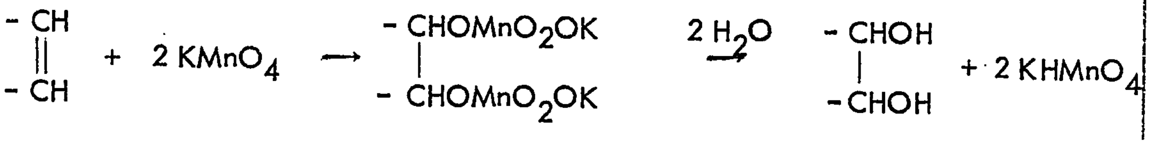
On the basis of his results, and following a suggestion by Lwoff (74), Wagner (75) proposed that the first product of permanganate oxidation was an addition compound (IV) between the permanganate and the olefin, and he predicted that the glycol formed in this reaction would be that which would be expected to arise if both the hydroxyl groups were added to one side of the planar olefinic bond,

(25)...



IV

In a later paper (76), in the mistaken belief that permanganate oxidation yields a trans-glycol, while hydration of an oxide yields a cis-glycol, Nametkin proposed an intermediate, (V), formed by the addition of two molecules of permanganate to the olefin,



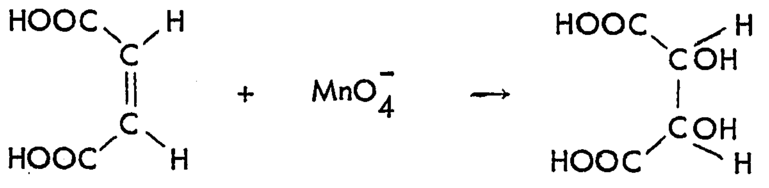
$$\begin{array}{l}-CH\\ \;\;\|\\ -CH\end{array} + 2\,KMnO_4 \longrightarrow \begin{array}{l}-CHOMnO_2OK\\ \;\;|\\ -CHOMnO_2OK\end{array} \xrightarrow{2\,H_2O} \begin{array}{l}-CHOH\\ \;\;|\\ -CHOH\end{array} + 2\,KHMnO_4$$

V

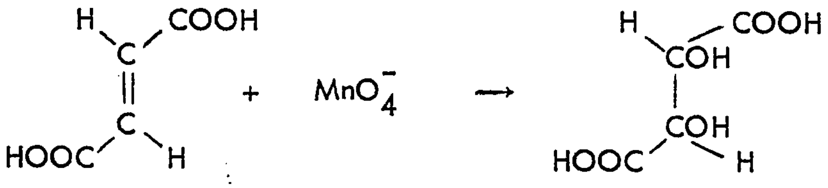
This mechanism agreed with the observation that, in alkaline medium, the permanganate was converted to a salt of manganic acid. It was thought that the permanganate addition was trans because of a naive notion of steric hindrance to cis-addition.

This contention was disproved by the elegant work of Boeseken (I).

In a lengthy series of papers, Boeseken described a method, based on complex formation with boric acid, for distinguishing between cis and trans glycols in alicyclic compounds and in sugars. Application of this method to a number of glycols formed by permanganate oxidation of the corresponding olefins established that permanganate oxidation gave the cis glycol in every case. This conclusion was supported, as seen earlier, by the results of the hydroxylations of fumaric and maleic acids. The glycol, m.p. 206°, obtained from the trans olefin (fumaric acid) could be resolved into optically active forms, while that from the cis olefin, m.p. 140°, was meso.



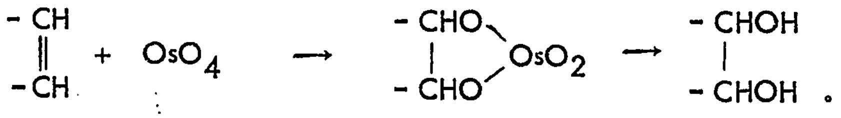
meso



dl form

The same result has recently been achieved with the 9,10-dihydroxystearic acids obtained from oleic and elaidic acids. Gensler and Schlein (77) showed that the 9,10-dihydroxystearic acid, m.p. 94-95°, isolated from permanganate oxidation of the *trans* olefin, elaidic acid, had the *threo* configuration, since the racemic form of the 9,10-octadecanedioic acids could be converted to this compound. Since oxidation of the *trans* olefin yielded the glycol with the *threo* configuration, the hydroxylation must have been *cis*. This conclusion substantiated the stereochemical interrelationships derived for these compounds by Swern (78), who based his conclusions on the assumed mechanisms of the permanganate and peracid oxidations of olefins.

Boeseken (1) suggested, on the basis of his results, that the formation of *cis* glycols was satisfactorily explained by assuming that a cyclic ester intermediate (IV) containing pentavalent manganese was formed, and was hydrolyzed without inversion of the carbon centres. Since the hydroxylation of olefins with osmium tetroxide (79) was also found to yield *cis* glycols, an analogous mechanism was postulated for this reaction,



$$\begin{matrix}-\mathrm{CH}\\ \| \\ -\mathrm{CH}\end{matrix} + \mathrm{OsO_4} \longrightarrow \begin{matrix}-\mathrm{CHO}\\ | \\ -\mathrm{CHO}\end{matrix}\!\!>\mathrm{OsO_2} \longrightarrow \begin{matrix}-\mathrm{CHOH}\\ | \\ -\mathrm{CHOH}\end{matrix}\ .$$

In 1936, Criegee (41) proved that the hydroxylation of olefins by osmium tetroxide did, in fact, proceed by way of this ester intermediate, since a 1 : 1 olefin-osmium compound could be isolated in quantitative yield. This complex was stable for long periods of time in refluxing acid or alkali, but rapidly decomposed to the cis glycol when treated with an aqueous solution containing an oxidizing or reducing agent. This is the behaviour expected if the compound contains Os(VI). This valence state is stable in aqueous medium, but since the Os(VIII)/Os(VI) couple has a potential of - 0.3 volt and the Os(VI)/Os(IV) couple has a potential of -.1 volt (80), hexavalent osmium can undergo oxidation and reduction very readily.

Criegee's work made the analogous intermediate in permanganate oxidations more acceptable, but there remained little information concerning the possible existence of pentavalent manganese or its behaviour under the conditions of the hydroxylation reaction.

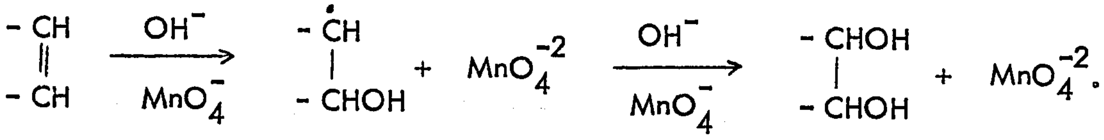
In their survey of the course of permanganate oxidations in alkaline media, Drummond and Waters (57) found that manganate was the first observed intermediate in the reaction with olefins. To rationalize this behaviour, they considered the possibility that initially-formed pentavalent manganese (hypomanganate) was rapidly oxidized by permanganate to manganate, but, in view of their lack of information concerning the chemistry of hypomanganate, they rejected this possibility, assuming that hypomanganate would decompose more rapidly than it could be oxidized by permanganate. That is, the reaction,

$$2\,\mathrm{Mn(V)} \longrightarrow \mathrm{Mn(IV)} + \mathrm{Mn(VI)}\,,$$

was considered to be much faster than the reaction,

$$\mathrm{Mn(V)} + \mathrm{Mn(VII)} \longrightarrow 2\,\mathrm{Mn(VI)}.$$

They explained the observation of manganate as the initial intermediate by proposing two successive one-electron exchanges with intermediate free radical formation,



$$\begin{matrix}-\mathrm{CH}\\ \Vert\\ -\mathrm{CH}\end{matrix} \xrightarrow[\mathrm{MnO}_4^-]{\mathrm{OH}^-} \begin{matrix}-\dot{\mathrm{C}}\mathrm{H}\\ |\\ -\mathrm{CHOH}\end{matrix} + \mathrm{MnO}_4^{-2} \xrightarrow[\mathrm{MnO}_4^-]{\mathrm{OH}^-} \begin{matrix}-\mathrm{CHOH}\\ |\\ -\mathrm{CHOH}\end{matrix} + \mathrm{MnO}_4^{-2}.$$

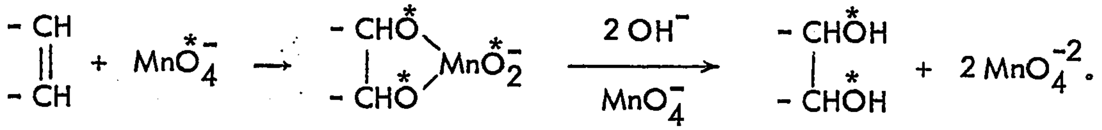
This mechanism seemed very likely to be incorrect, because the stereospecificity of the reaction requires that neither of the carbon atoms can possibly achieve the planar configuration which is to be expected for the postulated free radical intermediate. On the other hand, both of the carbon atoms could conceivably retain their configurational identities by way of a bridged structure for the free radical intermediate(see below). Nevertheless, these speculations seemed so implausible as to warrant immediate challenge and contributed much to our undertaking the present work.

In order to resolve the question of whether the initial reaction between permanganate and olefins involves one-electron or two-electron exchange, it is clear that more information is needed concerning the chemistry of manganate and hypomanganate under the conditions of the permanganate-olefin reaction. In particular, the objections of Drummond and Waters (57) to the postulate of a hypomanganate intermediate required experimental substantiation, and one of the first objectives of the present work was the study of this point.

Another approach to the question of whether the reaction involves one-electron or two-electron exchange would be to study the hydroxylation reaction using $KMnO_4 - O^{18}$. If the cyclic pentavalent ester is an intermediate, then the oxygen introduced into the glycol should come from the oxidizing agent. The performance of this experiment was considered at the beginning of this investigation. However, a private communication from Dr. R. Stewart advised us that the experiment was to be performed in the laboratories of Dr. K.B. Wiberg. The results of this work have recently been published by Wiberg and Saegebarth (81), who examined the hydroxylation of oleic acid with O^{18}-labelled permanganate. This olefin, at pH 12, gives an almost quantitative yield of the cis glycol, erythro-9,10-dihydroxystearic acid (2). Despite the fact that there is a rapid electron exchange reaction between manganate and permanganate (82),

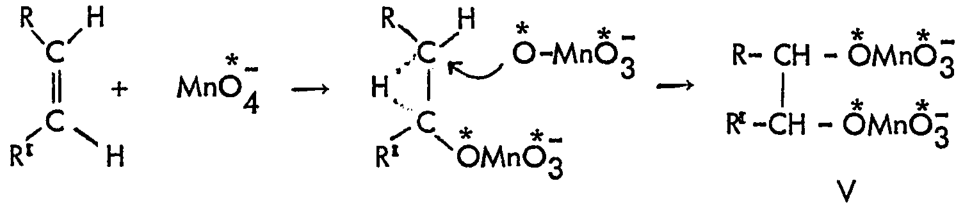
$$MnO_4^- + \overset{*}{Mn}O_4^{-2} \rightleftarrows MnO_4^{-2} + \overset{*}{Mn}O_4^- ,$$

and manganate will readily exchange its oxygen atoms with water (55), over 1.5 atoms of oxygen were transferred from the permanganate to the olefin when the stoichiometric quantities were used,



$$\begin{matrix}-CH\\ \|\\ -CH\end{matrix} + Mn\overset{*}{O}_4^- \longrightarrow \begin{matrix}-CH\overset{*}{O}\diagdown & \\ | & Mn\overset{*}{O}_2^-\\ -CH\overset{*}{O}\diagup & \end{matrix} \xrightarrow[MnO_4^-]{2\,OH^-} \begin{matrix}-CH\overset{*}{O}H\\ |\\ -CH\overset{*}{O}H\end{matrix} + 2\,MnO_4^{-2}.$$

This result comprises strong evidence in favour of an initial two-electron exchange reaction involving formation of the cyclic ester intermediate. The only alternative rationalization which can be envisaged would involve the type of mechanism outline below. Thus, the intermediate, V, postulated by Nametkin (76) would be formed,



V

Although a great many arguments can obviously be advanced against such a free radical mechanism, it is to be noted that it does have the virtue of rationalizing the results observed by Drummond and Waters (57).

The effect of pH on the initial stages of the permanganate-olefin reaction has received only little attention. Holde and Marcusson (83) were the first to consider this variable. They found that, though in alkaline medium permanganate oxidized oleic and elaidic acids to different glycols, when sufficient alkali was added to just neutralize the acid (pH 8), the two olefins gave the same compound, a yellow-coloured acid, m.p. 55-83°, which was difficult to purify, and which analyzed as hydroxyketostearic acid. This work was repeated by King (3), who established that, when the following conditions were observed, the oxidation of commercial oleic acid gave 20-35% yields of dihydroxystearic acid and 30-40% yields of the two 9-10-keto-hydroxystearic acids;

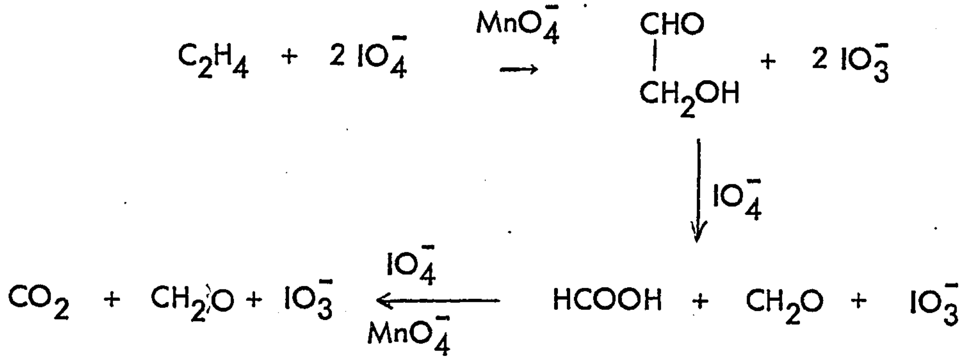
(1) the olefin and the alkali should be present in equivalent proportions, and the amount of permanganate subsequently added should be about two moles per mole of olefin;

(2) the concentration of the olefin should not be greater than 1 g. per litre of the reaction mixture;

(3) the duration of the oxidation should be 8-10 minutes at 8-10°.

King found that the two ketols were formed in about equal amounts, and the mixture, after repeated crystallization, melted at 64.5-65.5°. The products were separated by fractional crystallization of the semicarbazones, followed by regeneration of the ketols to give pure 9-hydroxy-10-ketostearic acid, m.p. 74°, and 9-keto-10-hydroxystearic acid, m.p. 75.5°.

Under the conditions of ketol formation, King observed that 9,10-dihydroxystearic acid was not attacked by permanganate. Hence the ketol was not formed by further oxidation of the glycol. It is evident, therefore, that the mechanism of the permanganate oxidation of olefins is strongly dependent on pH. The fact that, when the proper conditions are employed, the conversion of oleic acid to α -ketols is not an isolated case, was demonstrated by Lemieux and von Rudloff in their studies with the periodate-permanganate reagent (32, 84). By carrying out a limited oxidation at pH 7.7 and isolating the products after short reaction times, they isolated the expected ketols from oleic, elaidic and 10-undecenoic acids. Furthermore, the oxidation of ethylene resulted in the formation of only about one mole of formaldehyde on the consumption of oxidant equivalent to four oxygen atoms. If ethylene glycol alone had been produced in the first stage of the reaction, a consumption of oxidant equivalent to two atoms of oxygen would have yielded two moles of formaldehyde. The fact that formaldehyde was not oxidized under the conditions of the periodate-permanganate reaction supported this conclusion.



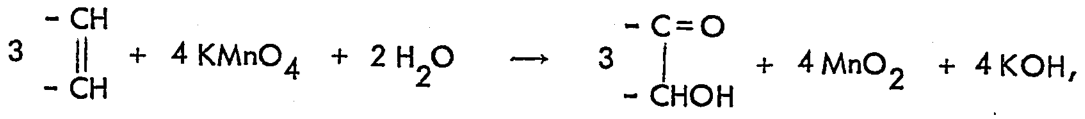
$$C_2H_4 + 2\,IO_4^- \xrightarrow{MnO_4^-} \begin{array}{c} CHO \\ | \\ CH_2OH \end{array} + 2\,IO_3^-$$

$$\downarrow IO_4^-$$

$$CO_2 + CH_2O + IO_3^- \xleftarrow[MnO_4^-]{IO_4^-} HCOOH + CH_2O + IO_3^-$$

The isolation of α-ketols from periodate-permanganate oxidations bears important implications on the mechanisms of the periodate-permanganate oxidation and the permanganate oxidation of olefins. First of all, the oxidation by periodate-permanganate must involve permanganate oxidation in its initial stages; this initial stage of the reaction would yield ketol and some reduced form of manganese. In the second stage of the reaction, the periodate cleaves the ketol and regenerates the permanganate. Since manganate was quantitatively oxidized to permanganate by periodate at pH 8.0, it could conceivably be the reduced state of manganese which is formed in the first stage of the reaction. The third stage of the periodate-permanganate-oxidation presumably involves permanganate oxidation of the products formed in the periodate cleavage.

Coleman, Ricciuti and Swern (85) recently reinvestigated the oxidation of oleic acid by neutral permanganate, and were able to explain, in part, the effect of pH on the course of the reaction. By controlling the pH of the reaction mixture, they increased the yield of the ketohydroxystearic acids from 30% to 55-75% in solutions twenty times more concentrated than those used by King (3). In accordance with the stoichiometric equation,



$$3\begin{matrix}-\mathrm{CH}\\ \| \\ -\mathrm{CH}\end{matrix} + 4\,\mathrm{KMnO_4} + 2\,\mathrm{H_2O} \longrightarrow 3\begin{matrix}-\mathrm{C{=}O}\\ | \\ -\mathrm{CHOH}\end{matrix} + 4\,\mathrm{MnO_2} + 4\,\mathrm{KOH},$$

the pH of a reaction solution containing 0.02 mole of oleic acid and 0.02 mole of potassium hydroxide in 60 ml. of water increased from about 10 to a maximum of 12 during the slow addition of 0.03 mole of permanganate in 75 ml. of water. This maximum pH was reached after only 25% of the calculated amount of permanganate had been added; when the reaction was worked up at this point, a 20% yield, based on olefin, of the ketohydroxystearic acids was isolated. However, when the addition of permanganate was continued, the major products were dihydroxystearic acid (50%), ketohydroxystearic acids (20%) and

9,10-diketostearic acid (3%). By maintaining the pH in the range 9.0-9.5 through neutralization of the liberated alkali as it formed, the yield of the ketols was raised to 55-75%; using these conditions, the yield of glycol was decreased to less than 10%, while the yield of diketostearic acid was about 7%. These results are readily explained if the mechanism of the reaction favours ketol in neutral medium and glycol at pH 12.

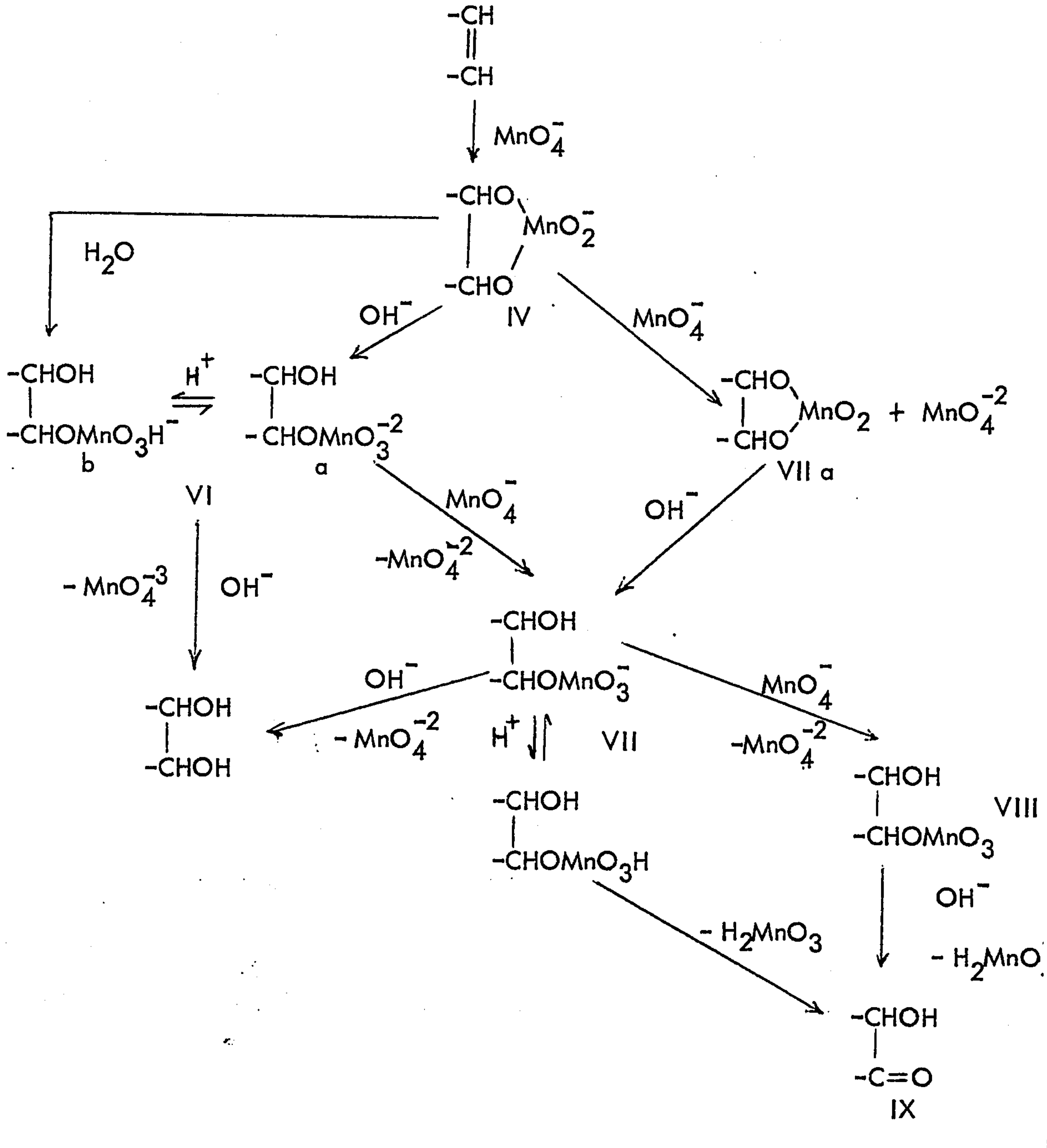
Without pH control during the reaction, it is evident why high dilutions are required for best yields of ketohydroxystearic acids. At high dilutions, the concentration of hydroxyl ions is reduced, and their undesirable effect, as far as formation of ketols is concerned, is diminished. This effect is explained by Coleman, Ricciuti and Swern, as being related to the rate of hydrolysis of the cyclic ester intermediate, which they assume to be the initial product of the reaction. They conclude that, in the presence of excess hydroxyl ions, this ester should be rapidly hydrolyzed at both CO - Mn bonds, more or less simultaneously, to yield 1,2-glycol. With pH control, the rate of hydrolysis of the ester should be reduced, and should proceed stepwise to yield an intermediate containing one hydroxyl group and one ester group. The competition between the permanganate and hydroxyl ions for this intermediate will favour the permanganate under these conditions, and further oxidation will then occur on the carbon atom still attached to manganese.

A mechanism embodying these principles was first proposed in 1955 by Lemieux (86,87), and with only minor modifications, by the author of this thesis in two reports to the National Research Council of Canada (88; see Table II).

On the basis of the evidence available at the time, it was considered that the initial stage of the permanganate-olefin reaction involved addition of the oxidizing agent to the double bond (1, 41) to form the pentavalent intermediate, IV. Since the hydroxylation reaction was stereospecific, the possibility of inversion during hydrolysis, due to incipient carbonium ion formation at one of the olefinic carbon atoms could be ruled out. Hence, the alkaline hydrolysis of this ester was normal; that is, fission occurred at the manganese-oxygen bonds (89). Since this hydrolysis presumably proceeds stepwise, the transient existence of the ester, VI, could be assumed. A consideration of King's work (3), and of the work of Lemieux and von Rudloff (32, 84) suggested that ketol could be formed directly from olefin in neutral medium by oxidation of a pentavalent ester (VI) by permanganate to a hexavalent ester (VII or VIIa) or to a heptavalent ester (VIII), which subsequently decomposed to ketol (IX) by a two-electron exchange. A step analogous to the VIII-IX step had been previously proposed by Wiberg and Stewart (7; see page 14). According to this mechanism, then, the yield of glycol in strongly alkaline medium was attributed to the rapid hydrolysis of VI under these conditions, while the high yield of the ketols in neutral medium was believed due to a much greater resistance to hydrolysis and susceptibility to oxidation possessed by VI.

TABLE II

Mechanism Proposed for the Permanganate Oxidation of Olefins (86 - 88)



The mechanism of the oxidation of olefins by permanganate in non-aqueous media has received little attention. Although many references can be found in the literature concerning oxidations under these conditions, in most of this work the permanganate oxidation has been part of some other problem in which, at some stage, the cleavage of an olefinic linkage was required. In general, this kind of work is difficult to locate, and, in any event, correlation of the results of various workers is almost impossible because of the different experimental techniques, concentrations and temperatures which can be used, and because the results of any systematic studies have not been published.

Two different kinds of experimental techniques seem to be favoured by most workers. In the first, the olefin, dissolved in dry acetone or glacial acetic acid or pyridine, is shaken with the calculated amount of powdered permanganate until the permanganate colour is discharged; in the second, an aqueous solution of permanganate is added to a solution of the olefin in some mixed solvent, usually aqueous acetone, ethanol or tertiary butyl alcohol. The latter solvent system is preferable, since t-butyl alcohol is oxidized only slowly by permanganate, while acetone and ethanol, particularly in alkaline media, are oxidized fairly readily. When acetone or ethanol must be used as the solvent, oxidation of the solvent can be minimized by dissolving the permanganate in water containing a molar equivalent of magnesium sulphate. Addition of magnesium sulphate to the reaction mixture enables the system to precipitate hydroxyl ions (as magnesium hydroxide) as rapidly as they are formed, and the pH remains near neutrality. Straus and Rohrbacher (90) appear to have been the first to use this technique.

When a completely anhydrous system is used, the major products of the oxidation are those which are formed by scission of the olefinic linkage, in accordance with the overall equations shown on page 7. To the author's knowledge, there is no mention in the published literature of a glycol ever having been isolated from reactions carried out under these conditions.

In mixed solvents, in addition to low yields of glycol, a variety of other products can be obtained. A complete survey of the literature is beyond the scope of this thesis, but a few of the more interesting reactions or reaction conditions which have been reported are summarized in Table III.

The experimental procedures used in the isolation of most of the products listed in Table III differ only slightly from one worker to another. The reaction mixture is either decolourized with sulphur dioxide, or the precipitated manganese dioxide is filtered off; the resulting colourless solution is concentrated and is then extracted with a suitable solvent such as ether, chloroform or methylene dichloride, etc. The extract is washed with water, sodium carbonate and water, and is worked up. The washing with sodium carbonate removes the acid products of the reaction, and these may be worked up separately. Unfortunately for our purposes, however, most workers have concentrated on

TABLE III

Oxidation of Olefins by Permanganate in Mixed Solvents

Olefin	Product(s)	Reaction Conditions	Reference
1,2-dimethylcyclopentene	cis glycol (45%)	90% acetone at -5°	91
cyclopentene	cis-1,2-cyclopentanediol (34%)	40% ethanol at - 40°; one mole of magnesium sulphate added as buffer.	92
cyclohexene	cis-1,2-cyclohexanediol (33%)		93
ergosterol	$\Delta^{7,14,22}$-ergostatriene-3β,5α,6α-triol (80%)	50% methylcyclohexane-water at 90-100°; aqueous phase contained 4% permanganate.	94
cholesterol	cholestane-3,6-dione-5α-ol (75%)	75% acetic acid, at 20-55°.	95
cholesterol	cholestane-3β,5α,6α-triol (4-5%)	benzene-water, with the aqueous phase containing alkaline permanganate	96
dehydroisoandrosterone acetate	androstane-(5,6)α-oxide-17-one-3β-ol-acetate (15%)	olefin was dissolved in acetic acid; the permanganate, dissolved in aqueous acetic acid, was added at 55°.	97
cholesterol acetate	cholestane-6-one-3β,5α-diol-3-monoacetate (14%) β-cholesterol oxide acetate (20%)	as above	97

TABLE III (contd.)

Olefin	Product(s)	Reaction Conditions	Reference
5-pregnene-20-one-3β-ol-acetate	pregnane-(5,6)-oxide-20-one-3β-ol acetate pregnane-20-one-3β,5α,6α-triol-3-acetate pregnane-6,20-dione-3β,5α,diol-3-acetate	as above	97
3β-acetoxypregna-5:16-diene-20-one	(A)-3β-acetoxy-16α,17α-dihydroxypregn-5-ene-20-one (B)- 3β-acetoxy-16α,17α-dihydroxypregna-5,14-diene-20-one	olefin was dissolved in acetone-acetic acid at 0°; permanganate in 85% acetone was then added; when no acetic acid was used, only A (5%) was isolated; when the ratio HOAc/MnO_4^- was 1.2, A (20%) and B (trace) were isolated; when the ratio HOAc/MnO_4^- was 15, only B (30%) was isolated.	98,99
2,2-dimethylpentene	2,2-dimethylpentanediol-4,5 (20%)	50% ethanol at − 40°	100
2,2,3-trimethylbutene-3	2,2,3-trimethylbutanediol-3,4 (28%)	a suspension of the olefin and aqueous permanganate was shaken for ten minutes.	
2-methylheptene-1	2-methylheptanediol-1,2 (20%)		100
bicyclo-[2.2.1]-2-heptene	exo-cis-bicyclo[2.2.1]-heptane-2,3-diol (40%)	50% t-butyl alcohol at 0-10° with one mole of added sodium hydroxide	101, 81
bicyclo-[2.2.1]-2-heptene	cyclopentane-1,3-dicarboxaldehyde (54-66%)	olefin was dissolved in 40% acetone at − 15 to −20°; an aqueous solution of permanganate and magnesium sulphate was added.	81

the neutral products of permanganate oxidation, and there is little reference in the literature concerning the nature of the acid products which are formed from the permanganate-olefin reaction in mixed solvents.

In connection with other problems in this Laboratory, Lemieux and co-workers have conducted several olefin-permanganate reactions in mixed solvents, and some of the results obtained from these studies have proved useful in interpreting the mode of action of permanganate under these reaction conditions. This work will be discussed later.

The isolation, by Wiberg and Saegebarth (81), of cyclopentane-1,3-dicarboxaldehyde from the oxidation of bicycloheptene in a buffered acetone-water mixture is of interest, since the result indicates a scission of the olefinic linkage. As will be seen later, the fact that carbon-carbon cleavage occurred at the olefinic linkage places important limitations upon the nature of the intermediate product of the reaction.

4. Some Aspects of the Chemistry of Manganate and Hypomanganate

Mention has been made several times in this thesis of the need for more specific information on the behaviour of pentavalent and hexavalent manganese, particularly under the conditions of alkaline permanganate oxidations.

Manganate, of course, is a well-known species, and various aspects of its chemistry have been reported for over one hundred years. The solid, K_2MnO_4 , may be prepared most readily by reduction of potassium permanganate in an alkaline melt (102). It forms a stable green solution in alkaline medium at pH values greater than 14. In the pH region 11-14, manganate can exist in solution for short periods of time, but is thermodynamically unstable with respect to the disproportionation reaction,

$$3\,MnO_4^{-2} + 2\,H_2O \longrightarrow 2\,MnO_4^- + MnO_2 + 4\,OH^- .$$

The equilibrium constant for this reaction,

$$K = [MnO_4^-]^2\,[OH^-]^4 / [MnO_4^{-2}]^3 ,$$

has been determined by Sackur and Taegner (103), and by Schlesinger and Siems (104); these workers find a value of the order of 25 at 25°.

The kinetics of this disproportionation reaction were studied by Duke (105). In the absence of added manganese dioxide, there was a pH-dependent induction period, followed by a rapid reaction which was zero order in manganate. The reaction was catalyzed by solid manganese dioxide, the catalyzed reaction being almost second order in hydrogen ion. The catalytic activity of the manganese dioxide decreased with ageing. Duke considered the following mechanism in explanation of his results;

$$MnO_4^{-2} + MnO_2 \rightleftharpoons MnO_2 \cdot MnO_4^{-2}$$

(adsorption; far to the left)

$$MnO_2 \cdot MnO_4^{-2} + 2\,H^+ \longrightarrow MnO_4^- + Mn(III)$$

(in the precipitate; the measured reaction)

$$\underset{\text{(ppte.)}}{2\,Mn(III)} + MnO_4^{-2} \longrightarrow 3\,MnO_2$$

$$MnO_2\ \text{(active)} \longrightarrow MnO_2\ \text{(inactive)}.$$

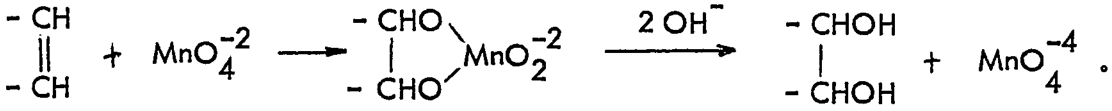
The reaction was considered to involve a kind of surface effect, the manganate being adsorbed on the surface of the manganese dioxide. This assumption was necessary in order to explain the zero order in manganate. The effect of manganese dioxide cannot be entirely due to a surface reaction, however, since ferric and aluminium hydroxides had no effect on the reaction. Since the catalysis was specific by manganese dioxide, the manganese dioxide can presumably enter chemically into the reaction.

The homogeneous reaction during the induction period was also studied (105), and equilibria such as the following were suggested by Duke,

$$2\,MnO_4^{-2} \rightleftharpoons Mn(V) + MnO_4^-$$

$$Mn(V) + MnO_4^{-2} \rightleftharpoons MnO_2 + MnO_4^- .$$

Potassium manganate has been little used in organic chemistry. Tcherniac used it for oxidation of naphthalene to phthalonic acid (106), the yield being one-third greater than when permanganate was used. Tursin and Rusakova oxidized diacetone-L-sorbose (107), the yield of diacetone-2-keto-L-gulonic acid (60-65%) being similar to that obtained with permanganate. In a survey of the oxidation of organic compounds by manganate (108), Pode and Waters observed that this oxidizing agent was no more specific than was alkaline permanganate, but was much slower in its action. The same authors, along with Rigby (109) and Wolfe (88) have reported that manganate hydroxylates olefins, the hydroxylation yielding <u>cis</u> glycols. This result suggests that manganate and permanganate hydroxylate olefins in the same way, and a mechanism involving a cyclic tetravalent ester intermediate has been proposed (88, 108),



$$\begin{array}{c}-\mathrm{CH}\\ \|\\ -\mathrm{CH}\end{array} + \mathrm{MnO}_4^{-2} \longrightarrow \begin{array}{c}-\mathrm{CHO}\\ |\\ -\mathrm{CHO}\end{array}\!\!>\mathrm{MnO}_2^{-2} \xrightarrow{2\,\mathrm{OH}^-} \begin{array}{c}-\mathrm{CHOH}\\ |\\ -\mathrm{CHOH}\end{array} + \mathrm{MnO}_4^{-4} .$$

This suggestion that manganate can oxidize via a two-electron exchange is supported by the work discussed earlier on the oxidations of the tertiary carbon-hydrogen bond (20) and aromatic aldehydes (7).

Although there have been reports in the literature for many years on oxo complexes of pentavalent manganese (110-112), and at least one worker attempted to use the results of this early work to prove the existence of pentavalent manganese as the intermediate in the oxidation of formate ion by permanganate (38; see page 11), only recently have well-defined methods been established for the preparation and proof of the structure of these compounds. The definitive work was done by Lux (113). He found that the action of manganese dioxide and sodium oxide on a sodium nitrite melt caused the formation of an intense blue colour. The hydrate, $Na_3MnO_4 \cdot 10\ H_2O$, crystallized from concentrated sodium hydroxide in the form of light blue prisms. These dissolved readily in concentrated potassium hydroxide but not in concentrated sodium hydroxide. The formation of mixed crystals with sodium phosphate, arsenate and vanadate was observed. When water was added to the solid material, the deep green manganate appeared at once, and at the same time manganese dioxide precipitated. A similar result was obtained on treatment of the solid with dilute sodium hydroxide or ammonium hydroxide, or on dilution or heating of the deep blue potassium hydroxide solution. Dilution of the potassium hydroxide solution gave a clear, light green solution from which manganese dioxide was quickly precipitated. Colorimetric determination of manganese showed that the ratio MnO_4^{-2}/MnO_2 was 0.95. Lux concluded, therefore, that in strongly alkaline media, and in the cold, pentavalent manganese was as stable as manganate or manganite and that, in fact, the equilibrium,

$$Na_2MnO_4 + MnO_2 + 4\,NaOH = 2\,Na_3MnO_4 + 2\,H_2O\,,$$

was entirely on the right hand side. That equilibrium does exist was demonstrated by mixing freshly precipitated manganese dioxide with manganate in 10 N sodium hydroxide at 0°. The blue hydrate of pentavalent manganese was quickly precipitated.

Further work has now established that alkali metal complexes containing the $MnO_4^{=3}$ anion can be prepared in a variety of ways (114-116): (a) reduction of an alkaline permanganate solution with iodide ion; (b) oxidation of a manganese (II) compound by means of potassium nitrate in an alkaline melt; (c) atmospheric oxidation of manganese dioxide in an alkaline melt; (d) reaction between permanganate ion and metal hydroxide, either in aqueous solution or in the anhydrous state at high temperatures; and (e) the interaction, at elevated temperatures, between a manganate compound and the appropriate metal hydroxide.

The anhydrous M_3MnO_4 compounds are dark, blue-green substances, soluble in concentrated alkali. Hydrated hypomanganate salts are recovered from these solutions. Anhydrous potassium hypomanganate, K_3MnO_4, is stable in an oxygen atmosphere to about 1000°.

Magnetochemical studies by Klemm (117) have shown that the compound $Na_3MnO_4 \cdot 10\ H_2O$ prepared by Lux (113) does in fact contain Mn(V) rather than an equimolecular mixture of Mn(IV) and Mn(VI). Miller and Rogers (118) have produced polarographic evidence for pentavalent manganese. A solution containing 1×10^{-3} M potassium permanganate and 0.01 M sodium hydroxide was examined. Three separate half-wave potentials could be detected, with the diffusion current of each corresponding to a one-electron change. The reaction was considered to be $Mn(VII) \rightarrow Mn(VI) \rightarrow Mn(V) \rightarrow Mn(IV)$.

Carrington and Symons have measured the electrode potential of the manganate-permanganate couple in aqueous alkaline solution at various ionic strengths, and that of the manganate-hypomanganate couple in concentrated potassium hydroxide solution. Their results, together with other pertinent data on the electrode potentials of the valence states of manganese (80) are shown in Table IV. The manganate-permanganate E_o was obtained by extrapolation of the data of Carrington and Symons to zero ionic strength, while the value for the manganate-hypomanganate couple is for ionic strengths between 6 and 12.

According to Latimer (80), the standard E_o potential refers to systems at 25° in which all gases are at unit fugacity and all dissolved substances are at unit activity. If the redox reaction,

$$A = B + mH^+ + ne,$$

has a potential E_o against the standard platinum-hydrogen electrode, the potential, E , effective under other conditions, is

$$(26)\ldots \qquad E = E_o - RT/nF \ln [B][H^+]^m / [A].$$

TABLE IV

Oxidation Potentials of Manganese Couples (80)

Couple	E_o (acid)	Couple	E_o (alkali)
$Mn - Mn^{+2}$	1.18 V	$Mn - Mn(OH)_2$	1.55 V
$Mn^{+2} - Mn^{+3}$	1.51	$Mn(OH)_2 - Mn(OH)_3$	- o.1
$Mn^{+3} - MnO_2$	- 0.95	$Mn(OH)_3 - MnO_2$	0.2
$Mn^{+2} - MnO_2$	- 1.23	$Mn(OH)_2 - MnO_2$	0.05
$Mn^{+2} - MnO_4^-$	- 1.51	$MnO_2 - MnO_4^{-1}$	- 0.588
$MnO_2 - MnO_4^-$	- 1.695	$MnO_2 - MnO_4^{-2}$	- 0.60
$MnO_2 - MnO_4^{-2}$	- 2.26	$MnO_2 - MnO_4^{-3}$	- 0.915
$MnO_2 - MnO_4^{-3}$	- 4.19	$MnO_4^{-3} - MnO_4^{-2}$	- 0.285
		$MnO_4^{-3} - MnO_4^{-1}$	- 0.43
		$MnO_4^{-2} - MnO_4^{-1}$	- 0.558

E_o is by convention a negative quantity for oxidants more powerful than hydrogen ion; R is the gas constant, T the absolute temperature and nF represents the Faradays of electricity involved when the reaction is carried out electrochemically. In a system containing an oxidized form and a reduced form, where no hydrogen ions are transferred, the familiar equation,

(27)... $$E = E_o - RT/nF \ln [\text{oxidized form}] / [\text{reduced form}] ,$$

is used.

The free energy change of a redox reaction is related to the electrochemical potential E_o by the equation,

$$(28)\ldots \qquad \underset{\text{(calories)}}{-\Delta F^o} = E_o \cdot n \cdot 23060 \, ,$$

where n is the number of electrons transferred.

The numbers shown in Table IV for the $MnO_2 - MnO_4^{-3}$ and $MnO_2 - MnO_4^{-2}$ couples were calculated using equation 28 and the hypothetical equilibria,

$$MnO_2 + 2\,H_2O \rightleftharpoons MnO_4^{-3} + 4\,H^+ + e$$

$$MnO_2 + 2\,H_2O \rightleftharpoons MnO_4^{-2} + 4\,H^+ + 2\,e$$

$$MnO_2 + 4\,OH^- \rightleftharpoons MnO_4^{-3} + 2\,H_2O + e$$

$$MnO_2 + 4\,OH^- \rightleftharpoons MnO_4^{-2} + 2\,H_2O + 2\,e \, ,$$

and the value - 111.1 Kcal. for the free energy of formation of manganese dioxide (80). The values calculated in this way suggest that manganate and hypomanganate should be extremely powerful oxidizing agents in acid medium. The consequences of this will be seen later on.

Carrington and Symons have used their values for the hypomanganate-manganate and manganate-permanganate couples to estimate the thermodynamic functions for the manganese oxyanions (52). These are reproduced in Table V. The S^o values which they obtained using Connick and Powell's formula (119) have been altered in this table to agree with the more recent work of Couture and Laidler (120).

TABLE V

Estimated Thermodynamic Data for Manganese Oxyanions

	ΔF^o (kcal.)	ΔH^o (kcal.)	S^o (cal./deg.)
MnO_4^- aq.	- 107.4	- 129.7	50.9
MnO_4^{-2} aq.	- 120.3	- 160.5	13.1
MnO_4^{-3} aq.	- 127.0*	- 185.8	- 28.1

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* Refers to MnO_4^{-3} in concentrated potassium hydroxide solution.

The action of hypomanganate on organic compounds has received little attention; this is not difficult to understand since the compound is stable only in cold 10 N alkali. Few organic compounds are sufficiently soluble under these conditions to enable useful information to be drawn from these experiments. Pode and Waters (108) and Wolfe (88) have reported that hypomanganate, unlike manganate and permanganate, does not attack olefins. This observation has some bearing on the mechanisms of the manganate and permanganate oxidation of olefins.

II. EXPERIMENTAL

Unless otherwise mentioned, all chemicals were highest purity reagent grade, and were used without further purification. Oleic acid was purchased from the Hormel Institute and was maintained at 0° in a sealed glass vial when not in use. Melting points were obtained with the Leitz hot stage apparatus, and are uncorrected. Spectra in the visible and ultraviolet regions were obtained with a Beckmann DK - 2 recording spectrophotometer. Infrared spectra were obtained with a Perkin-Elmer single beam double pass instrument. Volumetric solutions were prepared and standardized by conventional means.

1. Inorganic Preparations

A. Preparation of Hypomanganate with an Inorganic Reductant (113)

A mixture containing ten grams (0.0635 mole) of powdered potassium permanganate and 200 ml. of 10 N sodium hydroxide was stirred at room temperature for one hour, cooled to 0°, and 8.00 g. (0.0635 mole) of powdered anhydrous sodium sulphite was added all at once. The resulting viscous solution became greenish-coloured after about two minutes, and this colour did not change during one hour. The reaction mixture was left at -10° for 24 hours, and the precipitate was gathered on a fritted glass funnel. The blue prisms thus obtained were contaminated with some white material. The filtrate (I) was returned to the freezer, and the solid precipitate was washed on the filter with 300 ml. of 10 N sodium hydroxide. These aquamarine washings (II) were also left in the freezer. The residual material on the filter was slurried with 150 ml. of 10 N sodium hydroxide, and this mixture (III) was left at room temperature for one day and was then cooled to -10°.

Filtrate I yielded no crystalline deposit after two days at -10°. However, filtrates II and III yielded a light blue substance which crystallized in the form of needles. The material was air-dried, and was then dissolved in 450 ml. of 10 N sodium hydroxide. The blue solution of pentavalent manganese (analysis below) could be stored in the cold for several days without decomposition.

When the blue solution was allowed to stand at room temperature, decomposition to manganate and manganese dioxide generally occurred within one day. A similar decomposition occurred within two hours when the solid was kept in a vacuum desiccator. Hence, all work with hypomanganate was carried out with solutions in 10 N sodium hydroxide.

B. The Preparation of Potassium Manganate (102)

Potassium hydroxide, 50 g., was dissolved in 50 ml. of water, and 50 g. of powdered potassium permanganate was added slowly while the mixture was stirred and heated to 130-140°. Evolution of oxygen ceased after 15 minutes, and the dark green mixture was maintained at this temperature for 30 minutes more, with addition of a little water from time to time to keep the volume approximately constant. After cooling, 10 ml. of 12 N potassium hydroxide were added. The precipitate was collected and air-dried to a black solid.

When potassium manganate was desired for reactions, a small amount of the solid was dissolved in alkali of the desired strength and, after filtration to remove traces of manganese dioxide, the solution was standardized iodometrically (mM of manganate = mE/4).

C. Iodometric Analysis of Hypomanganate and Manganate Solutions

Hypomanganate should disproportionate in acid solution according to the equation, (29)... $3\,MnO_4^{-3} + 4\,H_2O \longrightarrow 2\,MnO_2 + MnO_4^{-} + 8\,OH^{-}$.

In terms of iodometric analysis involving reduction of manganese to the manganous level, this equation shows that hypomanganate (9valence units) yields manganese dioxide (4 valence units) and permanganate (5 valence units). If X is the number of ml. of thiosulphate solution required in the titration of Y ml. of hypomanganate solution, then, when Y ml. of hypomanganate solution is allowed to disproportionate in acid medium, the permanganate formed will require 5X/9 ml., and the manganese dioxide will require 4X/9 ml. of the thiosulphate solution.

Manganate disproportionates to manganese dioxide and permanganate in acid medium according to the equation,

(30)... $3\,MnO_4^{-2} + 2\,H_2O \longrightarrow 2\,MnO_4^{-} + MnO_2 + 4\,OH^{-}$.

If X ml. of manganate solution are equivalent to Y ml. of thiosulphate solution, then X ml. of manganate will yield, on disproportionation in acid medium, permanganate equivalent to 0.83 Y ml. of thiosulphate solution, and manganese dioxide equivalent to 0.17 Y ml. of thiosulphate solution.

To perform the analyses, 5 - ml. aliquots of the manganate or hypomanganate solution were added to acidified potassium iodide solution, and the iodine liberated was titrated with 0.008 N thiosulphate solution. Five ml. aliquots of the manganate or hypomanganate solution were then added to solutions containing 25 ml. of 2.5 N sulphuric acid. The resulting pink mixtures were centrifuged for 30 minutes, to help settle the manganese dioxide, which was collected on a fritted glass funnel. The amounts of permanganate in the filtrate and manganese dioxide on the filter were determined iodometrically. The results, shown in Table VI, were in rough agreement with expectation, based on equations 29 and 30.

TABLE VI

Iodometric Analysis of Manganate and Hypomanganate

Titer of MnO_4^- in the Filtrate	Titer of MnO_2 on the Filter	MnO_4^- Titer/ MnO_2 Titer
(a) Analysis of hypomanganate; total titration, 3.71 ml.; calculated MnO_4^- Titer/MnO_2 Titer, 1.25.		
2.00	1.70	1.18
2.05	1.45	1.41
1.80	1.85	0.97
Average,		1.19 ± .15 (13%)
(b) Analysis of manganate; total titration, 3.90 ml.; calculated MnO_4^- Titer/MnO_2 Titer, 5.00		
3.00	0.71	4.22
3.10	0.68	4.56
2.94	0.67	4.40
3.02	0.63	4.79
Average,		4.50 ± .18 (4%)

D. The Oxidation of Hypomanganate with Sodium meta-Periodate

Sodium meta-periodate, 2.0 g. (0.0094 mole), was dissolved in water, and the solution was made up to 100 ml. (approximately 0.094 mM/ml.). To 10 ml. of this solution and varying amounts of sulphuric acid was added rapidly 1 ml. of a 10 N alkaline solution containing 0.008 mM of hypomanganate per ml. The resulting pH was noted, along with any colour change during the reaction. The results are shown in Table VII.

A colour similar to that obtained as an intermediate in the periodate oxidation of hypomanganate in strongly alkaline medium was obtained by mixing manganate and permanganate in equal amounts; the same colour had a transient existence in permanganate oxidations in alkaline medium where permanganate was reduced to manganate.

E. The Oxidation of Hypomanganate with Permanganate

Five ml. (0.04 mM) of a hypomanganate solution, dissolved in 10 N alkali, were syringed into 125 ml. of water. The blue colour rapidly turned green, and a precipitate of manganese dioxide appeared. In a second experiment, 5 ml. of the hypomanganate solution were syringed into 125 ml. of water containing 0.04 mM of permanganate. The colour became green at

TABLE VII

Effect of pH on the Oxidation of Hypomanganate by Periodate

Ml. of 6 N Sulphuric Acid Added to 10 ml. of 0.094 M Periodate*	Final pH	Observations
0	14	The mixture became a very dark bluish-purple, and slowly (10 seconds) turned the colour of permanganate (spectrum). There was no precipitate.
1.6	14	The mixture was initially a slightly lighter bluish colour than the above, and then turned the colour of permanganate. No precipitate was formed.
1.8	13.5	Permanganate was obtained at once. There was no precipitate.
2.0**	6.85	Permanganate was obtained at once. There was no precipitate of manganese dioxide during one week.

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* Hypomanganate, 1 ml. of 0.008 M, was syringed into this solution.

** Ten ml. of ammonium acetate buffer were also added.

once, and there was no precipitate of manganese dioxide during one hour. Similar experiments at higher alkalinity produced the same results. At lower pH values (12–14), some manganese dioxide was obtained from the addition of hypomanganate to permanganate. The results obtained at the low pH are only qualitative, owing to the difficulties involved in adjusting the pH of the reaction mixture to the region 12–14. Buffer solutions could not be used, for when hypomanganate was added to buffered permanganate, no manganate was observed, and only permanganate and manganese dioxide were formed. To achieve these lower pH values, therefore, the hypomanganate, 5 ml. in 10 N alkali, was added to permanganate dissolved in a large volume (250–1000 ml.) of water.

F. The Attempted Oxidation of Hypomanganate by Molecular Oxygen

Hypomanganate, 0.04 mM, was dissolved in 75 ml. of 10 N alkali, and pure, dry oxygen was bubbled into this solution at 25°. The only reaction observed during 24 hours was the disproportionation of hypomanganate to manganate and manganese dioxide. Hence, this oxidation reaction is negligible.

G. The Preparation of Hypomanganate with Organic Reductants

(i) From Permanganate. A solution of 10.0 g. (0.063 mole) of potassium permanganate in 200 ml. of 10 N sodium hydroxide was cooled to 0°, stirred, and 4.28 ml. (3.66 g.; 0.063 mole) of allyl alcohol were added all at once. The mixture became clear green immediately, and after a few more seconds, a heavy precipitate appeared. After 40 minutes, the reaction mixture was filtered through sintered glass to yield blue needle-like crystals of hypomanganate, and a reddish-brown filtrate containing hydrated tetravalent manganese. A small amount of the blue material was recrystallized twice from 10 N sodium hydroxide, and the final sky-blue solution was analyzed for hypomanganate as described in Table VI. The observed MnO_4^- Titer/MnO_2 Titer was 1.2.

In a second experiment, the reaction mixture was filtered after one minute, and it was observed that there had been no precipitation of manganese dioxide during this time, although the filtrate was a deep reddish-brown in colour. The blue solid was washed with 100 ml. of 10 N sodium hydroxide and was then added to 500 ml. of 4 N sulphuric acid. This mixture was allowed to stand overnight. At this time, the manganese dioxide was filtered off; the filtrate contained 13.3 mM of permanganate, determined iodometrically. The precipitate of manganese dioxide was dissolved in acidified potassium iodide; titration of the resulting iodine solution indicated that 23.4 mM of manganese dioxide had been formed when the solid was caused to disproportionate. This established that the blue material was hypomanganate; calcd. for MnO_4^{-3}, mM of MnO_2/ mM of MnO_4^- $=$ 2; calcd. for MnO_4^{-2}, mM of MnO_2/mM of MnO_4^- $=$ 0.5. Found, mM of MnO_2/mM of MnO_4^- $=$ 1.76.

The tetravalent manganese formed in the initial reaction precipitated on standing and was gathered by filtration. The manganese dioxide was reduced to the manganous level with hot sodium bisulphite, and an aliquot of the resulting colourless solution was oxidized to permanganate with acid periodate. Colorimetric determination of this permanganate indicated that the yield of tetravalent manganese from the initial reduction of permanganate by allyl alcohol had been 42%.

(ii) From Manganate. To a solution of 0.063 mole of manganate (concentration determined iodometrically) in 200 ml. of 10 N sodium hydroxide, cooled to 0°, was added with stirring 4.28 ml. (0.063 mole) of allyl alcohol. The mixture was filtered after 45 seconds to yield hypomanganate , and manganese dioxide in the filtrate. The filtrate was diluted with 50 ml. of water, and 5.0 g. of sodium bisulphite were added to hasten precipitation of the manganese dioxide. This was then filtered and estimated colorimetrically as permanganate; yield, 35.2%.

The hypomanganate was reduced to manganese dioxide by addition to 500 ml. of N hydrochloric acid. This precipitate contained 42 mM of manganese dioxide. Hence, the yield of hypomanganate was 42/63, or 64%.

(iii) Using Various Olefins and Permanganate. Permanganate, 0.4 ml. of a 0.02 M solution, was added continuously over a 20 minute period to a solution or suspension of 0.5 mM of an olefin in 50 ml. of 10 N alkali at 0°. The reaction mixture was stirred during the addition of the permanganate. When the addition of permanganate was complete, the spectrum of the resulting system was read on the Beckmann DK - 2 recording spectrophotometer for comparison with the spectrum of hypomanganate (see Fig. 1). The results obtained from these experiments using several olefins are shown in Table VIII.

(iv) Using Various Olefins and Manganate. When the above series of experiments was repeated with 0.4 ml. of a 0.02 M solution of manganate in 10 N sodium hydroxide and the olefins allyl alcohol and cis-4-cyclohexenedioic acid, hypomanganate was again obtained from a slow addition of the oxidizing agent at both 0° and 25°. When the manganate was added rapidly, the initial colour was green, but the reaction mixture slowly took on the colour of hypomanganate.

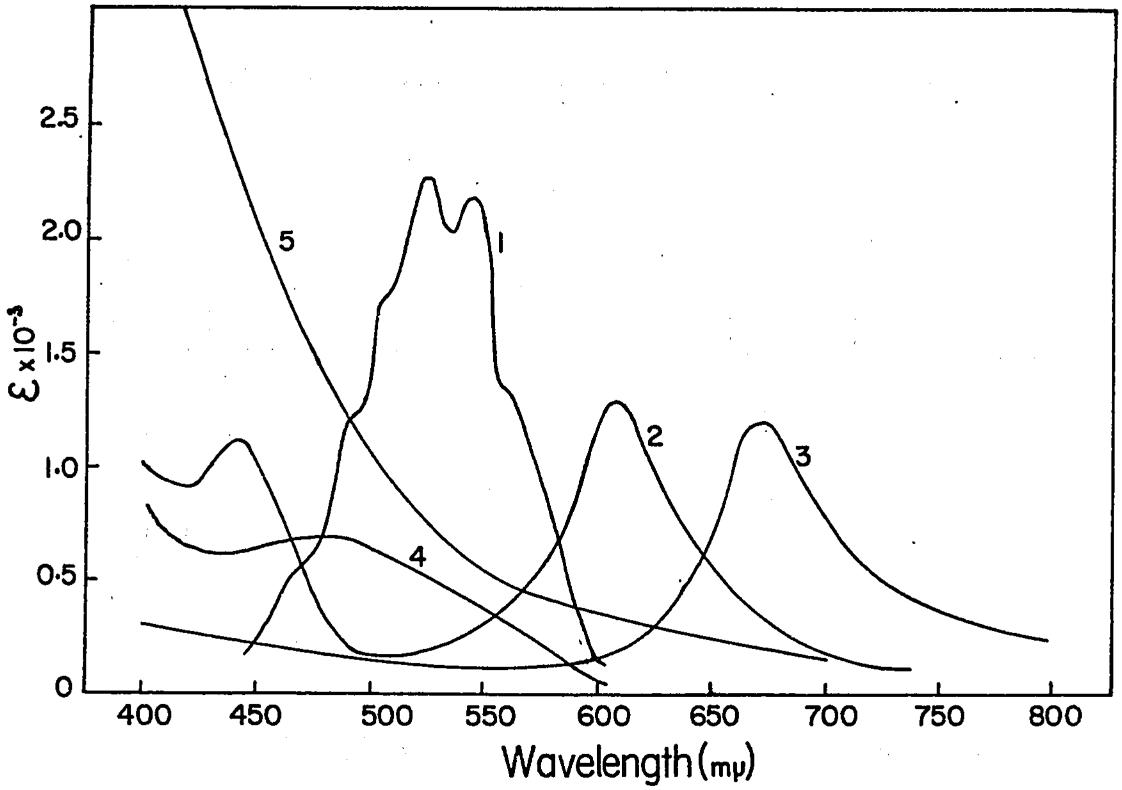

Fig. 1 - Spectra of the valence states of manganese.
Plot 1, permanganate in aqueous solution. Plot 2, manganate in 10 N sodium hydroxide. Plot 3, hypomanganate in 10 N sodium hydroxide. Plot 4, manganite-tellurate complex in 3 N alkali. Plot 5, colloidal manganese dioxide at pH 8.

TABLE VIII

Addition of 0.4 Ml. of 0.02 M Permanganate to Various Olefins

Olefin (0.5 mM in 50 ml. of 10 N alkali)	λ max. (mμ)	Conc. of MnO_4^{-3} ($M \times 10^5$)	Yield (%)
allyl alcohol	675	7.9	50
cis-4-cyclohexene-dioic acid	675	9.0	57
sorbic acid	675	12.5	78

(v) Using Added Tellurate or Barium Ions. Experiments in which solutions of manganate (0.4 ml. of 0.02 M) or permanganate (0.4 ml. of 0.02 M) in N sodium hydroxide were added slowly to a 10 N alkaline solution containing an olefin (0.5 mM) and tellurate ion (0.5 mM) also failed to give a difference in the colour of the final mixture, both oxidizing agents being reduced to hypomanganate. However, the addition of telluric acid to the reaction mixtures caused them to remain homogeneous when the hypomanganate was allowed to disproportionate to tetravalent manganese and manganate. When no telluric acid was added to the reaction mixtures, manganese dioxide precipitated from these reaction mixtures after one day at room temperature.

Thus, as Issa and co-workers have shown (121-124), telluric acid may be a useful reagent for achieving homogeneity in these reaction mixtures. The complexing action between the tellurate and manganite ions evidently is not strong enough to prevent a reaction between manganite and manganate to form hypomanganate.

The slow addition of 0.4 ml. of 0.02 M solutions of either manganate or permanganate in N alkali to a solution containing 0.5 mM of cis-4-cyclohexenedioic acid and 1.0 mM of barium nitrate in 50 ml. of ice-cold 10 N sodium hydroxide yielded hypomanganate in each case.

2. Organic Preparations

A. The Reaction of Permanganate with cis-4-Cyclohexenedioic Acid

A solution of potassium permanganate, 7.9 g. (50 mM), in 350 ml. of 0.2 N potassium hydroxide was added all at once to a solution of 4.25 g. (25 mM) of cis-4-cyclohexenedioic acid dissolved in 250 ml. of 0.2 N potassium hydroxide. After two minutes, 200 ml. of a 0.4 M potassium sulphite solution were added, and the resulting manganese dioxide was then separated by filtration and thoroughly washed with hot water.

The filtrate was concentrated to 150 ml.; 22 ml. of 6 N sulphuric acid were then added and the slightly acid solution was evaporated to dryness. The residue was extracted twice with 200 ml. of boiling ethyl alcohol and the extract was evaporated to dryness. The solid residue was extracted with 150 ml. of ethanol and, after filtration, was evaporated to dryness. The procedure was continued until the solid residue was soluble in 80 ml. of boiling ethanol. This solution, on standing overnight at room temperature, deposited long needle-like crystals, 0.05 g., m.p. 122.8-123.5°.

The mother liquor from this crystallization was concentrated to 20 ml. and, after standing several hours at -10°, yielded a total of 1.67 g. (36%) of material which, after recrystallization from water gave 1.58 g. of massive crystals, m.p. 233-235°. Calcd. for $C_8H_{12}O_6$: neutral equivalent, 102. Found: neutral equivalent, 101.

In a second experiment, a 38% yield of this compound was obtained, along with 1.00 g. (24%) of recovered cyclohexenedioic acid.

Treatment of this 4,5-dihydroxy-1,2-cyclohexanedioic acid, 204.2 mg. (1 mM), with excess 0.05 M periodate, resulted in the consumption of 2.09 milliequivalents of oxidant. Calculated for $C_6H_8(COOH)_2(OH)_2$ with the hydroxyl groups free, 2.0.

B. The Reaction of Manganate with cis-4-Cyclohexenedioic Acid

A solution of 5.79 g. (34 mM) of cis-4-cyclohexenedioic acid was dissolved in 100 ml. of 0.2 N potassium hydroxide, and to this solution at 25° was added a solution of 67.9 mM (by titration) of potassium manganate in 275 ml. of 0.2 N potassium hydroxide. The reaction mixture was stirred for 15 minutes, filtered, and the manganese dioxide washed with 1000 ml. of hot water. The reddish-brown filtrate was concentrated to 50 ml., 35 ml. of 6 N sulphuric acid were added, and the resulting pale yellow acid solution was evaporated to dryness. The residue was triturated with 200 ml. of water, and the insoluble material (0.85 g., m.p. 230-235°), after recrystallization from ethyl alcohol, gave 0.58 g. of long needle-like crystals, m.p. 232-234°, neutral equivalent, 105. A mixture melting point with the compound prepared by permanganate oxidation of cis-4-cyclohexenedioic acid was not depressed.

The aqueous filtrate from the trituration was evaporated to dryness and the residue extracted with 500 ml. of boiling ethanol. Norit was added and, after clarification, the pale yellow solution was concentrated to 10 ml., and 50 ml. of benzene were added. The resulting white crystalline deposit was recrystallized from water to give 1.51 g. of plates, m.p. 225-226°, identical with the first product. The total yield was 34%. The residual mother liquors were oily, and chromatography on alumina failed to yield any further product.

C. The Oxidation of cis-4-Cyclohexenedioic Acid by Neutral Permanganate

A solution of 8.5 g. (50 mM) of cyclohexenedioic acid and 6.9 g. (50 mM) of potassium carbonate was diluted to 1000 ml. with water, cooled to 10°, and a solution of potassium permanganate, 15.8 g. (100 mM), in 500 ml. of water was added all at once. The reaction mixture was stirred for two minutes, and excess oxidizing agent was then precipitated by addition of 200 ml. of 3% hydrogen peroxide solution. The manganese dioxide was filtered with the aid of Celite, and the filtrate was concentrated to a yellowish-brown syrup. Extraction of the syrup with hot acetone or ethanol failed to yield any material. The syrup gave a positive test with 2,4-dinitrophenylhydrazine reagent. A portion of the syrup was heated on the Leitz melting point apparatus; at 130°, the material appeared to evolve water and appeared to polymerize to an amorphous solid.

The main portion of the syrup was then passed through Amberlite-IRC - 50 - H cation exchange resin and the column was eluted with 1000 ml.

of water. The eluate was degassed by sweeping with nitrogen, and was then concentrated to a clear brown syrup. This was dried by azeotropic distillation of the water with benzene and ethanol to yield a yellow amorphous resin, m.p. $>$ 250°.

D. The Oxidation of Oleic Acid

(i) By Permanganate in Alkaline Solution. Oleic acid, 282.4 mg. (1 mM), and potassium hydroxide, 56 mg. (1 mM), were dissolved in water, and the solution was diluted to 250 ml., cooled to 0° by the addition of ice, and the pH was adjusted to 12 by the addition of solid potassium hydroxide. A solution of potassium permanganate, 316 mg. (2 mM), in 50 ml. of ice-cold water was added all at once and, after two minutes, the green reaction mixture was decolorized by the addition of 5 g. of sodium sulphite and 10 ml. of 6 N sulphuric acid. The precipitate was filtered, washed with water, air dried and weighed. The yield was 285 mg. (90%), m.p. 126-128°. For purification, the erythro-9,10-dihydroxystearic acid was dissolved in 1 ml. of ethyl alcohol, and the solution was diluted to 100 ml. with ether and cooled to -10°. One recrystallization raised the melting point to 132-134°. (Lit., m.p. 132-134° (2)).

(ii) By Manganate in Alkaline Medium. To a solution of 157.8 mg. (0.558 mM) of oleic acid in 250 ml. of 0.2 N potassium hydroxide was added a solution of 0.9 mM of potassium manganate in 15 ml. of 0.2 N potassium hydroxide. The green reaction mixture was stirred at 25° for 12 minutes, and 25 ml. of ethyl alcohol were then added to stop the reaction. The manganese dioxide was removed by filtration and the filtrate was acidified with 15 ml. of 6 N sulphuric acid. The resulting precipitate, on recrystallization from ethanol-water, was erythro-9,10-dihydroxystearic acid, m.p. 130-131°, undepressed on admixture with an authentic specimen melting at 132.5-134°. The yield was not determined due to some loss on working up the reaction.

In a second experiment, 291.4 mg. (1.04 mM), of oleic acid were dissolved in 250 ml. of 0.1 N potassium hydroxide. A solution of 1.0 g. (ca. 5.0 mM) of potassium manganate, dissolved in 50 ml. of 0.1 N potassium hydroxide , was added all at once, and the reaction mixture was left at room temperature for three hours, by which time precipitation of manganese dioxide was complete. Working up the reaction in the usual way gave 180 mg. (55%) of the 9,10-dihydroxystearic acid, m.p. 128-130°. The acid filtrate was treated as described on page 82 to determine the composition of the cleavage products of the reaction. These products are shown on page 262 .

(iii) With Periodate-Permanganate in Alkaline Medium. Oleic acid, 144.6 mg. (0.509 mM), was dissolved in 350 ml. of 0.01 N potassium hydroxide. This solution was stirred, and a solution of 39.5 mg. (0.25 mM) of potassium permanganate and 427.8 mg. (2.0 mM) of sodium metaperiodate in 100 ml. of water was added all at once. The pH of the resulting solution was 11.5. After stirring for 90 seconds, 15 ml. of 6 N sulphuric acid and 5 g. of sodium bisulphite were added. The white solid product was separated by filtration and air-dried. The yield was 133.1 mg., m.p. 56-65°. Two recrystallizations from 70% ethanol yielded a total of 106 mg. (70%) of the 9,10-ketohydroxystearic acids, m.p. 63.5-65°, undepressed on admixture with an authentic specimen (3).

(iv) By Excess Permanganate at Various pH. Oleic acid, 500 mg. (1.77 mM), was dissolved in 500 ml. of 0.001 N potassium hydroxide, and the pH was adjusted to 10.2. The solution was cooled to 5°, and an ice-cold solution of 1.106 g. (7.0 mM) of permanganate in 100 ml. of water was added all at once. The mixture was stirred for 90 seconds, and the reaction was then stopped by the addition of bisulphite and sulphuric acid. The white solid was collected and air-dried. Extraction of the material with 300 ml. of cold ether gave 487 mg. (87.5%) of the 9,10-ketohydroxystearic acids, identified by melting point and mixture melting point determinations and preparation of the semicarbazones (3). The ether-insoluble material was recrystallized from ethanol-ether to give 16 mg. (3%) of erythro-9,10-dihydroxystearic acid, m.p. 128-130°, which was identified by melting point and mixture melting point determinations.

An experiment conducted using the same conditions, except that the pH was 9.3, gave an 88% yield of the ketols and a 5% yield of the glycol.

(v) At Elevated Temperature. Four solutions were prepared, each containing 1 mM of oleic acid in 200 ml. of 0.001 N potassium hydroxide; two of these were adjusted to pH 9.6 and the other two were adjusted to pH 13 by the addition of small amounts of 6 N sulphuric acid or 12 N potassium hydroxide. The solutions were then heated either to 50° or to 100°, and solutions of 0.63 g. (4 mM) of permanganate in 100 ml. of water, heated to the same temperature (either 50° or 100°), were added all at once to each of the olefin solutions. The resulting reaction mixtures were maintained at the desired temperatures until the permanganate was completely reduced to the tetravalent stage. At pH 9.6 and 50°, some permanganate was still present after 12 hours, and the reaction was stopped at this time by the addition of acid and bisulphite. The relative rates of these oxidations are indicated by the data shown in Table IX.

TABLE IX

The Reaction of Permanganate (4 mM) with Oleate Ion (1 mM) at Elevated Temperatures

pH	Temp.	Time after Addition of Permanganate	Observations
13	52	1 min.	The reaction mixture contained manganate and permanganate.
		7 min.	The reaction mixture contained manganate, permanganate and precipitated manganese dioxide.
		24 min.	The reaction mixture contained only manganate and manganese dioxide.
		110 min.	The reaction mixture contained only manganese dioxide.
13	95-100	1 min.	The reaction mixture contained only manganate and manganese dioxide.
		4 min.	The reaction mixture contained only manganese dioxide.
9.6	50	12 hr.	The reddish-brown system was decolourized with bisulphite.
9.6	95-100	3 min.	The permanganate was completely reduced to colloidal manganese dioxide.

The oxidations at pH 13 resulted in the formation of precipitated manganese dioxide. The reaction mixtures were filtered with the aid of Celite, and the filter cakes were washed with 100 ml. of hot water. The filtrates were acidified and cooled. In the case of the oxidations at pH 9.6, colloidal manganese dioxide was formed and, since this material was difficult to remove by filtration, acid bisulphite was added to decolorize the reaction mixtures.

The precipitates were collected, washed with water, air-dried, and the composition determined by fractional crystallization of the glycol and ketol fractions from ethanol-ether. The aqueous filtrates were continuously extracted with ether for 24 hours, and the extracts, after drying over anhydrous sodium sulphate and treatment with ethereal diazomethane, were evaporated to dryness and weighed. The composition of the mixtures of methyl esters obtained in this way was determined by vapour phase chromatography on a Podbielniak instrument, the column being packed with 20% D.C. high vacuum silicone grease on Celite.*

The aqueous phases remaining after the ether extraction were concentrated to approximately 75 ml. and were tested for the presence of oxalic acid with resorcinol and concentrated sulphuric acid.

The results of the above analyses are given in Table XXXIII page 262 .

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* The author wishes to acknowledge the assistance of Mr. F. Cooper of the Division of Applied Biology, National Research Council, in carrying out these determinations.

(vi) At High Concentrations. Oleic acid, 565 mg. (2.01 mM) was dissolved in 30 ml. of 0.001 N potassium hydroxide, and the pH was adjusted to 9.6 by the addition of sulphuric acid. The solution was cooled to zero degrees, and an ice-cold solution of 4.74 g. (30 mM) of permanganate in 100 ml. of water was added all at once. The reaction was stopped after 60 seconds by the addition of 10 g. of sodium bisulphite and excess sulphuric acid. The insoluble material, 488 mg. (77%), was yellow-coloured, and melted at 80-100°. The solid was dissolved in 2 ml. of hot ethanol, and 250 ml. of ether were then added. This solution was cooled to -10° and deposited 153 mg. (24%) of pure erythro-9,10-dihydroxystearic acid, m.p. 130-132°. The ether filtrate was evaporated to dryness, and the yellow solid, m.p. 60-68°, was separated into the 9,10-ketohydroxystearic acids and 9,10-diketostearic acid in the following way. The solid was dissolved in 5 ml. of hot ethanol, and water was added dropwise to the first sign of turbidity. The solution was then cooled at 0° to give a product, m.p. 65-85°, which was rich in the diketo compound. The filtrate was diluted with water and was filtered to yield material, m.p. 55-60°, rich in the ketohydroxy compounds. Each solid fraction was treated again in the same way until pure 9,10-diketostearic acid, m.p. 82-84°, 140 mg. (22%) and 9,10-ketohydroxystearic acid, m.p. 62-64°, 142 mg. (22%) were obtained.

The aqueous filtrate obtained after removal of the 488 mg. of of solid material was analyzed for cleavage products as described on page 82. The results are shown on page 262 .

Oxidations of 9,10-Dihydroxystearic Acid and the 9,10-Ketohydroxystearic Acids

The compounds, about 0.75 mM, in 0.001 N potassium hydroxide , 150 ml., were treated at pH 9.5 and 100° with a 4:1 molar excess of permanganate in 50 ml. of water. The ketols were also treated at room temperature at pH 13. The reaction mixtures were worked up as described on page 82, and the products of these oxidations which could be identified are reported in Table XXXIII, page 262 .

3. Kinetic Methods

A. Photometric Experiments

(i) Oxidation of Oleate Ion by Permanganate. The addition of telluric acid to alkaline mixtures containing permanganate or manganate and an organic reductant caused these mixtures to remain homogeneous due to the complexing action between tellurate ion and tetravalent manganese (see page 73; also references 121-124). When the concentration of permanganate was of the order of 3×10^{-4} M, the mixtures also remained homogeneous in the absence of telluric acid, but the colour of uncomplexed manganite was much more intense. This is seen by the data plotted in Fig. 2. Since, in the presence of tellurate ion, there was an appreciable change in the optical density during a run, and the system remained homogeneous, it seemed worthwhile to try to develop a photometric method of following the reaction, based on the addition of telluric acid to the reaction mixtures.

Oleic acid was the olefin used in most of the kinetic runs. A stock solution, 0.015 M in potassium oleate, was prepared from the oleic acid and, kept in a well-stoppered container, was shown to be stable for several weeks. The photometric data were obtained on a Coleman Junior Spectrophotometer at 525 mμ. The reaction of permanganate with the olefin was so fast that the mechanical manipulations prior to taking readings had to be kept to a minimum, and this instrument, while perhaps not as precise as might have been desired, helped in the fulfillment of this requirement.

The following procedure was used in carrying out a run. The desired amounts of olefin and telluric acid were pipetted into a 50 ml. beaker and the solution was diluted to about 45 ml., and was magnetically stirred while the pH was adjusted to the desired value by the addition of either potassium hydroxide or sulphuric acid, using a Beckmann glass electrode pH meter. The resulting solution was transferred to a 50 ml. volumetric flask, and the volume

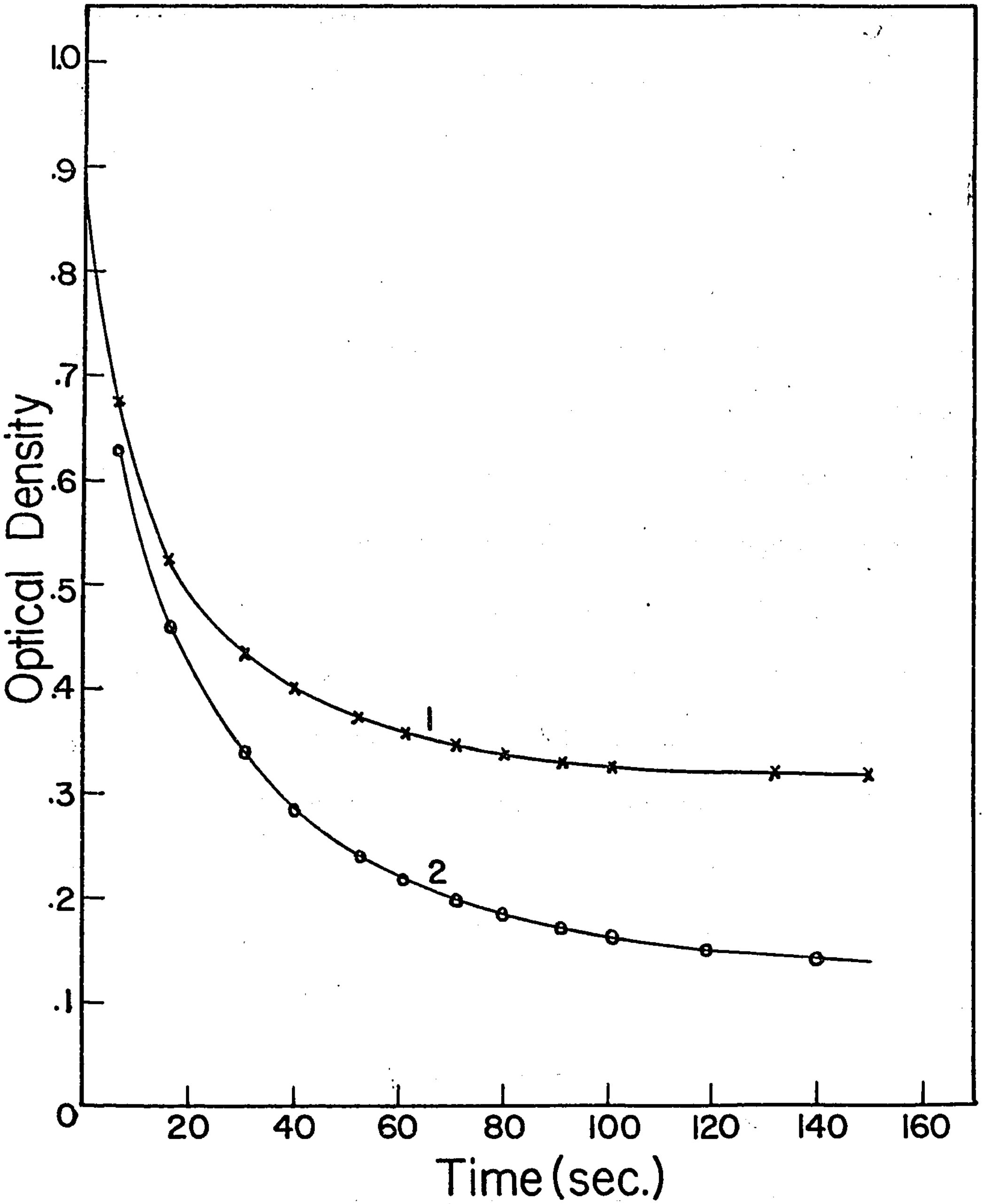


Fig. 2 - Effect of tellurate ions on the optical density of reaction mixtures containing permanganate (3×10^{-4}M) and oleate ion (3×10^{-4}M) at pH 9.5. Plot 1, no added tellurate ions; plot 2, tellurate concentration, 5×10^{-3}M.

was made up to a calibration at 48.5 ml. The flask was then stoppered and placed in a constant temperature bath controlled to ± 0.05° for at least one hour.

Rapid and reproducible introduction of the permanganate was possible using a 10 cc. syringe, fitted onto a metal holder, which could be adjusted so that the syringe delivered a known volume of solution. The reactions were started by rapidly syringing 1.500 ml. of the permanganate solution into the volumetric flask containing the olefin solution. Time readings were made with a "Time-it" electric timer, manufactured by the Precision Scientific Company, and the reaction was always started with the timer running. Addition of the permanganate required less than one-half second, and the force of the addition was generally sufficient to provide complete mixing of the two reactants. Nevertheless, the reaction flask was stoppered, rapidly shaken, and the solution was poured into a photometer tube for reading. Stabilized readings could be taken about six seconds after the photometer tube was placed in the spectrophotometer, and the initial handling usually required about 10 seconds. The first readings were, therefore, recorded twenty seconds after beginning the reaction.

Since the half-life of the reaction was generally between 20 and 30 seconds, this method enabled the reaction to be followed only from 40-100% of reaction. The experimental method was modified in the following way in order to obtain readings in the first part of the reaction. The desired amounts of olefin and telluric acid were placed in a 10 ml. beaker and the solution was diluted to about 8 ml. The pH was adjusted to the desired value and the solution was made up to volume in a 10 ml. volumetric flask. These volumes could be scaled upwards if desired. The solution was transferred to a burette, 8.50 ml. was added to a photometer tube and the tube was set in the temperature bath for 30 minutes. The tube was then removed, dried and inserted into the spectrophotometer, and the instrument was adjusted to zero. Then the permanganate (1.50 ml.) was syringed in as before, and readings were taken. The syringing provided complete mixing of the two solutions.

In the pH region 7-10.5, the only manganese species present in the reaction mixture were permanganate and the manganite-tellurate complex. Since the manganite-tellurate complex, the product of the oxidation reaction, had a finite absorption at 525 mμ, the expression,

$$(31)\ldots \qquad X = X_o (D_t - D_\infty)/(D_o - D_\infty) ,$$

was used to calculate the permanganate concentration, X , at any time, where D_t , D_∞ , and D_o were the optical densities at times t, infinity and zero, respectively. This expression is derived in the following manner.

Let X_o and X be the molar concentrations of permanganate at times zero and t, respectively, and X' the molar concentration of the manganite-tellurate complex at time t. Then,

(32)... $$X + X' = X_o .$$

Let E and E' be the extinction coefficients of permanganate and the manganite-tellurate complex at 525 mμ. Then, since Beer's Law could be shown to be valid for these solutions (see below), the optical densities (D) can be expressed in terms of the extinction coefficients (E) and concentrations (X),

$$D = EX .$$

The extinction coefficient for the permanganate can be expressed as,

$$E = D_o/X_o ,$$

while that (E') for the manganite-tellurate complex is related to the optical density of the solution (D_∞) when all the permanganate has disappeared,

$$E' = D_\infty/X_o .$$

It is assumed that the optical density (D_t) at any time t is the sum of the optical densities of permanganate and the manganite-tellurate complex.

Therefore,

$$\begin{aligned} D_t &= EX + E'X' \\ &= D_o X/X_o + D_\infty/C_o (X_o - X) \\ &= X/X_o (D_o - D_\infty) + D_\infty. \end{aligned}$$

When X_o, the initial concentration of permanganate, was greater than $4Y_o/3$, where Y_o is the initial concentration of oleate ion, this expression had to be modified for the presence of excess permanganate in the reaction mixture at the end of the reaction. To calculate the concentration of permanganate under these conditions, the expression,

(33)... $$X = X_o - (4Y_o/3)(D_o - D_t)/(D_o - D_\infty),$$

was employed. This may be derived as follows, where the symbols have the same meaning as in equation 31,

(34)... $$D_\infty = 4Y_oE'/3 + E(X_o - 4Y_o/3)$$

$$\begin{aligned} E' &= 3/4Y_o\ (D_\infty - D_o + 4D_oY_o/3X_o) \\ &= D_o/X_o + 3/4Y_o\ (D_o - D_\infty). \end{aligned}$$

$$\begin{aligned} D_t &= EX + E'X' \\ &= D_oX/X_o + (D_\infty - D_o)(X_o - X)(3/4Y_o) + D_o(X_o - X)/ \end{aligned}$$

(35)... $$= D_o + 3/4Y_o\ (D_\infty - D_o)(X_o - X).$$

At pH values higher than 12, manganate was also a product of the reaction. Under these reaction conditions, the concentrations of permanganate, manganate and the manganite-tellurate complex could be determined by following the reaction at both 525 $m\mu$ and 600 $m\mu$. In the concentration range studied (1-5×10^{-4} M), Beer's Law was obeyed by all three of these manganese species. The extinction coefficients of permanganate, manganate and the manganite-tellurate complex were determined at 525 mμ, and at 600 mμ, and these values are shown in Table X. The extinction coefficients of the manganite-tellurate complex were determined by adding a known amount of manganate or permanganate to excess oleate ion, and allowing the reaction to run to completion; the optical density was then read at both wavelengths.

TABLE X

Extinction Coefficients

Species	Extinction Coefficient 525 mμ	 600 mμ
permanganate	2940	535
manganate	747	2160
manganite-tellurate	498	127

The concentrations of each of these three species at a given time t could then be calculated by solving the following equations,

(36)... $$X + X'' + X' = X_o$$

(37)... $$E \cdot X + E''X'' + E'X' = D_t$$

(38)... $$E_1X + E_1''X'' + E_1'X' = D_{t_1} ,$$

where X , X'' , and X' are the concentrations of permanganate, manganate and the manganite-tellurate complex, respectively. These species have extinction coefficients E , E'' and E' at 525 mμ and E_1 , E_1'' and E_1' at 600 mμ ; D_t and D_{t1} are the optical densities at time t read at 525 mμ and at 600 mμ , respectively.

(ii) Oxidations by Manganate. For kinetic runs with manganate, potassium manganate was dissolved in N potassium hydroxide solution, and the concentration of this solution was adjusted until the syringe (set at 1.50 ml.) delivered the desired amount of oxidant. Otherwise the technique was the same.

(iii) Disproportionation of Hypomanganate to Manganate and Manganite. The rate of the disproportionation of hypomanganate was followed at 670 mμ, using tellurate ion to solubilize the products of this reaction. The reactions were conducted at 0°, using a 5×10^{-3} M solution of hypomanganate in 10 N sodium hydroxide. To start the reaction, 2 ml. of this solution were diluted to 10 ml. with a solution containing 0.25 mM of tellurate ion and sodium hydroxide of known concentration. The resulting mixture was transferred to a photometer tube and the optical density was read.

B. Titrimetric Experiments

The high rate of the reaction of permanganate with olefins, and the fact that manganese dioxide was often precipitated from the reaction mixtures precluded the use of the usual chemical means for following the reaction. Therefore, a quenching method was used in this work. In a typical experiment, 6 ml. of 0.015 M potassium oleate solution were pipetted into a 400 ml. beaker and, after the pH was adjusted to the desired value, the solution was diluted to 291 ml. and was set in the temperature bath for equilibration to the desired temperature. Aliquots (48.5 ml.) of this solution were then removed to 125 ml. erlenmeyer flasks, and each of these aliquots in turn was allowed to react with permanganate. The solutions were stirred magnetically and, with the timer running, the desired amount of permanganate (1.50 ml.) was syringed into this stirred solution. To stop the reaction, an excess of acidified potassium iodide solution was poured into the reaction flask. The iodine thus liberated was titrated immediately, using a micro syringe pipette manufactured by Burrell Corporation and N thiosulphate solution. The concentrations for the titrimetric experiments were the same as those used in the photometric work, and experiments were conducted in the presence and absence of telluric acid. End points in the presence of telluric acid were not sharp, but were reproducible. The results of these experiments, using this quenching technique, were also reproducible to within about 2%. It was estimated that the addition of the permanganate and the mixing of the two reactants required less than half a second, and the quenching of the reaction required about the same length of time.

The results were plotted (Figs. 14 - 16) as equivalents of oxidant consumed per mole of olefin against time in seconds. In the pH range where permanganate and manganite were the only manganese species present, the concentration of permanganate could be calculated from the following expression (equation 39).

If the titrations at times zero, t and infinity are V_o , V_t and V_∞, respectively, and N/50 represents the normality of the thiosulphate solution divided by the volume of the reaction mixture, then

$$X_o = NV_o/5 \times 50$$
$$X' = N/50\ (V_o - V_t)/3 ,$$

where X_o and X' are the initial concentration of permanganate and the concentration of tetravalent manganese at time t, respectively. The concentration of permanganate, X , at time t is given by

$$\begin{aligned} X &= X_o - X' \\ &= (V_o/5 - V_o/3 + V_t/3)(N/50) \\ &= N/3 \times 50\ (V_t - 2V_o/5) . \end{aligned} \quad (39)...$$

This equation was used by Wiberg and Stewart (7) in their study of the oxidation of aromatic aldehydes by permanganate.

When manganate was used as the oxidizing agent, the concentration , Z , of this species, derived in the same way, was given by the equation,

$$(40)\ldots \qquad Z = N/50\,(2V_t - V_o)/4 \,.$$

4. The Oxidation of Ethylene and 1,1-Dideuteroethylene

A. Apparatus

An apparatus was desired in which the oxidation of small amounts of gas by an aqueous solution of periodate-permanganate could be studied. The vacuum line shown in Fig. 3 was constructed for this purpose. The ethylene used in these experiments was reagent grade material supplied by the Matheson Company in a lecture bottle. The 1,1-dideuteroethylene (99% isotopically pure) was provided by Dr. L.C. Leitch of the National Research Council at atmospheric pressure in a one-litre round-bottomed flask. The cross-sectional area of the burette of Fig. 3 was determined by attaching a stopcock to the bottom; with the column filled with mercury, and using a cathetometer to measure the difference in height, various

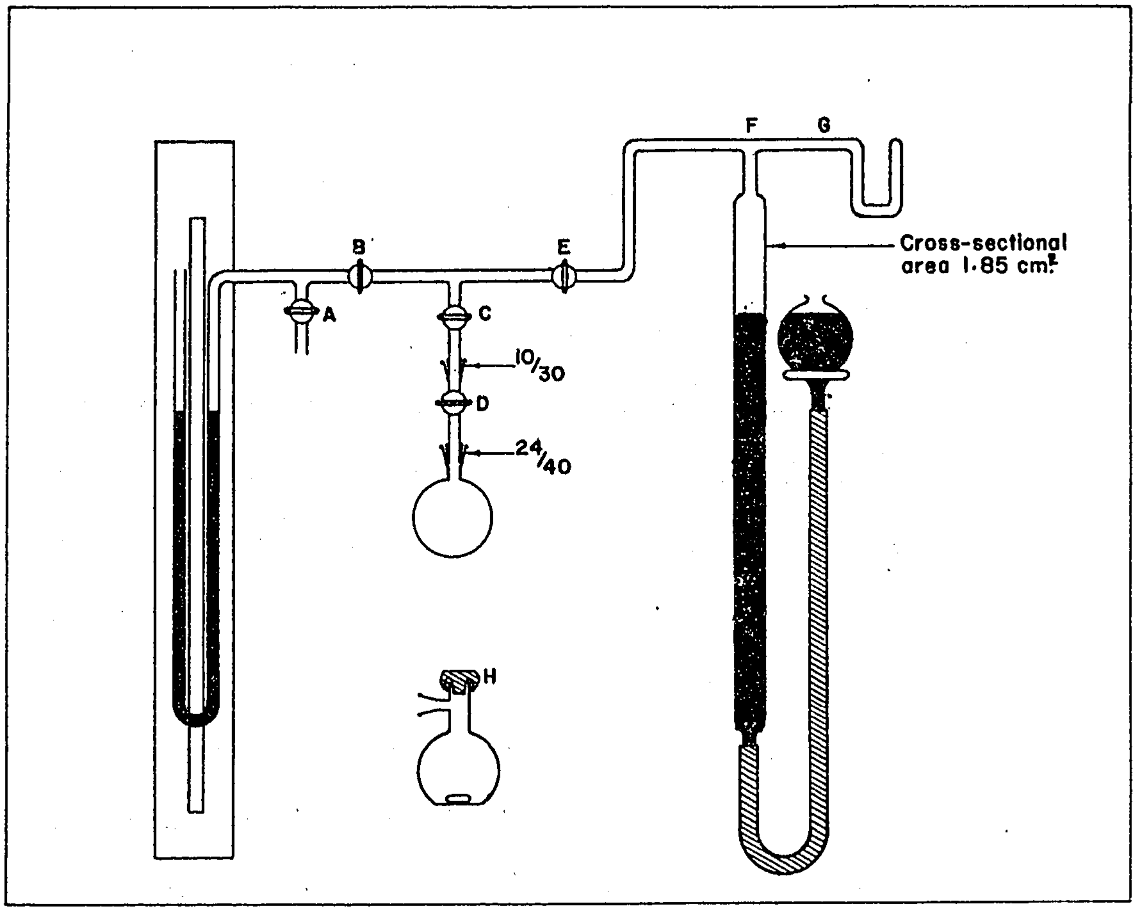


Fig. 3 - Vacuum line constructed for the oxidation of ethylene and 1,1-dideuteroethylene.

quantities of liquid were run out of the burette and weighed. A uniform area of 1.85 $cm.^2$ was obtained.

B. Procedure

(i). In the initial experiments, a measured volume of gas was introduced into the reaction flask containing periodate-permanganate solution buffered at the desired pH. The flask was sealed and mechanically shaken for the desired length of time, opened and the contents were analyzed for consumption of oxidant and yield of formaldehyde.

The following procedure was employed to measure the gas into the reaction flask. The mercury reservoir was raised, with all stopcocks open, until the mercury level was at F. Then stopcock E was closed, and the reservoir was lowered. With stopcocks E and C closed and stopcocks A and B open, the system was evacuated at A. Then E was opened and the burette was partially evacuated. E was then closed, and the ethylene cylinder was attached at C. With A, B and C open, some gas was allowed to pass through the system. B was closed and E was opened, admitting some gas to the burette. E and C were then closed, and the cylinder was replaced by a 500 ml. round-bottomed flask, attached to the system by means of the adaptor D. The flask contained the periodate-permanganate solution, previously frozen at -70°. With E closed and A, B, C and D open, the system was evacuated for two or three minutes to degas the contents of the reaction flask. Then A and D were closed and E was opened, permitting the gas to circulate through the system up to stopcock D. The initial burette reading was taken, and the periodate-permanganate solution was allowed to thaw. D was opened, admitting some gas to the reaction flask, then closed and the burette reading was taken again after readjustment to atmospheric pressure. The volume of gas introduced into the reaction flask was 1.85 Δh cc., where Δh was the difference, in cm. in the two cathetometer readings at atmospheric pressure. This volume was corrected to S.T.P.; the number of millimoles of gas used was then this corrected volume divided by 22.4. The flask and adaptor were removed from the line and the contents were mechanically shaken for the desired length of time. The ground glass joints were sealed with Kronig cement during this period.

(ii) Since procedure (i) required 1-2 days for complete oxidation of the gas, the apparatus was modified to enable the reaction to be conducted with an excess gas pressure over the system. A modification of the apparatus was desired which would permit an increase in the rate of the reaction, but yet would be adequate for runs with deuterated ethylene, and would permit measurement of the consumption of gas. A stopcock was sealed onto the vacuum line at G and led to a 10/30 male joint, K. The reaction flask, H , was a 50 ml. flat-bottomed flask with a 10/30 female side-arm. The outlet C of the vacuum line was bent at a 90° angle to the line, and the reaction flask, containing a small magnet, and covered with a self-sealing rubber seal was sealed onto the vacuum line with Kronig cement. The system was evacuated at A with G closed and all other stopcocks open. Then A was closed and the reading on the U-tube was taken immediately. When the rubber seal was properly adjusted, there was no increase in pressure during one hour.

The ethylene cylinder was attached at K and, after flushing the portion GK, stopcock G was opened and ethylene was admitted to the whole system. A gas pressure of about 760 mm. was introduced, and stopcock E was then closed. The mercury was levelled to atmospheric pressure, and the burette reading was taken with the cathetometer. For introduction of the oxidizing agent to the reaction system, the constant delivery addition syringe, used in the kinetic experiments, with a hypodermic needle attachment, was employed. The rubber seal was pierced, and a solution of periodate buffered with potassium carbonate, followed by a solution of permanganate, were syringed into the reaction flask. The mercury reservoir was readjusted to atmospheric pressure and the level was read. The progress of the reaction could then be followed by observing the mercury levels on the U-tube. Reaction did not usually commence until the contents of the flask were stirred, and the efficiency of the stirring appeared to be the main factor governing the rate of consumption of the olefin.

C. Analysis of the Reaction Mixture

The consumption of oxidizing agent was determined by removing an aliquot of the reaction mixture and adding about 0.5 g. of sodium bicarbonate, followed by a measured excess of arsenite solution and a few crystals of potassium iodide. After this solution was left for at least 10 minutes, the excess arsenite was determined by slow titration of the stirred solution with standard iodine solution to the starch end point. The difference between the titers for a run and a reagent blank was taken as equivalent to the oxidant consumed.

The yield of formaldehyde was determined by transferring an aliquot of the reaction mixture to a 25 ml. volumetric flask and adding an excess of M sodium arsenite solution, followed by sufficient 6 N sulphuric acid to make the system acidic. Under these conditions, the periodate was completely reduced to iodide, and manganese was completely reduced to manganous ion. These did not interfere with the colorimetric determination(126). The colourless solution was allowed to stand for 15 minutes, and was then made up to volume and a 1 ml. aliquot was transferred to a 25x200 mm. test tube. The chromotropic acid reagent (1 g. of chromotropic acid in 100 ml. of water, filtered and the filtrate made up to 500 ml. with 2:1 V/V concentrated sulphuric acid-water mixture), 10 ml., was added, and the test tube was tightly sealed with aluminum foil and then heated in a boiling water bath in diffuse light for 30 minutes. A reagent blank was run with every determination. When the contents of the test tubes had cooled to room temperature, they were transferred to photometer tubes and the optical density was read at 570 mμ. Erythritol and mannitol were used as standards for the production of known amounts of formaldehyde (2 moles of formaldehyde per mole of polyol) in the setting up of a standard curve. The two compounds gave identical results.

D. Attempted Isolation of Products

Using procedure (ii), 30 ml. (2 mM) of a solution 0.066 M in sodium meta-periodate and 0.066 M in potassium carbonate (prepared just before use by mixing one part of 0.2 M periodate with one part of 0.2 M carbonate and one part of water) were syringed into the flask H in an atmosphere of ethylene. This solution was stirred and a solution of 10 ml. of 0.002 M permanganate was syringed in. The reaction mixture was stirred for 30 minutes, during which time about 11 cc. (ca. 0.5 mM) of gas was absorbed. The reaction flask was then removed from the ethylene atmosphere and the reaction was stopped by the addition of 30 ml. of N arsenite solution and 50 ml. of 2 N sulphuric acid. The resulting clear, colourless solution was extracted with small portions of ether, and the ether extracts were combined and tested with ethereal solutions of phenylhydrazine, 2,4-dinitrophenylhydrazine and dimedone. No carbonyl derivative was obtained. Ether extraction of an aqueous solution containing 10 mg. of glyoxal followed by treatment in the same way yielded the derivative with each of the carbonyl reagents.

In a second experiment, carried out in the same way, but allowed to run until the permanganate decolourized (86 minutes), the reaction mixture was filtered to remove manganese dioxide, and was then concentrated to about 6 ml. The composition of the resulting solution was investigated by descending paper chromatography, using the butanol-water system. The paper was sprayed with the periodate-permanganate spray reagent (127), consisting of four parts of 2% periodate solution and one part of 1% permanganate solution, buffered to pH 8 with potassium carbonate. Spots developed very slowly. Since the paper is rapidly oxidized once the spray reagent dries, the freshly-sprayed paper was suspended in a moist atmosphere in a closed bell jar during the development period. Under these conditions, spots developing as slowly as 30 minutes after the initial spraying could still be detected.

Three spots were detected, with R_f values of 0, 0.22 and 0.48, respectively. Since ethylene glycol had an R_f of 0.50 on irrigation with butanol-water, a spot of the reaction mixture, along with a spot of ethylene glycol were run together. A single spot of R_f 0.48 was obtained in addition to the two spots with low R_f. Therefore, ethylene glycol appeared to be one of the products of the periodate-permanganate oxidation of ethylene. The spot with R_f zero was attributed to formate ion, which, using this solvent mixture, did not move on the paper chromatogram.

This experiment was repeated several times, and the spot with R_f 0.48 was always obtained. However, when the reaction mixture was allowed to stand for several hours before being concentrated and chromatographed, spots with R_f 0.05 and 0.13 were obtained along with that of R_f 0.48. The spot with R_f 0.22 had disappeared.

This behaviour can be explained if glycollic aldehyde is a product of the reaction. An aqueous solution of glycollic aldehyde was found to be stable, giving a single spot with R_f 0.66. However, addition of either sodium bicarbonate (to pH 7.6) or potassium carbonate (to pH 8.5) caused a rapid self-condensation of the glycollic aldehyde. The data in Table XI are the results of a paper chromatographic study of the effect of addition of dilute alkali to aqueous solutions of glycollic aldehyde. Solutions (40 mg./ ml.) of the compound were allowed to stand at room temperature at the desired pH, and spots were placed on paper at various times. The chromatograms were irrigated with butanol-water and sprayed with periodate-permanganate. The results of a similar study with solutions containing glycollic aldehyde (40 mg./ ml.) and formaldehyde (20 mg./ ml.) are shown in Table XII. No spots were detected when only formaldehyde was maintained at pH 8.5 for one hour.

An attempt was then made to estimate the products of the oxidation of ethylene quantitatively using the technique of Celite partition chromatography as described by Lemieux, Bishop and Pelletier (128). Ethylene was oxidized with 2 mM of periodate, 2 mM of potassium carbonate and 0.02 mM of permanganate until the manganese dioxide precipitated. The reaction mixture was concentrated to 1 ml. and 1 g. of acid-washed Celite was added. This mixture was stirred until it was uniform and was then pressed onto the top of a 1.95x20 cm. tapered column prepared with 15 g. of acid-washed Celite and the butanol-water solvent system. The amount of top phase required to separate the components of the reaction mixture was calculated from the equations (128),

$$\begin{aligned} R_v &= 300\,R_f + 15 \\ &= dr^2/v \ \text{mm.}^3 \times \text{ml.}^{-1}, \end{aligned}$$

where R_f is obtained from the paper chromatogram, and v is the volume (in ml.) of developing phase required to move a band a distance d mm. from the

TABLE XI

Effect of pH on the Paper Chromatographic Behaviour of Glycollic Aldehyde

Time - hr.	R_f of Spots pH 7.6	pH 8.5
0.5	.02, .05, .30	.29, .68
1.0	.02, .05, .28	.28, .66
21.0	.05, .13, .31	.15, .31
72.0	.03, .10	.04, .11, .25

TABLE XII

Effect of pH on the Paper Chromatographic Behaviour of Solutions Containing Equimolecular Amounts of Glycollic Aldehyde and Formaldehyde

Time - hr.	R_f of Spots pH 7.6	pH 8.5
0.1	.033, .100, .307	.308, .645
0.25	.033, .054, .292	.283
1.0	.046, .108, .296	.292

top of a column of radius r. It was calculated that 65 ml. of developing phase would move the band corresponding to R_f 0.48 a distance of 10 mm. from the top of this column. Hence 65 ml. of top phase were passed through this column under a slight pressure at a rate of 1 ml. per minute. Excess solvent was then forced out of the column and the column was extruded and sprayed (using a metal shield) with a solution of 1% permanganate in 2 N sodium hydroxide. A narrow red line is thus obtained which rapidly turns green due to reduction of the permanganate by residual butanol on the column. This green line rapidly turns reddish-brown in the zones where a high concentration of a reducing agent is present on the column.

Two bands, corresponding to the two spots found by paper chromatography, were located on the column in this way. These bands were cut out of the column, slurried with water, and the slurries were filtered. The filtrates were made up to 100 ml. in volumetric flasks and aliquots were treated with excess periodate.

The consumption of oxidizing agent and yield of formaldehyde were determined as described above. The results obtained from these estimations served as a quantitative check on the conclusions arrived at from paper chromatography alone. These results are described on page 243 .

The Reduction of Periodate-Permanganate by Excess Ethylene

A solution of sodium meta-periodate, 10.7 g. (50 mM), potassium permanganate, 0.79 g. (5 mM), and potassium carbonate, 6.9 g. (50 mM), was diluted to 1500 ml., cooled to 10°, stirred and ethylene was rapidly bubbled in. Manganese dioxide precipitated in 10 minutes. The reaction mixture was filtered with the aid of Celite and, after concentration to 1200 ml., was deionized by passing successively through Amberlite-IRC-50H cation exchange resin and Dowex-1-X10 anion exchange resin. The columns were eluted with 2000 ml. of water and the total eluate was evaporated to dryness. The product still contained a small amount of inorganic salt, most of which was removed by extraction with ethanol. The ethanol extract was evaporated to dryness leaving a clear, colourless syrup. The infrared spectrum of this syrup was identical in every respect with that of ethylene glycol.

Preparation of Formaldehyde-2,4-Dinitrophenylhydrazone

Para-formaldehyde, 2.5 g. (10 mM), was added to a solution prepared from 2.0 g. (10 mM) of 2,4-dinitrophenylhydrazine in 10 ml. of concentrated sulphuric acid, 15 ml. of water and 50 ml. of ethanol. The resulting suspension was heated to boiling, whence the p-formaldehyde depolymerized, dissolved, and the derivative immediately precipitated. The compound was recrystallized four times from ethyl acetate-ethanol, m.p. 167.0-167.8°.

Preparation of Formaldehyde-d_2-2,4-Dinitrophenylhydrazone

The above procedure was unsuccessful when applied to a sample of deuterated paraformaldehyde supplied by Dr. L.C. Leitch of the National Research Council. The compound was therefore depolymerized in a Sargent combustion train at 500°, the vapour being swept into a bubbler containing ethanol by use of a positive pressure of nitrogen. The derivative was readily prepared from this ethanolic solution.

Formaldehyde-2,4-Dinitrophenylhydrazone from the Oxidations of Ethylene and 1,1-Dideuteroethylene

Using procedure (ii), page 97, a quantity of gas (0.5-1.0 mM) was oxidized. The reaction was stopped at the desired time, and excess arsenite and sulphuric acid were added to decolourize the reaction mixture. The resulting clear, colourless solution (ca. 75 ml.) was divided into five parts, each of which was treated with 2 ml. of a solution prepared by dissolving

2.5 g. of 2,4-dinitrophenylhydrazine in 12 ml. of concentrated sulphuric acid, 18 ml. of water and 60 ml. of ethanol. The formaldehyde derivative readily precipitated under these conditions, and was recrystallized from ethanol to constant melting point. The product, 1 mg., was dissolved in 3 ml. of freshly-distilled dioxane and the infrared spectrum was determined as described below.

Infrared Spectra of Formaldehyde-2,4-Dinitrophenylhydrazone and Formaldehyde-d_2-2,4-Dinitrophenylhydrazone

Several different techniques were examined for the quantitative determination of the spectra of mixtures of these two compounds. Since the two dinitrophenylhydrazones crystallized as fine needles, which could not be easily ground, the spectra in Nujol mull were not extensively studied. The dinitrophenylhydrazones were not soluble in any of the ordinary solvents used in infrared analysis. The compounds were quite soluble in dimethyl sulphoxide, but the infrared spectrum of this compound indicated that it was unsuitable as a solvent for infrared analysis. The potassium bromide pressed disc technique was then investigated. This technique, invented independently by Schiedt and Reinwein (129) and by Stimson and O'Donnell (130) in 1952, has since received much attention and wide application (131-134). In this method, the usual procedure involves grinding the sample with powdered potassium bromide. The mixture is then placed in a die, which is evacuated, and the die is compressed. Evacuation eliminates occluded air which would expand when the pressure is released and produce an undesirable milkiness in the pellet. The resulting clear or translucent pellet gives an infrared spectrum free from interfering bands of solvents or mulling agents.

In the present work, a rectangular Baird die was used in the preparation of the discs. A hydraulic press, capable of a hydrostatic pressure of 10,000 lbs. per sq. in. was used to press the discs. The potassium bromide was reagent grade material and a 10% solution was prepared in conductivity water. In the initial experiments, 3 ml. (300 mg. of potassium bromide) were freeze-dried (135), and a solution of the dinitrophenylhydrazone in chloroform (1 mg. in 0.5 ml.) was added to this potassium bromide. The resulting mixture was stirred under a heat lamp while the chloroform evaporated and, after drying at 120° for a few minutes, was transferred to the die, tamped evenly with a microspatula, and the die was assembled and placed in the press. The system was evacuated for one minute, and the pressing was commenced; the pressure was gradually increased to 1000 pounds over a two minute period. The pressure was then immediately released and the die was opened and the disc extruded. The two spectra shown in Fig. 4 were obtained using this procedure.

Though discs prepared in this way gave satisfactory spectra, a

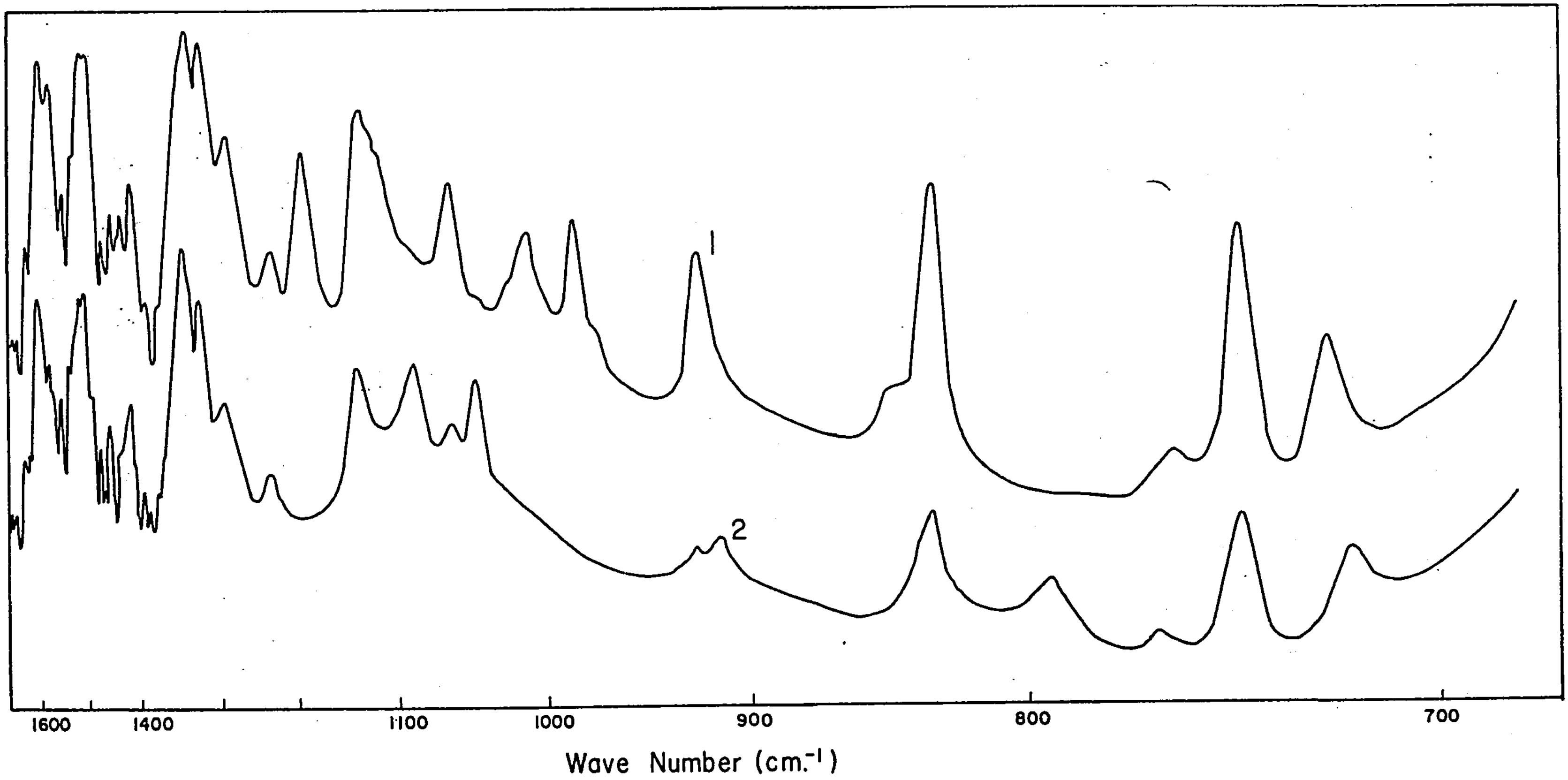


Fig. 4 - The infrared spectra of CH_2O-2,4-dinitrophenylhydrazone (curve 1) and CD_2O-2,4-dinitrophenylhydrazone(curve 2).

more efficient method was sought for the preparation of the potassium bromide-dinitrophenylhydrazone mixtures. Since the lyophilized potassium bromide was extremely hygroscopic, the particle size increased during the preparation of the sample. This made the amount of scattering caused by the disc, and thus the position of the baseline, difficult to reproduce (see reference 136 for a study of the effect of particle size on quantitative disc spectroscopy). A procedure was desired which would eliminate, as much as possible, handling of the sample between the freeze-drying and the final pressing of the disc. The procedure developed to satisfy this requirement, which was employed in all subsequent work, involved freeze-drying of a solution of 1 mg. of dinitrophenylhydrazone and 300 mg. of potassium bromide from 1:1 dioxane-water. This solvent system gave a homogeneous solution which could be uniformly frozen and thawed, and which could be satisfactorily freeze-dried provided certain conditions were followed. Since the melting point of the mixed solvent was appreciably less than 0°, it was necessary to guard against thawing of the sample before the freeze-drying was complete. Thus the freeze-drying was conducted in the dark, at a room temperature of 0-10°.

The dioxane used for this work was distilled immediately before use, since ordinary reagent grade material gave unsatisfactory results. Blank discs prepared using this freshly-distilled dioxane were not completely free from absorption maxima, but in the region 1400-600 cm.$^{-1}$, the system was ideally suited for quantitative work(see Fig. 5). Indeed, discs obtained by pressing

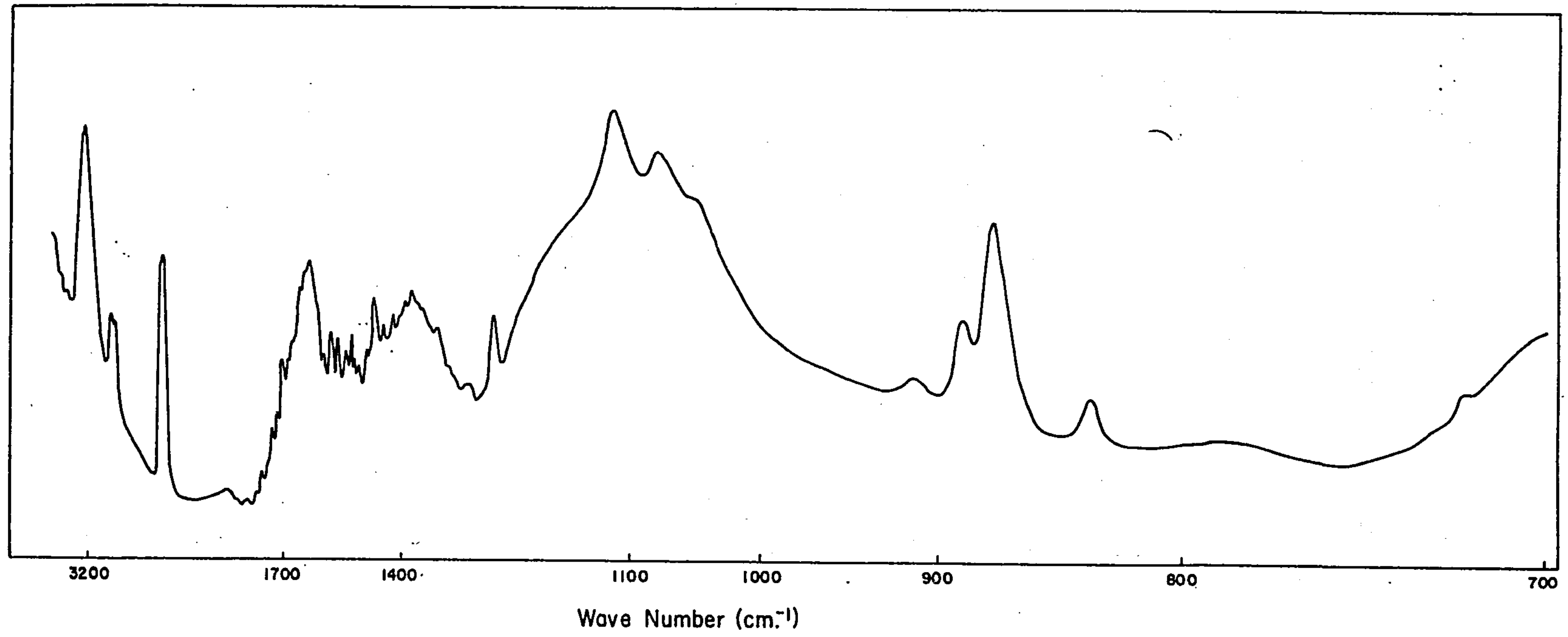


Fig. 5 - Infrared spectrum of a pressed disc prepared from a freeze-dried solution of 300 mg. of potassium bromide in 50% dioxane.

the solid which resulted when a solution of 1 mg. of compound in 3 ml. of dioxane and 3 ml. of aqueous potassium bromide (10%) was freeze-dried, gave spectra which were completely superimposable. Solutions 0.0033% in formaldehyde-2,4-dinitrophenylhydrazone and formaldehyde-d_2-2,4-dinitrophenylhydrazone were then mixed in the proper proportions to prepare the standard curves. The spectrum of the 1:1 mixture is shown in Fig. 6. The formaldehyde-2,4-dinitrophenylhydrazone had a maximum at 723 $cm.^{-1}$, while the formaldehyde-d_2-2,4-dinitrophenylhydrazone had a maximum at 717 $cm.^{-1}$ (Fig. 4). Mixtures of the two compounds showed a band containing two maxima in this region, and the appearance of this band easily gave the concentration of formaldehyde-d_2-2,4-dinitrophenylhydrazone in unknown mixtures. This can be seen by the curves shown in Fig. 7, which show the effect, on this band, of variation of the concentrations of the two compounds.

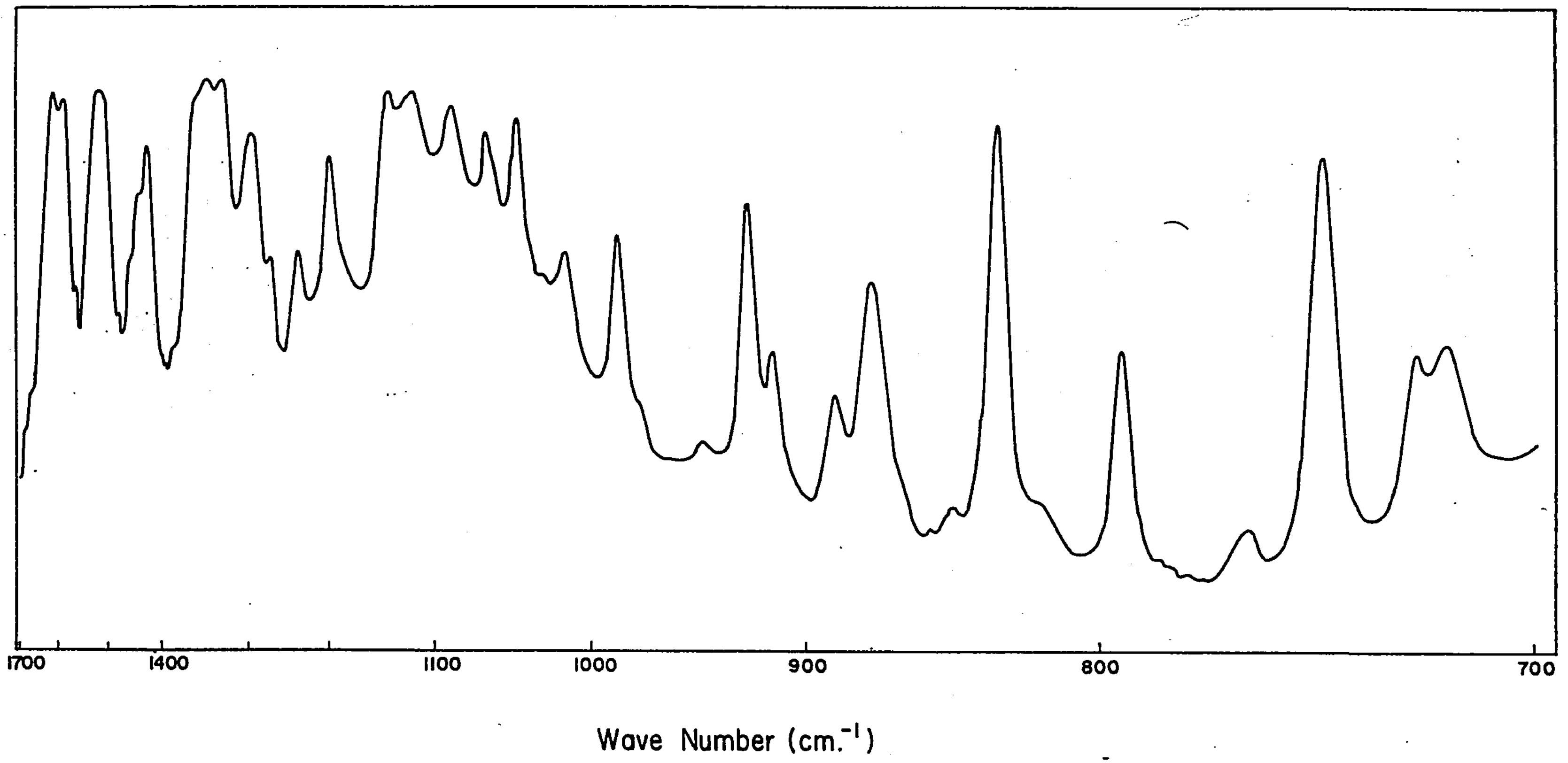


Fig. 6 - Infrared spectrum of a pressed disc containing a 1:1 mixture of formaldehyde-2,4-dinitrophenylhydrazone and formaldehyde-d_2-2,4-dinitrophenylhydrazone; the disc was prepared using the same conditions as Fig. 5.

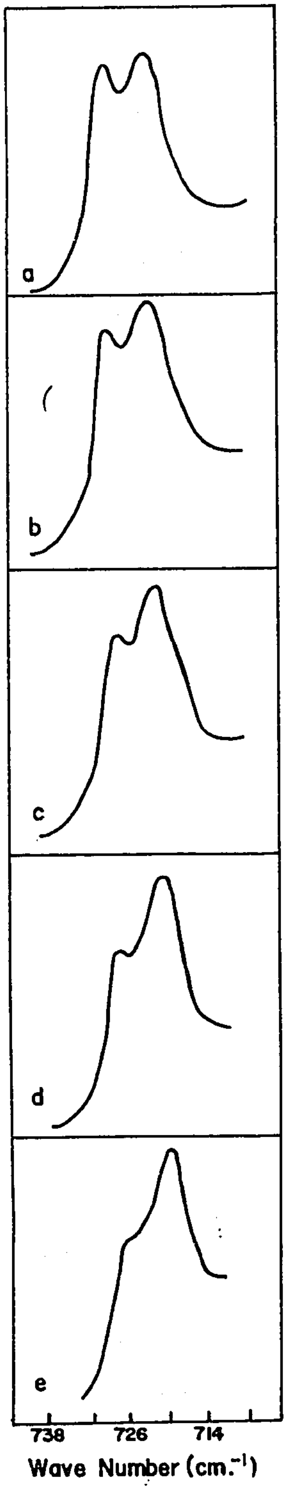


Fig. 7 - Effect of concentration of the components on the infrared spectra of mixtures of formaldehyde-2,4-dinitrophenylhydrazone and formaldehyde-d_2-2,4-dinitrophenylhydrazone in the 725-715 cm.$^{-1}$ region.

a. 50% deuterium

b. 54% deuterium

c. 58% deuterium

d. 64% deuterium

e. 68% deuterium

III. RESULTS AND DISCUSSION

1. The Disproportionation of Hypomanganate to Manganate and to Permanganate

Duke (105) has studied the kinetics of the disproportionation of manganate to permanganate and manganese dioxide. It was felt that a study of the analogous reactions of hypomanganate might provide information on the stability of hypomanganate which would assist in the interpretation of the role of this valence state in the oxidation of olefins by permanganate. Above pH 12, where manganate ions are stable, the disproportionation proceeds according to the following equation,

$$2\,H_2O + 2\,MnO_4^{-3} \longrightarrow MnO_2 + MnO_4^{-2} + 4\,OH^- .$$

This reaction is reversible in 10 N alkali (113). At pH values below 12, the overall transformation can be approximately represented as follows,

$$3\,MnO_4^{-3} + 4\,H_2O \longrightarrow 2\,MnO_2 + MnO_4^- + 8\,OH^- .$$

A. Disproportionation of Hypomanganate in Alkaline Medium

The disproportionation to manganate and manganese dioxide was studied kinetically, using tellurate ion to solubilize the tetravalent manganese. Tellurate ion has been shown by Issa and co-workers (121-124) to form a soluble complex with tetravalent manganese. The principal observations made in these experiments are summarized by the three curves shown in Fig. 8. In 10 N alkali, hypomanganate was stable for long periods of time. However, dilution of the solution caused a rapid disproportionation. As shown by curve 3, Fig. 8, there was an induction period for the disproportionation, the length of which decreased as the alkalinity decreased until, near 2 N alkali, it either disappeared completely, or was too short to observe.

The induction period infers a slow initial process in which a product(s) is formed which can catalyze the disproportionation. That a product of the disproportionation, manganese dioxide, possessed this property, was demonstrated by observing the effect of added manganese dioxide on the stability of hypomanganate in 10 N sodium hydroxide. The hypomanganate was stable for several days at 0°; however, when a small amount of freshly-precipitated manganese dioxide (prepared by the addition of methyl alcohol to alkaline permanganate) was added, the disproportionation commenced immediately, and there was a heavy precipitate of manganese dioxide in less than one day. The catalytic effect of manganate ions was not studied.

The discontinuity in curve 2, Fig. 8, after about 20% of reaction, was reproducible. The decrease in rate is attributed to a decrease

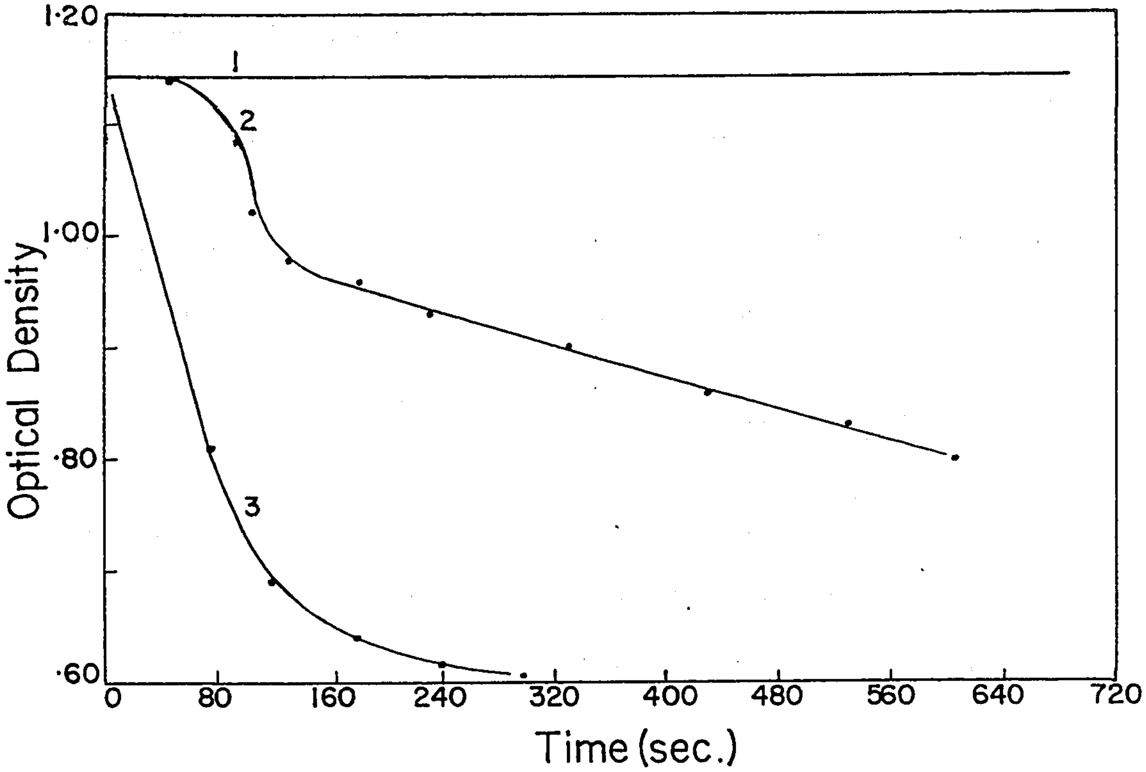


Fig. 8 - The disproportionation of hypomanganate (1×10^{-3}M) to manganate and manganese dioxide in the presence of tellurate ions (2.5×10^{-3}M).

Plot 1, 10 N sodium hydroxide. Plot 2, 3.66 N sodium hydroxide.

Plot 3, 1.83 N sodium hydroxide.

in the concentration of the catalyst which was formed in the induction period. It is believed that the reaction,

(41)...
$$\mathrm{MnO_4^{-2}} + \mathrm{MnO_4^{-4}} \longrightarrow 2\,\mathrm{MnO_4^{-3}}\ ,$$

which Lux (113; see page 54) established in 10 N alkali was occurring here also, and was competing with the complexing reaction,

(42)...
$$\mathrm{MnO_4^{-4}} + \text{tellurate} \rightleftharpoons \mathrm{MnO_4^{-4}}\cdot\ \text{tellurate}\ .$$

The apparent absence of a discontinuity in curve 3, Fig. 8, reflects the pH dependence of the reactions shown in equations 41 and 42.

Among the possible reactions occurring in the disproportionation of hypomanganate are the following three,

(a)
$$\begin{array}{lcl} \mathrm{MnO_4^{-3}} + \mathrm{MnO_4^{-3}} & \rightleftharpoons & \mathrm{MnO_4^{-4}} + \mathrm{MnO_4^{-2}} \\ & & \quad \updownarrow\ 2\,\mathrm{H_2O} \\ & & \mathrm{MnO_2} + 4\,\mathrm{OH^-}\ , \end{array}$$

(b)
$$\begin{array}{lcl} \mathrm{MnO_4^{-3}} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2MnO_5^{-3}} & \rightleftharpoons & \mathrm{OH} + \mathrm{HMnO_4^{-3}} \\ & & \quad \downarrow \mathrm{MnO_4^{-3}} \\ & & \quad \mathrm{MnO_4^{-2}} + \mathrm{OH^-}\ , \end{array}$$

(c)
$$\begin{array}{lcl} 2\,\mathrm{H_2O} + 2\,\mathrm{MnO_4^{-3}} + \mathrm{MnO_4^{-2}} & \rightleftharpoons & \mathrm{MnO_4^{-4}} + \mathrm{MnO_4^{-1}} + \mathrm{MnO_4^{-3}} + 2\,\mathrm{H_2} \\ & & \qquad\qquad\qquad \updownarrow \\ & & \qquad \mathrm{MnO_2} + 2\,\mathrm{MnO_4^{-2}} + 4\,\mathrm{OH^-}. \end{array}$$

The first route (a), which represents the transfer of an electron between two hypomanganate ions, may well be that responsible for the induction period. According to the third route (c), manganate, formed in the induction period, would have the ability to catalyze further disproportionation of the hypomanganate. Unfortunately, this possibility was not tested. However, it was demonstrated that under the conditions of these experiments, the reaction,

(43)... $$MnO_4^{-3} + MnO_4^{-1} \longrightarrow 2\,MnO_4^{-2}\ ,$$

was rapid and quantitative. Such a reaction would occur in the second stage of route (c).

A reaction route such as (b) is somewhat speculative, but is, nevertheless, supported by the experimental facts in a number of ways. First, the oxidation potential for the hypomanganate-manganese dioxide couple in alkaline medium is -0.92 V. (see Table IV, page 56). Since, in alkaline medium, the potential of the water-hydroxyl radical couple is -0.89 V. (80), it is evident that the reaction is thermodynamically possible. Secondly, Symons has found that manganate readily exchanges its oxygen atoms with water (55), and has postulated an intermediate species $H_2MnO_5^{-2}$ in this reaction; this kind of species is similar to that proposed as an intermediate in route (b) above. Thirdly, addition of permanganate to acrylonitrile in 3 M alkali, followed by neutralization of the reaction mixture, resulted in the formation of a polymer (56). This could conceivably have arisen during the disproportionation of a hypomanganate intermediate, which was formed in the oxidation of the monomer.

B. Disproportionation of Hypomanganate in Acid Medium

During experiments on the iodometric analysis of hypomanganate, it was observed that the amount of iodine liberated depended on the order of addition of the potassium iodide. When hypomanganate was added to acidified potassium iodide solutions (using sulphuric, nitric and hydrochloric acids), more iodine was liberated than when the hypomanganate was first caused to disproportionate in excess acid, and potassium iodide then added. Many experiments were conducted with several different preparations of hypomanganate to establish that this effect was not a spurious one, due to the presence of traces of reducing agent in the hypomanganate (which could then reduce the permanganate as it formed). The results shown in Table XIII, obtained from one solution of hypomanganate, are typical. Excess potassium iodide was used for all the titrations.

The effect on the thiosulphate titer of rapid and slow addition of hypomanganate, and the effect of variation in the nature of the alkali were also studied. The results, shown in Table XIV, are the average of at least three determinations in each case.

TABLE XIII

The Disproportionation of Hypomanganate in Acid Medium

Amount of Acid Used in the Disproportionation Reaction[a]	Method	Ml. of Thiosulphate Required to Titrate the Liberated Iodine
45 ml. of 2.7 N sulphuric acid[b]	A[c]	1.10
"	A	1.08
"	A	1.07
"	B[d]	0.50
"	B	0.48
35 ml. of 1.5 N sulphuric acid[e]	A	1.08
"	B	0.50
35 ml. of 3 N hydrochloric acid	A	1.05
"	B	0.46
50 ml. of 2 N nitric acid	A	1.09
"	B	0.50

---

[a] Five ml. of a solution of hypomanganate in 10 N sodium hydroxide was treated with this acid.

[b] The pH of the resulting mixture was less than 1.

[c] The hypomanganate was added to acidified potassium iodide

[d] The hypomanganate was allowed to disproportionate, and the potassium iodide was then added

[e] The pH of the reaction mixture was 1-3.

TABLE XIV

Effect of Method of Addition and Variation in the Alkali on the Disproportionation of Hypomanganate in Acid Medium

The hypomanganate solution, 5 ml., was added to 45 ml. of 2.7 N sulphuric acid, under the conditions described in the footnotes.

Method	Thiosulphate Titer	% Difference in Titer
(i) Using a solution of hypomanganate in 10 N sodium hydroxide.		
A[a]	1.738 ± .008	-
B[b]	1.588 ± .018	8.6
C[c]	1.738 ± .005	-
D[d]	1.558 ± .014	10.4
(ii) Using a solution of hypomanganate in 12 N potassium hydroxide.		
A	1.738 ± .009	-
B	1.362	21.6

---

[a] The hypomanganate was added dropwise to acidified potassium iodide.

[b] The hypomanganate was added dropwise to acid, and potassium iodide was then added

[c] The hypomanganate was added rapidly through a syringe to acidified potassium iodide.

[d] The hypomanganate was added rapidly through a syringe to acid, and potassium iodide was then added.

The same behaviour was shown to a lesser extent by manganate and not at all by permanganate. A solution of manganate in 10 N sodium hydroxide required 4.79 ±.04 ml. (average of four) of thiosulphate solution using method A (see Table XIII for a description of this method), and 4.53±.03 ml. of thiosulphate (average of three) using method B of Table XIII.

When hypomanganate was allowed to disproportionate in alkaline medium, and the mixture of manganate and manganese dioxide was then added to acidified potassium iodide, the resulting titration was the same as that obtained by adding the hypomanganate to acidified potassium iodide.

Thus, the disproportionation in acid medium and in the absence of a reducing agent of hypomanganate and, to a lesser extent, manganate, to permanganate and manganese dioxide, results in a loss of oxidizing agent. The exact amount of this loss of oxidizing agent depends only slightly on whether the hypomanganate is added rapidly or slowly to the acid, but varies appreciably between solutions of hypomanganate in potassium hydroxide and sodium hydroxide, and between solutions in sodium hydroxide prepared from different batches of the solid.

The route of the reaction was studied by causing hypomanganate and manganate to disproportionate in excess acid, and centrifuging and filtering the resulting mixtures. The manganese dioxide and permanganate were then estimated iodometrically (Table VI). Quantitative recoveries of manganese dioxide were obtained, but the recovery of permanganate was low in each case, being 95% of theoretical from hypomanganate and 93% of theoretical from manganate. These differences from theoretical were outside the average experimental error of 2.8% and appear to be real.

The loss of oxidizing agent must, therefore, be due to formation of some soluble species of manganese which is not detected by the iodometric analysis. This can only be manganous ion.

That some of the manganese is, in fact, reduced to the manganous level during the disproportionation of hypomanganate was established by photometric means. A solution of hypomanganate in 10 N sodium hydroxide was prepared and the concentration, determined iodometrically, was found to be 0.0038 M. Five ml. of this solution were then treated with acid bisulphite, and the resulting solution of manganous ion was oxidized with hot periodate to permanganate(137). The solution was diluted to 100 ml., and the optical density was read at 525 mμ on the Coleman Junior Spectrophotometer. The optical density was 0.526, corresponding to a concentration of hypomanganate of 0.0036 M. The satisfactory agreement between the photometric and the titrimetric analyses established the reliability of the photometric method of detecting manganous ion which is described below. Additional evidence of the reliability of this photometric procedure was obtained by demonstrating that aqueous solutions of permanganate could be reduced to the manganous level, and then reoxidized quantitatively to permanganate.

Five ml. aliquots of the above hypomanganate solution were then added to solutions containing 45 ml. of 2.7 N sulphuric acid. The resulting mixtures were centrifuged for 30 minutes and were then filtered through sintered glass. The permanganate filtrates were diluted to 100 ml. and the optical densities were determined. The average of three determinations was 0.086 ± .003. These solutions were then reduced with acid bisulphite to manganous ion, reoxidized to permanganate with hot periodate, diluted to 100 ml. and read again; the optical density was now 0.167 ± .008.

This increase in optical density must have been caused by oxidation of the manganous ion which was present in the original filtrate. If the disproportionation of hypomanganate had obeyed the stoichiometric equation,

$$3\,MnO_4^{-3} + 4\,H_2O \longrightarrow 2\,MnO_2 + MnO_4^- + 8\,OH^-,$$

the optical density of the permanganate obtained by filtering the disproportionation mixture and diluting the filtrate to 100 ml. would have been 1/3 x 0.526 or 0.175. Only half this amount was actually obtained. However, the oxidation by periodate gave the theoretical amount of permanganate, in agreement with the idea that the difference from theoretical was due to manganous ion.

This observation that some of the hypomanganate is reduced to the manganous level during the disproportionation reaction has a number of immediate and important implications. Since the presence of traces of reducing agent in the hypomanganate solution may be ruled out, the reduction of the oxidizing agent must have been caused by the solvent. Since hydrogen peroxide, in acid medium, will reduce the higher valence states of manganese to the manganous level, the results are satisfactorily accounted for by the assumption that small amounts of hydrogen peroxide are formed by oxidation of the water solvent when hypomanganate is added to acid.

The water-hydrogen peroxide couple has an oxidation potential of -1.77 V. in acid medium and -0.88 V. in alkaline medium, while the water-hydroxyl radical couple has a potential of -2.82 V. in acid medium(80). The oxidation potential of the hypomanganate-manganese dioxide couple in acid medium was calculated to be -4.19 V. (see page 56). The manganate-manganese dioxide couple has been reported (80) to have an oxidation potential of -2.26 V. in acid medium. On the basis of these calculations, hypomanganate is theoretically capable of oxidizing water to hydroxyl radicals in acid medium, and the foregoing experimental results indicate that such a reaction may constitute a first step in the disproportionation of hypomanganate to permanganate and manganese dioxide in acid medium.

The fact that different solutions of sodium hydroxide or potassium hydroxide give different amounts of reduction to the manganous level is surprising. It is noteworthy, however, that Symons (51) has suggested that traces of heavy metal ions such as are present in "analar grade" sodium hydroxide can affect the rate of decomposition of hydrogen peroxide.

The results suggest that manganate, in acid media, also oxidizes water to hydrogen peroxide. In this case, since the oxidation potential of the manganate-manganese dioxide couple is not sufficiently great to produce hydroxyl radicals in high concentration, the reaction route may proceed by way of a direct transfer of oxygen to the water. Since manganate rapidly exchanges its oxygen atoms with water (55), albeit in alkaline medium, the oxidation of water by manganate to hydrogen peroxide can conceivably occur by addition of a molecule of water to the manganate, followed by decomposition of the resulting species to hydrogen peroxide and a manganite anion, thus,

$$MnO_4^{-2} + H_2O \rightleftharpoons H_2MnO_5^{-2} \rightleftharpoons H_2O_2 + MnO_3^{-2} .$$

The possibility that the disproportionation of hypomanganate to permanganate and manganese dioxide can give rise to hydroxyl radicals could be employed to rationalize a variety of permanganate oxidations in which free radical species appear to be formed (7, 19, 21).

2. Evidence for the Cyclic Intermediate in the Oxidation of Olefins by Permanganate

A. Isolation of Hypomanganate from the Oxidation of Olefins by Manganate and Permanganate

With the increased understanding of the behaviour of hypomanganate gained by the foregoing experiments, it was possible to devise conditions which would permit the isolation of hypomanganate from the oxidation of olefins by permanganate. It was believed that formation of hypomanganate, if it were an intermediate, would be favoured by operating in the cold, in 10 N alkali and in the presence of excess olefin.

These expectations were confirmed. The slow addition of permanganate at 0° to concentrated alkaline solutions of allyl alcohol, cyclohexenedioic acid and sorbic acid, using a 1:100 molar ratio of permanganate to olefin, yielded the blue hypomanganate, $\lambda_{max.} = 675$ mμ. In each case, the yield, estimated photometrically, was at least 50% of that expected on the assumption that the permanganate was quantitatively reduced to hypomanganate. These results are summarized in Table VIII, page 72. The following observations were also recorded:

(i) when the rate of the addition of the permanganate was increased, the initial product was manganate, rather than hypomanganate;

(ii) when the addition of the permanganate was too slow, the concentration of hypomanganate was increased to a sufficiently high level that it, rather than the olefin, reacted with the permanganate, and the initial product was manganate;

(iii) the solutions containing hypomanganate and excess olefin were stable.

Thus, by adopting favourable experimental conditions, permanganate could be reduced by an over-all two electron exchange. To determine whether this reduction occurred directly, or in stages with intermediate formation of manganate, the experiments were repeated using the same olefins and manganate. Hypomanganate was again obtained. When the manganate was added rapidly, the initial colour was green, but the reaction mixture slowly took on the colour of hypomanganate. The results do not allow a decision as to whether the reaction proceeded by one-electron or two-electron exchanges since, under the conditions of these reactions (10 N alkali), oxidation of hypomanganate by permanganate to form manganate was quantitative and immeasurably fast. Indeed, this reaction was quantitative, even in 1N alkali. Below this alkalinity, the reaction was still evident, but some manganese dioxide was also obtained, indicating that disproportionation of the hypomanganate had also occurred. The objections raised by Drummond and Waters (57) to the postulate of a hypomanganate intermediate are, therefore, not completely consistent with these experimental results and, as Pode and Waters (108) now agree, the occurrence of the reaction shown in equation 43 (in competition with the disproportionation reaction) under the conditions of the hydroxylation reaction, shows that a two-stage reaction with over-all reduction of the oxidizing agent by one valence unit is consistent with the experimental facts. As was seen above, the formation of hypomanganate is highly sensitive to the rate of addition of the permanganate to the olefin. This fact agrees with the idea of a two-stage reaction.

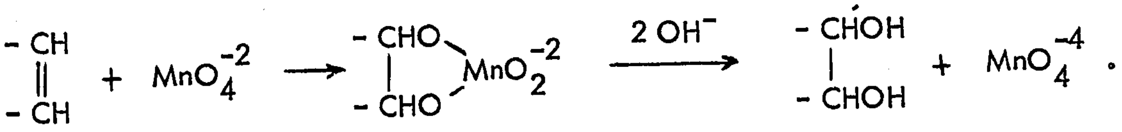
The manganate oxidation of an olefin may also proceed by way of a two-electron transfer, since an over-all reduction of manganate by one valence unit could also conceivably occur in two stages,

(44)... $MnO_4^{-2} + \text{olefin} \longrightarrow MnO_4^{-4} + \text{product}$,

(41)... $MnO_4^{-4} + MnO_4^{-2} \rightleftharpoons 2\,MnO_4^{-3}$.

The second of these reactions (equation 41) has been shown to occur (see reference 113; also page 119 of this thesis).

It was found in this work that oxidation of oleic acid and <u>cis</u>-4,5-cyclohexenedioic acid by manganate in alkaline solutions gave in each case the <u>cis</u> glycol. The analogous results reported by Pode and Waters (108) and by Rigby (109) indicate that this is probably a general reaction. Thus the arguments employed by Boeseken (1) for the hypothesis of a cyclic ester intermediate in the case of the permanganate oxidation of olefins can be applied to the manganate oxidations,



$$\begin{array}{l}-\mathrm{CH}\\ \;\| \\ -\mathrm{CH}\end{array} + \mathrm{MnO}_4^{-2} \longrightarrow \begin{array}{l}-\mathrm{CHO}\diagdown\\ \;\;| \qquad \mathrm{MnO}_2^{-2}\\ -\mathrm{CHO}\diagup\end{array} \xrightarrow{2\,\mathrm{OH}^-} \begin{array}{l}-\mathrm{CHOH}\\ \;\;| \\ -\mathrm{CHOH}\end{array} + \mathrm{MnO}_4^{-4} .$$

The effects of complexing and precipitating agents on the oxidations by manganate and permanganate in strongly alkaline media were studied in the hope that they would have some effect on the reactions and enable more definite conclusions to be drawn concerning the initial stage of the hydroxylation reaction. Addition of barium ions to the permanganate-olefin reaction mixtures had no effect on the formation of hypomanganate either at 25° or at 0°. Apparently under these conditions precipitation of barium manganate was not rapid enough to prevent oxidation of the olefin by some of the manganate, since manganate was also reduced to hypomanganate under these conditions. Telluric acid was added to the reaction mixtures in the hope that, by complexing with tetravalent manganese, it might inhibit a second stage of the manganate reaction (equation 41), and so prevent the formation of hypomanganate in this way. Again there was no difference between the oxidations by manganate and permanganate, and the yield of hypomanganate was unchanged. Therefore, either the tetravalent stage in the reduction of manganate was never reached and the oxidation proceeded by way of a single one-electron exchange, or the complexing action of tellurate had no effect on the oxidation of the tetravalent manganese by manganate. That complexing did occur under these conditions was shown by warming the hypomanganate-olefin solutions, whence disproportionation to manganate and manganese dioxide occurred; in the absence of tellurate, the manganese dioxide precipitated, while the system remained homogeneous in the presence of the complexing agent.

Though the experiments described in the foregoing paragraphs did not definitely resolve the question of the number of electrons transferred in the initial stage of the permanganate-olefin reaction, the results seemed to point towards the scheme involving two-electron exchanges and, in any event, the experiments were of value in demonstrating the kinds of problems which had to be overcome. Furthermore, an increase in the concentrations of materials from the micro scale to the macro scale led to a novel synthesis of solid hypomanganate. Allyl alcohol was sufficiently soluble in cold 10 N alkali to permit preparative experiments to be carried out. The addition of a molar equivalent of allyl alcohol to a solution of manganate or permanganate in cold, 10 N sodium hydroxide resulted in a rapid precipitation of hypomanganate. The yields of hypomanganate were 22% from permanganate and 64% from manganate. Separation of the insoluble hypomanganate from the manganese dioxide which was also formed in these reductions was made possible by the fact that the initial tetravalent product could be filtered through sintered glass. Presumably the reaction,

$$(45)\ldots \quad MnO_4^{-4} + 2H_2O \longrightarrow MnO_2 + 4OH^- ,$$

was not instantaneous under these conditions.

This method of preparation of hypomanganate is particularly useful, since the solid product is obtained uncontaminated by coprecipitation of inorganic salts. Traces of allyl alcohol are removed simply by washing the solid with alkali.

B. Evidence for the Two Electron Exchange

The observation that addition of telluric acid to olefin-permanganate reaction mixtures rendered the mixtures homogeneous was made the basis of a photometric study of the kinetics of the reaction. In the pH region 7-10.5, where α-ketol is the initial product of the reaction of oleate ion with permanganate, the only valence states of manganese which could be detected were permanganate and the manganite-tellurate complex. In the pH region 10.5-12, while there was some darkening of the reaction mixture, due to the transient formation of manganate, this was very short-lived, and the manganate could not be detected photometrically. Above pH 12, where glycol was the product of the reaction, manganate was an intermediate stage. It is this high pH region with which we are concerned in the present section.

The data plotted in Fig. 9 show the variation in the concentrations of permanganate (read at 525 mμ) and manganate (read at 600 mμ)

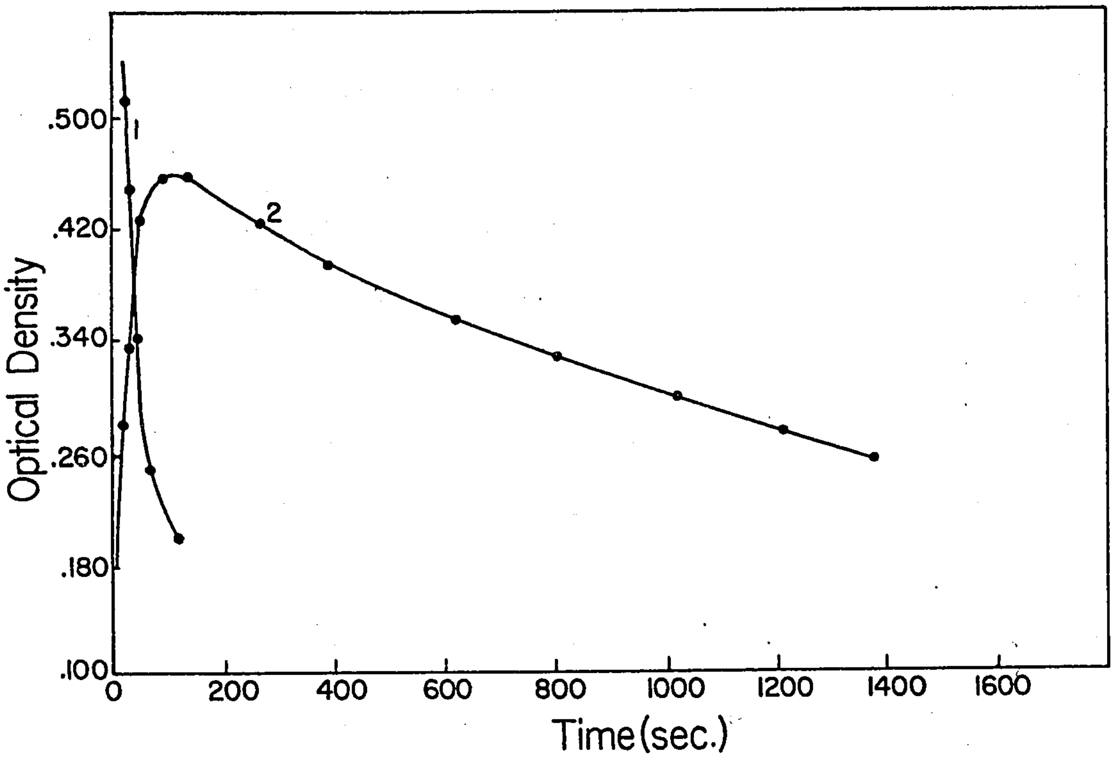


Fig. 9 - The reaction of permanganate (3×10^{-4} M) with oleate ion (3×10^{-4} M) at pH 12.2. Plot 1, optical density at 525 mμ. Plot 2, optical density at 600 mμ.

in a mixture containing initially 0.015 mM of permanganate, 0.015 mM of oleate ion and 0.25 mM of telluric acid in 50 ml. of solution at pH 12.2 and 25°. This data comprised confirmation of the work of Drummond and Waters (57) since the rapid initial consumption of permanganate was accompanied by a rapid formation, of manganate. Superficially, at least, it was quite clear how this result might suggest that, under the conditions of this reaction, the initial step was a one-electron exchange. However, when the data of Fig. 9 were recalculated using equations 36-38, page 90, and then were replotted in Fig. 10 as mole fraction of manganese against time, an entirely new effect was observed.

Manganate was indeed an initial product of the reaction, but at the same time, an appreciable concentration of manganite was also produced. There are only three possible explanations for this result. Permanganate could be reduced initially by a three-electron exchange, or manganate could be formed and subsequently reduced to manganite, or manganate and manganite could both be produced as the result of secondary reactions. The first of these possibilities is highly improbable and can certainly be ruled out. The second can also be ruled out since, in the same time period (see page 270), there was effectively no reaction with manganate. Therefore, manganate and manganite must both be produced as the result of secondary reactions. These can only be reactions involving hypomanganate.

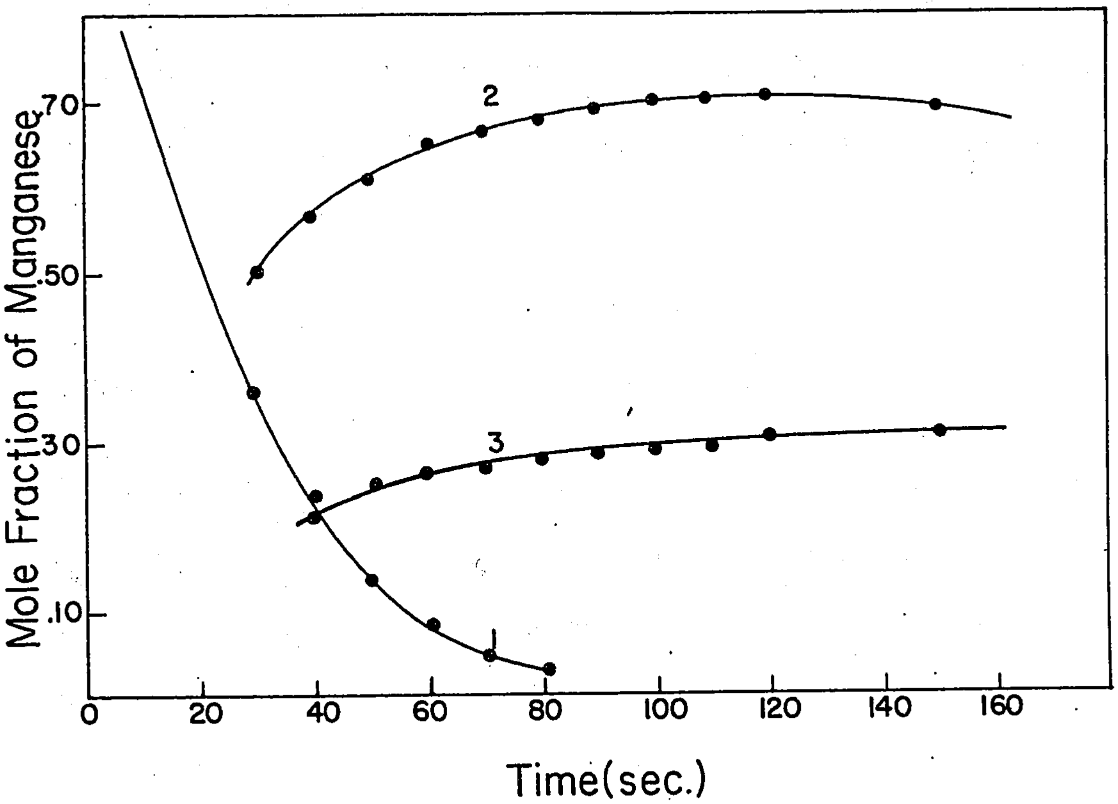


Fig. 10 - A replot of the data of Fig. 9 in terms of mole fraction of manganese. Plot 1, Mn(VII). Plot 2, Mn(VI). Plot 3, Mn(IV).

As was shown previously, hypomanganate can undergo two reactions in the pH region 12-14, and both of these are fast, since the addition of permanganate to hypomanganate in this pH region yields both manganate and manganese dioxide,

(43)... $\mathrm{Mn(V)} + \mathrm{Mn(VII)} \rightarrow 2\,\mathrm{Mn(VI)}$

(46)... $2\,\mathrm{Mn(V)} \rightarrow \mathrm{Mn(IV)} + \mathrm{Mn(VI)}$.

The results shown in Fig. 10 are then satisfactorily explained by the assumption that hypomanganate is the initial reduced species in the reaction, and that formation of this species is followed by reactions 43 and 46, with 43 slightly more rapid under the conditions of Fig. 10. Since the yield of manganite is appreciable, the rates of the two reactions, 43 and 46, are of the same order of magnitude.

Now, if this reasoning is correct, changes in the reaction conditions should affect the relative yields of manganate and manganite according to the known properties of hypomanganate. For example, since the stability of hypomanganate is increased by an increase in the alkalinity, then an increase in the alkalinity with all other conditions constant should decrease the rate of reaction 46, resulting in a decrease in the proportion of manganite. Likewise, an increase in the initial concentration of permanganate at constant pH should increase the proportion of hypomanganate which reacts by way of reaction 43, and an increased yield of manganate should be obtained.

As is seen by the data shown in Fig. 11 and Fig. 12, these

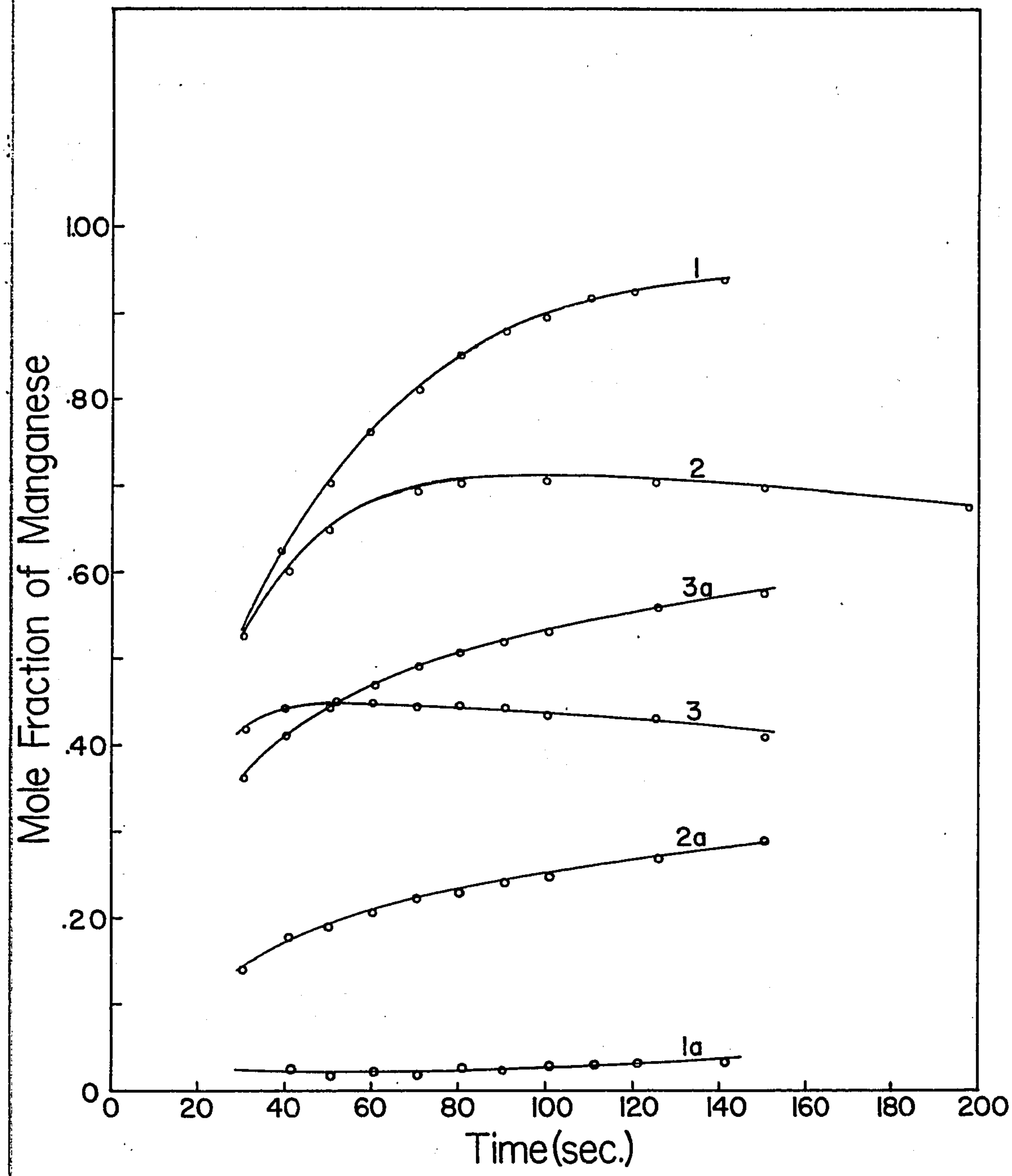


Fig. 11 - Effect of pH on the yields of Mn(VI) and Mn(IV) in the reaction of permanganate (3.09×10^{-4} M) with oleate ion (3×10^{-4} M) at 25°. Plots 1, 2 and 3 are the yields of Mn(VI) at pH 13.0, 12.5 and 12.0, respectively. Plots 1a, 2a and 3a are the yields of Mn(IV) obtained under the conditions of plots 1, 2 and 3.

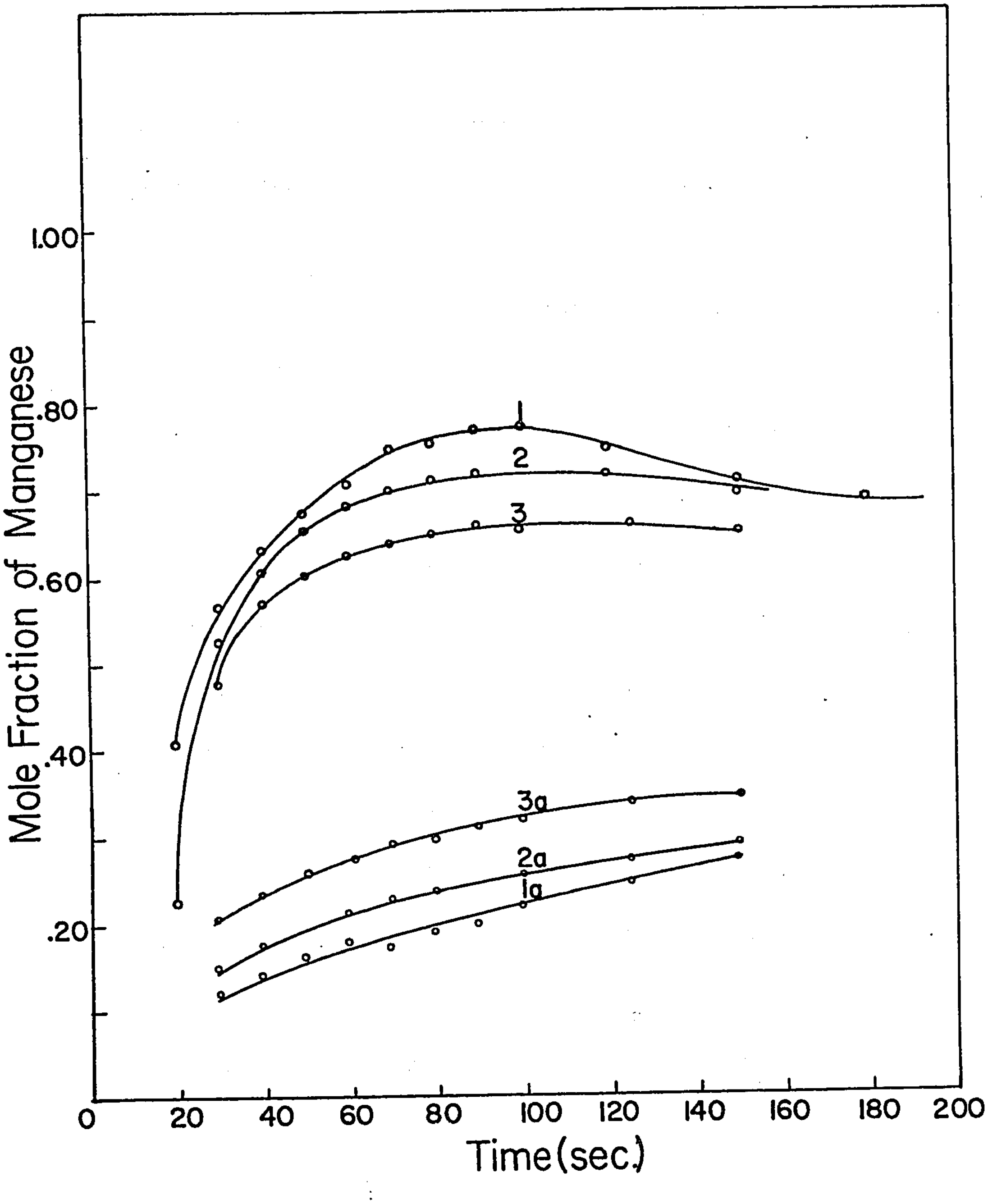


Fig. 12 - Effect of variation of permanganate concentration on the yields of Mn(VI) and Mn(IV) from the oxidation of oleate ion (3×10^{-4}M) at pH 12.5. Plots 1,2 and 3 represent the yields of Mn(VI) from initial permanganate concentrations of 5.10×10^{-4}M, 3.09×10^{-4}M and 1.55×10^{-4}M, respectively. Plots 1a, 2a and 3a represent the yields of Mn(IV) obtained under the conditions of plots 1,2 and 3.

expectations were entirely substantiated. Variation of the pH caused a large change in the relative amounts of manganate and manganite, the trend being in the proper direction; that is, decreasing amounts of manganite with increasing pH. Also, as expected, the yield of manganate was increased by an increase in the initial concentration of permanganate.

The data of Figs. 10-12, therefore, are taken as unequivocal evidence that the initial reaction of permanganate with oleate ion in this pH region involves a two-electron transfer. The success of this method of analysis is due primarily to the facts that in the pH region 12-13, and using these concentrations of permanganate and oleate ion, the rates of reactions 43 and 46 are of the same order of magnitude, and these, in turn, are of the same order of magnitude as the initial reduction of the permanganate to hypomanganate.

The fact that hypomanganate does not oxidize olefins (108; see also page 130) supports these conclusions. If the hydroxylations by permanganate and manganate had proceeded by way of one-electron exchanges, it would have been anticipated that hypomanganate would also hydroxylate olefins. However, if the oxidations by permanganate and manganate proceeded by way of two-electron exchanges, then a hypomanganate-olefin reaction would yield trivalent manganese as the initial reduced stage. Since not even the strong inorganic reducing agents such as sodium sulphite or iodide ion will reduce manganese beyond the tetravalent stage in alkaline medium, it seems rather improbable that this reduction to a valence state lower than four can be accomplished by an organic reductant. Hence, if these reactions can proceed only via initial two-electron exchanges, then hypomanganate, lacking a mechanism, should not attack an olefin.

C. Extension of this Analytical Method to Other Systems

The method described above for the determination of the number of electrons exchanged in the initial step of the permanganate-olefin reaction was successfully extended to the oxidation of the 9,10-ketohydroxystearic acids by alkaline permanganate. This work is discussed on page 265 . An attempt to extend the method to the oxidation of alcohols by alkaline permanganate was unsuccessful, but served to stress the fact that the combination of three fast reactions was necessary for successful application of this method of analysis.

In his study of the oxidation of benzhydrol by alkaline permanganate, Stewart (8; see page 20) obtained evidence in support of a mechanism in which the initial step was the transfer of a hydride ion to the permanganate, to form hypomanganate. It was, therefore, anticipated that application of the method described above to the oxidation of benzhydrol by permanganate would provide additional support for the mechanism adduced by Stewart. However, the rate of this reaction was not great enough to give satisfactory results, even when a saturated solution (sevenfold molar excess of benzhydrol) was employed. Thus, even at pH 12.0, the reduction of permanganate to manganate was quantitative. However, using these reaction conditions, the reaction was at least twenty times slower than the reaction with the olefin at this pH. This comparatively slow initial reduction of permanganate means that the hypomanganate would be produced during most of the reaction in the presence of a large excess of permanganate; the oxidation to manganate would then be favoured over the disproportionation reaction.

No such solubility problem existed in the oxidation of ethyl alcohol, and by employing a 350-fold excess of this alcohol, it was possible to reduce the half-life of permanganate to about ten seconds. However, an additional problem arose here, in that the intermediate product (presumably acetaldehyde) should readily undergo oxidation by manganate (compare the results of Wiberg and Stewart, page 18). Manganate was, indeed, the initial product of the reaction, but was rapidly reduced to the tetravalent stage. Pending further work, no conclusions can be drawn from experiments with this alcohol but, as the data of Fig. 13 show, it may prove significant that no manganite was detected until after the secondary oxidation by manganate had commenced.

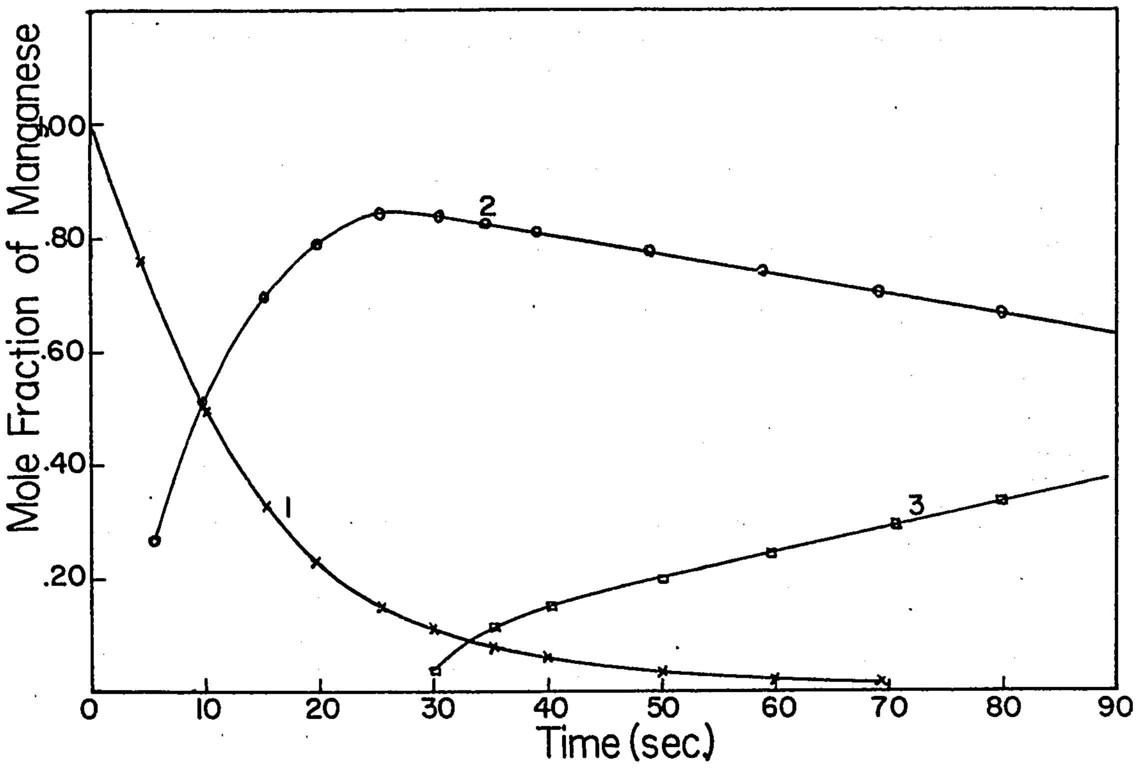
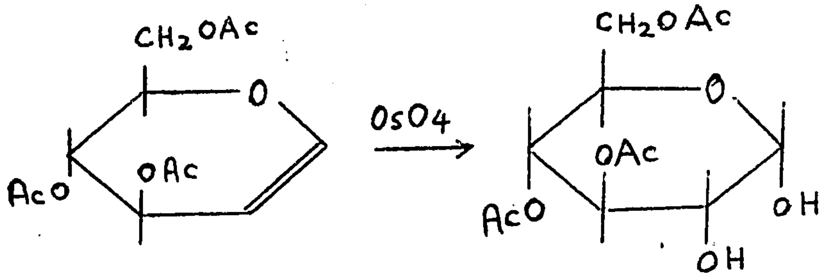


Fig. 13 - The oxidation of ethyl alcohol (0.085 M) by permanganate (2.6×10^{-4}M) in the presence of tellurate (5×10^{-3}M) at pH 12.5 and 25°. Plot 1, Mn(VII). Plot 2, Mn(VI). Plot 3, Mn(IV).

D. Stereochemistry of the Hydroxylation Reaction and Route of the Hydrolysis of the Intermediate

The facts that the hydroxylation reaction involves an initial two-electron exchange, and a direct transfer of oxygen from the permanganate to the olefin (81) comprise strong evidence in favour of the cyclic intermediate. This evidence becomes overwhelming when the mass of experimental data on the stereochemistry of the reaction is also considered. In addition to the cis-stereospecificity of the reaction, there is also a steric cis-effect due to the formation of the five-membered ring of the hypomanganate intermediate. The effect may be illustrated by a consideration of the reaction of some unsaturated sugar acetates with osmium tetroxide, which is known to proceed by way of a cyclic intermediate(41). Hockett and co-workers (138) have found that the oxidation of glycal with osmium tetroxide leads to the glucose derivative rather than the mannose derivative because of steric interaction with the C3 acetoxyl group,

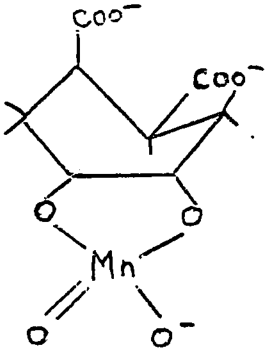


Wieman and Gardan (139) have found the same effect in the hydroxylation of cyclic α-unsaturated alcohols with osmium tetroxide. Permanganate oxidations follow similar reaction routes. For example, the hydroxylations of 3-ethoxycyclohexene (140) and 3-methoxycyclohexene (141) by permanganate gave in each case the glycol with the arabo configuration. There was no trace of the compounds with the ribo configuration. Hydroxylation of bicyclo [2.2.2]-oct-2-ene with permanganate and with osmium tetroxide (142) gave the same glycol, reported to have the exo (less hindered) configuration. Likewise, the hydroxylation of norbornylene by permanganate yielded the glycol with the exo configuration (143).

The hydroxylation of cis-4-cyclohexenedioic acid was studied in the present work. The hydroxylation of this compound is of interest for two reasons. First, the configuration of the glycol should be easy to prove since formation of the all cis compound should result in lactonization (144). Secondly, the proximity of the two carboxylate ions to the double bond could affect the route of the hydrolysis of the cyclic ester intermediate.

This olefin yielded the glycol with the cis-anti-cis configuration when treated with permanganate in the pH region 12-14. The hydroxyl groups were shown to be free, since the compound readily consumed the theoretical amount of acid periodate. This is the configuration expected for this compound, since the cis-syn-cis compound could be formed only by way of a highly strained intermediate.

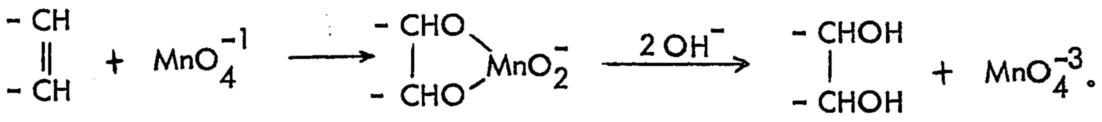
The fact that no worker has ever reported the isolation of a trans glycol from the hydroxylation of an olefin by permanganate in aqueous medium shows that hydrolysis of the ester intermediate occurs at the Mn – O bonds. If hydrolysis occurred at the C – O bonds, a carbonium ion or incipient carbonium ion intermediate would be anticipated and some trans diol would result. This is particularly true in the case of oxidation of the compound, cis-4-cyclohexenedioic acid. The intermediate product of this reaction,



contains a carboxylate ion in very close proximity to a carbon centre of the ester, and this would therefore be able to readily participate in any cleavage of the C – O bond. Since this did not occur, it may be concluded that the cyclic manganese intermediate undergoes normal ester hydrolysis.

E. The Mechanism of the Hydroxylation Reaction

Since the cyclic intermediate is a short-lived species, the curves in Figs. 10-12 undoubtedly refer to inorganic manganese rather than to manganese ester intermediates. This assumption enables some answer to be given to the question of whether the pentavalent intermediate is hydrolyzed directly, or is oxidized to a manganate intermediate before being hydrolyzed. At the lower pH studied, 12-12.5, the detection of appreciable amounts of manganite shows that hypomanganate itself must have been present in the reaction mixture. At the higher pH (12.5-13), the formation of a high proportion of manganate can be due either to hydrolysis of a manganate intermediate or to a rapid oxidation of initially-formed inorganic hypomanganate. There is no way of differentiating between these two possibilities, although it is likely that a tenfold increase in the hydroxyl ion concentration will favour hydrolysis of the cyclic pentavalent intermediate, followed by oxidation of the inorganic hypomanganate,

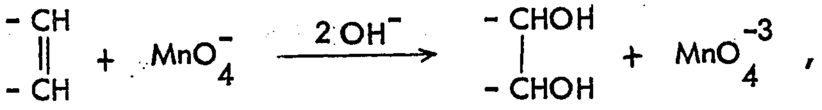


The mechanism of the hydrolysis was not studied. Presumably both water and hydroxyl ion can cause hydrolysis of the cyclic intermediate.

3. The Mechanism of Ketol Formation. A Kinetic Study of the Oxidation of Oleate Ion by Permanganate in the pH Region 8-11

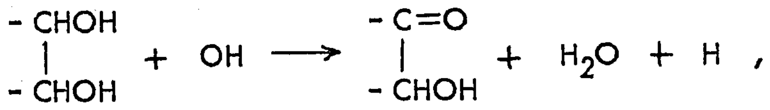
The oxidation of an olefin to a ketol requires the transfer of four electrons to the oxidizing agent. Since the permanganate is reduced by only three valence units, at least two molecules of permanganate must be involved in this reaction. The results already discussed indicate that the transfer of two of these four electrons is associated with the formation of the cyclic ester intermediate. The problem was to determine the route of the subsequent reactions which lead to the formation of the two ketols.

As King (3) pointed out, and as the present study confirmed, the ketol did not result from further oxidation of an initially-formed glycol, since the glycol was not oxidized under the conditions of ketol formation. The possibility remained that the ketol was formed as the result of oxidation of initially-formed glycol by the disproportionation products of the initial hypomanganate intermediate. That is, the following could be considered a plausible route for the reaction, in view of the behaviour of hypomanganate when it disproportionates,



$$\begin{matrix}-\mathrm{CH}\\ \|\\ -\mathrm{CH}\end{matrix} + \mathrm{MnO}_4^- \xrightarrow{2\,\mathrm{OH}^-} \begin{matrix}-\mathrm{CHOH}\\ |\\ -\mathrm{CHOH}\end{matrix} + \mathrm{MnO}_4^{-3},$$

(47)... $$MnO_4^{-3} + H_2O \longrightarrow HMnO_4^{-3} + OH ,$$



$$\begin{array}{c}-CHOH\\ |\\ -CHOH\end{array} + OH \longrightarrow \begin{array}{c}-C{=}O\\ |\\ -CHOH\end{array} + H_2O + H ,$$

particularly since the Fenton reagent, which is believed to contain the free hydroxyl radical (145, 146), is known to oxidize ethylene glycol to glyoxal and glycerol to glyceraldehyde (147).

A reaction route of this kind was ruled out by oxidizing mixtures containing various proportions of oleate ion and dihydroxystearate ion. In these reaction mixtures, varying amounts of hypomanganate (from the oxidation of the olefin) would be disproportionating in the presence of excess glycol and, if a reaction such as that shown in equation 47 occurred to any significant extent, the consumption of oxidant would differ from that expected on the assumption that the olefin was the sole reducing species. For glycol to olefin ratios from one to fifteen and using excess permanganate, the consumption of oxidant was always exactly equivalent to that expected on the basis that the olefin was the only reducing species; that is, the consumption was 4.0 equivalents of oxidant per mole of olefin, regardless of the glycol to olefin ratio. The ketol must, therefore, be formed by direct oxidation of the olefin, with no isolable intermediate stage. Since it was shown that the cyclic pentavalent ester is an intermediate in the reaction, the ketol may result from further oxidation of this intermediate.

Coleman, Ricciuti and Swern (85) studied the effect of pH on ketol formation and pointed out that the fate of the cyclic ester intermediate may depend on the competition for it between the permanganate and hydroxyl ions. As already pointed out on page 43, this rather obvious idea had occurred to other workers, but was without experimental proof.

The curves of Figs. 14–16 were obtained by plotting the consumption of oxidant versus time for the reaction of oleate and dihydroxystearate with permanganate. Since the oxidation of oleate at pH 9.3 gives a near-quantitative yield of the 9,10-ketohydroxystearates, the over-oxidation of the olefin shown in plot 1, Fig. 14, is a measure of the rate of oxidation of the ketohydroxystearate ions.

The data plotted in Fig. 14 show that, below pH 10, the oxidations of the ketols and the glycol were slow. The oxidations were also slow at pH 12. Therefore, since the oxidation of the oleate ion to these products was complete in 10-50 seconds, depending on the relative concentrations of olefin and permanganate, quantitative yields of the initial products should be possible by stopping the reaction after 1-2 minutes.

The results plotted in Fig. 15 show the effect of pH on the course of the oxidation of the oleate ion by a fourfold molar excess of permanganate ions. The proportions of glycol and ketol formed in the initial rapid oxidation

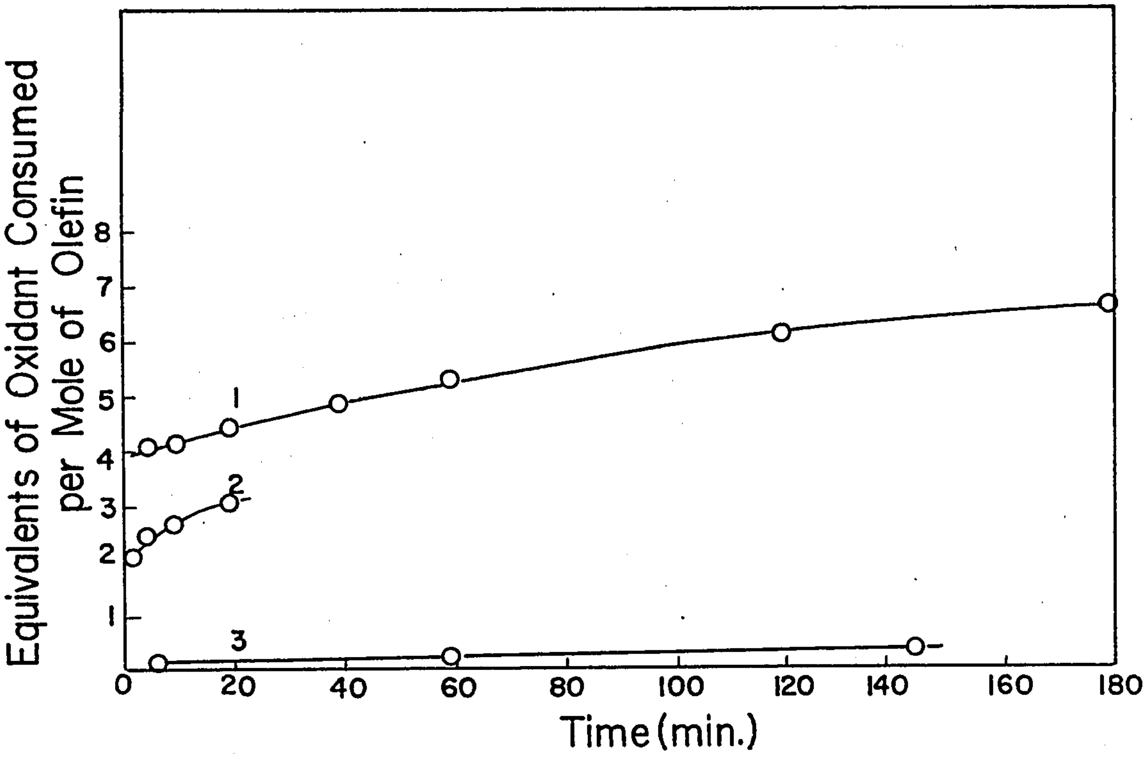


Fig. 14 – Extended oxidation of oleate ion (3×10^{-4}M) and dihydroxystearate ion (3×10^{-4}M) by permanganate (12×10^{-4}M). Plot 1, oxidation of oleate ion at pH 9.3. Plot 2, oxidation of oleate ion at pH 12.0 Plot 3, oxidation of dihydroxystearate ion at pH 9.5.

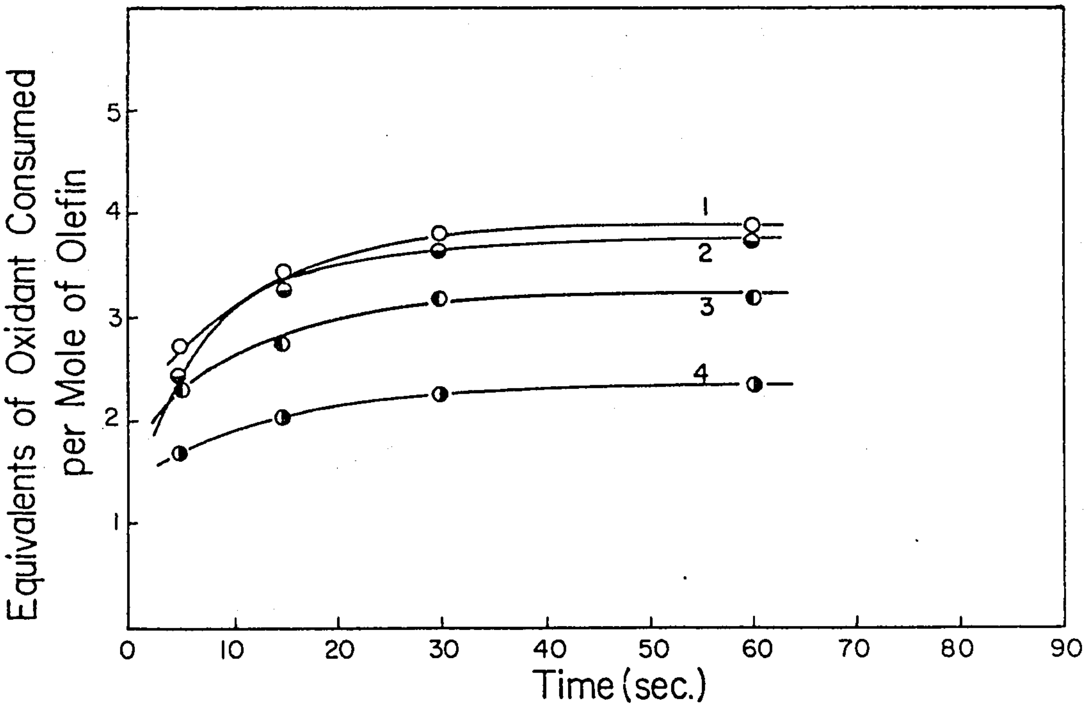


Fig. 15 - The oxidation of oleate ion (3×10^{-4}M) by permanganate (12×10^{-4}M) at pH 9.3 (Plot 1), 10.2 (Plot 2), 11.0 (Plot 3) and 12.0 (Plot 4).

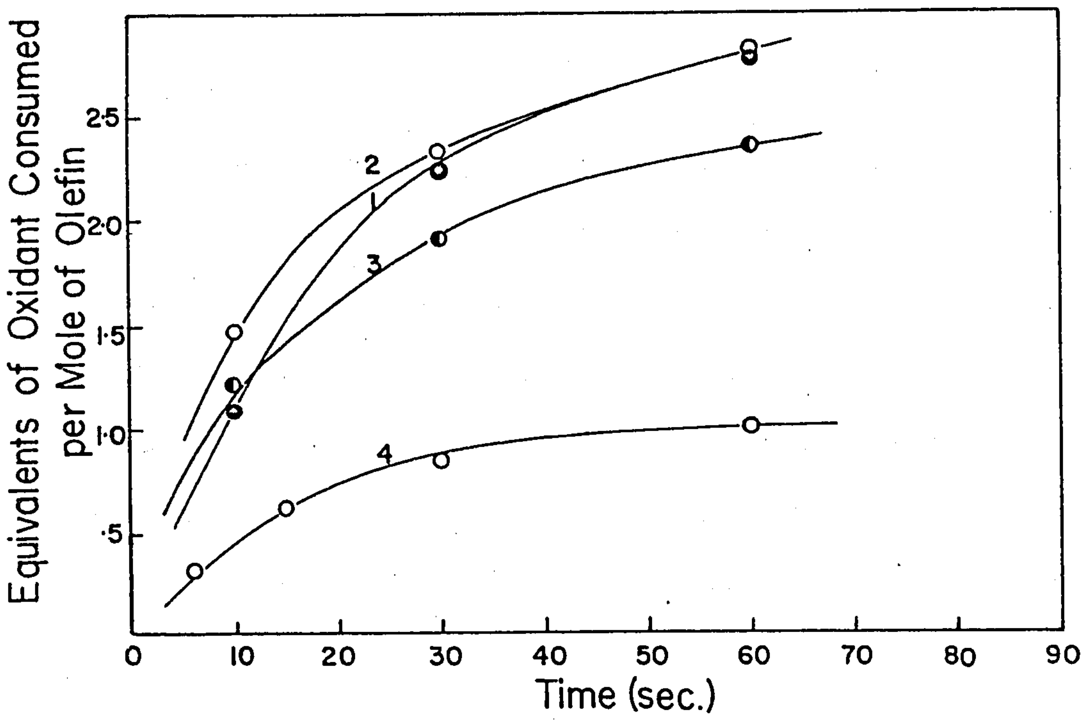


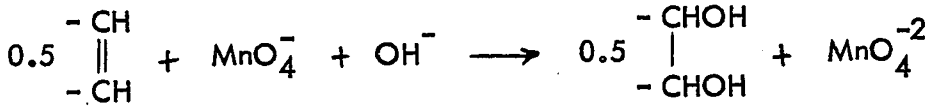
Fig. 16 - The oxidation of oleate ion (3×10^{-4}M) by permanganate (3×10^{-4}M) at pH 9 (Plot 1), 10 (Plot 2), 11 (Plot 3) and 12.2 (Plot 4).

were calculated using equation 48,

$$(48)\ldots \qquad 2a + 4(1 - a) = E ,$$

where a is the proportion of glycol, (1 - a) is then the proportion of the ketols and E is the consumption of oxidant in equivalents per mole of olefin. The value for E was taken as the amount of oxidant consumed after the initial rapid reaction, and corresponds to the horizontal portions of the plots in Fig. 15. The data indicate that, above pH 12, the initial product was glycol (only two equivalents of oxidant were consumed). On the other hand, at or below pH 10.2, substantially only the ketols were formed (four equivalents of oxidant were consumed).

The effects of both pH and permanganate concentration are illustrated by the data plotted in Fig. 16. It is seen that, when one mole of oxidant was available at pH 12.2 for the oxidation of a mole of oleate ion, only one equivalent of oxidant was consumed. The reason for this is that, as noted previously, manganate ions are stable at pH 12.2, and oxidize olefins only slowly as compared to permanganate (see page 270). Therefore, at this level of oxidant, only half of the olefin is oxidized by permanganate.



$$0.5\ \begin{matrix}-\mathrm{CH}\\ \| \\ -\mathrm{CH}\end{matrix} + \mathrm{MnO}_4^- + \mathrm{OH}^- \longrightarrow 0.5\ \begin{matrix}-\mathrm{CHOH}\\ | \\ -\mathrm{CHOH}\end{matrix} + \mathrm{MnO}_4^{-2}$$

However, below pH 11.5-12, manganate is not stable, and one mole of permanganate can provide three equivalents of oxidant for permanganate oxidation. (It is for these reasons that a fourfold molar excess of permanganate was used in the oxidations reported in Fig. 15). Since only three equivalents of oxidant are available per mole of olefin, and four equivalents of oxidant are required for ketol formation, all the permanganate should be consumed in the initial fast reaction, unless a greater than 50% yield of glycol is formed. Therefore, the fact that, at pH 11 (plot 3, Fig. 16), the oxidation slowed down before all the permanganate was consumed, indicates that at this pH the yield of glycol was greater than 50%. The rapid consumption of 2.35 equivalents of oxidant per oleate ion indicates that glycol was actually formed in 80% yield. Plot 3 of Fig. 15 illustrates the effect of the permanganate concentration on the yield of glycol at this pH. It is seen that 3.2 equivalents of oxidant were consumed in the oxidation of the oleate ion. Thus, using equation 48, the yield of glycol was 40% as compared to the 80% yield when the initial concentration of permanganate was one-quarter as great.

The results discussed in the foregoing paragraphs are summarized in Table XV, and they illustrate rather well the competition between the hydroxyl and permanganate ions for the initial intermediate of the reaction.

TABLE XV

Apparent Effect of Permanganate and Hydroxyl Ion Concentrations on the Route of Oxidation of Oleate Ion

Initial pH	Ratio of the $[OH^-]:[MnO_4^-]:[olefin]$ Concentrations	Product(s)
12	33:4:1	90% glycol
	33:1:1	90% glycol
11	3:1:1	80% glycol; 20% ketols
	3:4:1	40% glycol; 60% ketols
10	1:3:3	uncertain since the permanganate was completely reduced
	1:12:3	14% glycol; 86% ketols

These conclusions were confirmed by the results of preparative experiments conducted at 0–10°. Since the ketols were not rapidly oxidized by excess permanganate below pH 12, the olefin could be treated with excess permanganate with no complications due to secondary reactions. The oxidations were stopped after 90 seconds and the products were isolated and analyzed. In agreement with the reasoning behind the use of fast reaction times, the yield of (ketol + glycol) was 90–95% in all of the experiments.

Using stoichiometric quantities of permanganate, and reaction conditions as described on pages 39 and 41, other workers obtained yields of the ketols of 40-45% (3) and 55-75% (85). However, by employing an excess of permanganate and a 0.1% concentration of olefin, the yield of the ketols was raised to 87% at pH 10.2 and 88% at pH 9.3.

An attempt to extend these reaction conditions to high concentrations of the reactants such as were employed by Coleman, Ricciuti and Swern (85) led to a different set of products. The results of this experiment and their implication on the mechanism of the reaction are best presented in a later part (see page 251).

Another striking example of the competition between the oxidizing agent and hydroxyl ions for the initial pentavalent intermediate was seen in the effect of added periodate on ketol formation. As reported on page 40, Lemieux and von Rudloff (32) isolated ketols in good yield from the periodate-permanganate oxidations of two olefins at pH 7.6. In addition, they showed that under their reaction conditions, manganate was quantitatively oxidized by periodate to permanganate. Since it was now established that hypomanganate was the initial reduced stage in the oxidation of olefins by permanganate at pH 12, it was anticipated that hypomanganate would also be oxidized by periodate to permanganate. This was confirmed. The oxidation of hypomanganate to permanganate by periodate was quantitative and rapid, even at pH 6.8. In the absence of periodate, hypomanganate was instantly hydrolyzed to permanganate and manganese dioxide in the pH region 6.8-10. Therefore, the rate of the oxidation of hypomanganate by periodate must be very great and must be at least an order of magnitude greater than the rate of the hydrolysis of this valence state. The same relative reactivities should hold for a hypomanganate ester intermediate. Since, as demonstrated above, the product of the oxidation of the olefin depends on the result of the competition between the hydrolysis and oxidation reactions of the initial pentavalent intermediate, it is clear that formation of ketols at a given pH should be favoured in the presence of excess periodate. The product of the reaction could conceivably be changed from glycol to the ketols, even at pH 12. At pH 12, in the absence of periodate, the product of the oxidation of oleate ion was 9,10-dihydroxystearic acid (96%). However, repetition of the reaction at the same pH using a system containing periodate, permanganate and olefin in the molar proportions respectively, 2.0 : 0.25 : 1.0, gave the 9,10-keto-hydroxystearic acids in 70% yield as the only insoluble products isolated after a 30 second reaction time.

A. Reduction of Permanganate to Manganite and the Manganite-Tellurate Complex

As the data plotted in Fig. 2 show, tellurate ion, by virtue of its complexing action on tetravalent manganese (see page 85), had a marked effect on the optical densities of reaction mixtures containing permanganate and oleate ions, and indicated that it might be possible to establish a photometric method for studying the kinetics of the reaction. However, the kinetics were extremely complex in the presence of tellurate ion. The effect apparently was only a kinetic one, since the quantitative character of the products was unchanged. In view of the complexity introduced by the addition of telluric acid, it was also necessary to study the kinetics of the reaction in the absence of the complexing agent.

Though it is generally believed that tetravalent manganese is insoluble, either as the result of rapid hydrolysis of the manganite ion (equation 45), or as the result of a polycondensation process which favours the ultimate separation of pyrolusite, a three-dimensional polymer (52), under certain conditions this valence state can exist as a stable colloid (148). A number of the earlier workers studied the properties of this colloid, the work of Witzemann (148) being particularly detailed. The colloid is readily prepared by the action of various organic and inorganic reducing agents on neutral permanganate and is stable in the absence of added acids or salts. Homogeneous solutions were readily prepared in the present work from the action of permanganate (3×10^{-4}M) on oleate ion (3×10^{-4}M), and these dark brown reaction mixtures presumably contained the colloid. The spectra of solutions containing manganite and the manganite-tellurate complex are shown in Fig. 1, plots 5 and 4, respectively.

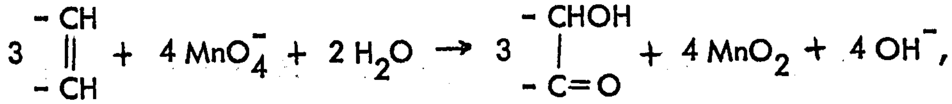
Since these solutions containing colloidal manganese dioxide were found to obey Beer's Law at 525 mμ, it was possible, using equation 31, to calculate the concentration of permanganate at any given time. A check on the results obtained by the photometric method was made by following the reaction using a titrimetric procedure.

B. Order of the Reaction in the Absence of Tellurate Ion

The data obtained at pH 9.0-9.5 from the photometric and the titrimetric procedures were treated in two different ways, and the four sets of results showed the reaction to obey second order kinetics — first order in olefin, and first order in permanganate ion. Satisfactory agreement between the two methods of treating the data was obtained, within the limits of experimental error.

It follows from the stoichiometric equation of the reaction,

(49)...



$$3\begin{array}{c}-\mathrm{CH}\\ \| \\ -\mathrm{CH}\end{array} + 4\,\mathrm{MnO_4^-} + 2\,\mathrm{H_2O} \rightarrow 3\begin{array}{c}-\mathrm{CHOH}\\ | \\ -\mathrm{C{=}O}\end{array} + 4\,\mathrm{MnO_2} + 4\,\mathrm{OH^-},$$

that Y, the molar concentration of olefin after time t, is given by

(50)...
$$Y = Y_o - 3(X_o - X)/4 = nX_o - 3(X_o - X)/4$$
$$= \left[(4n - 3)X_o + 3X\right]/4 \quad ,$$

where X_o is the initial molar concentration of permanganate, X the molar concentration after time t, and Y_o, the initial molar concentration of olefin, is nX_o. The second order rate expression for the reaction is given by

(51)...
$$v = -dX/dt = k_2[X][Y]$$
$$= k_2[X][(4n - 3)X_o + 3X]/4 \ .$$

Integration of this equation yields the rate equation

(52)...
$$\frac{4}{(4n - 3)X_o} \ln\left[\frac{(4n - 3)X_o + 3X}{4nX}\right] = k_2t \ ,$$

where k_2 is then the second order rate constant in litres $\text{moles}^{-1}\text{sec.}^{-1}$

When the rate of the reaction was followed titrimetrically, the expressions

$$X_o = V_o/5$$

and

$$X = (V_t - 2V_o/5)/3$$

were substituted into equation 52, where V_o (ml.) was the initial thiosulphate titration and V_t was the titration after time t.

The results shown in Table XVI represent the effect of variation of the permanganate to olefin ratio on the reaction at 24.8° and an initial pH of 9.2. The reaction mixtures were not buffered for reasons which will become evident later on. The data were obtained using the titrimetric procedure.

The fact that the calculated second order rate constant remained constant during a run demonstrates that the overall reaction is indeed second order. Since the constancy of k_2 during a run was nearly independent of the relative proportions of permanganate and olefin, the kinetics of the reaction are satisfactorily accounted for by equation 52, and the reaction, therefore, is first order in olefin and first order in permanganate.

The data in Table XVII were obtained using the photometric procedure and the same reaction conditions; that is, pH 9.2 and 24.8°. The constancy of k_2 during the first 75% of reaction for three different concentrations of olefin confirms the conclusion that the reaction is first order in olefin and first order in permanganate. In addition, the rate constant for the reaction of permanganate (3×10^{-4}M) with oleate ion (3×10^{-4}M) was the same using the photometric procedure (268 ± 5) and the titrimetric procedure (257 ± 14), within the limits of experimental error.

TABLE XVI

The Reaction of Oleate Ion (3×10^{-4}M) with Permanganate at pH 9.2 and 24.8°

Time (sec.)	Titration (ml.)	$f_a \times 10^3$*	k_2
(a) Initial permanganate concentration, 3×10^{-4}M.			
0	7.00	-	-
5	5.83	8.22	252
10	5.16	7.70	237
20	4.31	8.01	246
40	3.48	9.01	277
60	3.19	8.86	272
		$f_b \times 10^3$**	
(b) Initial permanganate concentration, 12×10^{-4}M			
0	28.22	-	-
10	24.38	38.4	175
15	23.65	39.1	178
30	22.87	37.5	171

---

* $f_a = 2.303/t \log \left[3(V_t - V_o/5)/4(V_t - 2V_o/5)\right]$

** $f_b = 2.303/t \log \left[(V_t - 2V_o/5)/3(V_t - 4V_o/5)\right]$

TABLE XVII

The Reaction of Oleate Ion with Permanganate (3×10^{-4}M)

at pH 9.3 and 24.8°

Time (sec.)	Optical Density	X ($\times10^{4}$M)	$f_c \times 10^{3}$ [a]
(a) Initial concentration of oleate ion, 1.5×10^{-4}M			
22	.735	2.06	5.55
30	.700	1.82	5.77
40	.678	1.72	5.39
50	.659	1.61	5.27
60	.628	1.42	6.31
70	.608	1.30	7.10
80	.595	1.22	7.72
90	.588	1.18	7.87
100	.579	1.12	8.73
			$f_d \times 10^{3}$ [b]
(b) Initial concentration of oleate ion, 3.0×10^{-4}M			
20	.508	1.03	8.77
30	.449	0.72	8.62
40	.408	0.51	8.85
50	.382	0.37	8.94
60	.364	0.28	9.05
70	.350	0.21	9.26
80	.342	0.17	9.14
			$f_e \times 10^{3}$ [c]
(c) Initial concentration of oleate ion, 12.0×10^{-4}M			
20	.305	0.27	48.9
30	.262	0.07	52.7
40	.252	0.01	61.0

---

[a] $f_c = 1/t \log\left[(3X - X_o)/2X\right]$; [b] $f_d = 1/t \log\left[(3X + X_o)/4X\right]$

[c] $f_e = 1/t \log\left[(13X_o + 3X)/16X\right]$

The order of the reaction was also determined by the half-time method. Using this procedure, when the initial concentrations of the two reactants are the same,

(53)... $$\tau \propto a^{1-n} ,$$

where a is the initial concentration of the two reactants, and τ is the time when a given fraction of the reaction has been completed (149). In most of the runs, the reaction was too fast to permit direct determination of the half-life of the reaction; when necessary, this was obtained by extrapolation of the concentration-time plots. The two-thirds time of the reaction could be measured directly, and the order was determined using the two-thirds time as well.

It follows from equation 53 that

(54)... $$\log\tau = \log C + (1 - n)\log a ,$$

and the plot of $\log\tau$ against log a should be linear with slope $1 - n$. The results of experiments conducted using this method of treating the data are shown in Table XVIII and the appropriate data have been plotted in Fig. 17 and Fig. 18.

The slope of the straight line of Fig. 17, determined by the root mean square method, was -1.01 ± 0.10. Hence the order of the reaction, determined by the photometric procedure, is 2. The slopes of the two lines of Fig. 18 were almost the same, indicating that the order of the reaction was constant for at least 67% of the reaction. The slopes of the two lines of Fig. 18 were -0.98 and -1.11 for the half-life plot and the two-thirds life plot respectively, and the order of the reaction was, therefore, 2.05 ± 0.06.

To complete this work, it was necessary to show that equation 53 which, for $n = 2$, leads to the expression $\tau \propto X_o^{-1}$ when there is unit stoichiometry, was also valid for a reaction such as the conversion of oleate ion to ketol. This could be readily accomplished. If we consider equation 52, the half-time, for $X_o = Y_o$, is given by

$$\tau_{\frac{1}{2}} = 1/k_2 X_o \; 4 \ln 5/2 \text{ , or } \tau_{\frac{1}{2}} \propto X_o^{-1}.$$

The two-thirds time, for $X_o = Y_o$, is given by

$$\tau_{2/3} = 1/k_2 X_o \; 4 \ln 3/2 \text{ , or } \tau_{2/3} \propto X_o^{-1}.$$

The fact that the two methods of obtaining the data gave numerical results which were in satisfactory agreement with each other and with the theoretical second order rate expression enabled the data obtained from reactions conducted in the presence of telluric acid to be accepted with some confidence.

TABLE XVIII

Order of the Reaction of Permanganate with Oleate Ion at pH 9.5 and 24.8°

Photometric Experiments

Initial Concentration of Reactants ($\times 10^4$M)	Two-thirds Life (sec.)
1.5	37.3
3.0	20.0
4.5	16.7*
6.0	14.3*
7.5	5.2*

Titrimetric Experiments

Initial Concentration of Reactants ($\times 10^4$M)	Half-life (sec.)	Two-thirds Life (sec.)
1.5	19.4	44.0
3.0	9.6	20.0
4.5	7.0	12.2
6.0	5.0	9.4

---

* Obtained by extrapolation of the concentration-time plot.

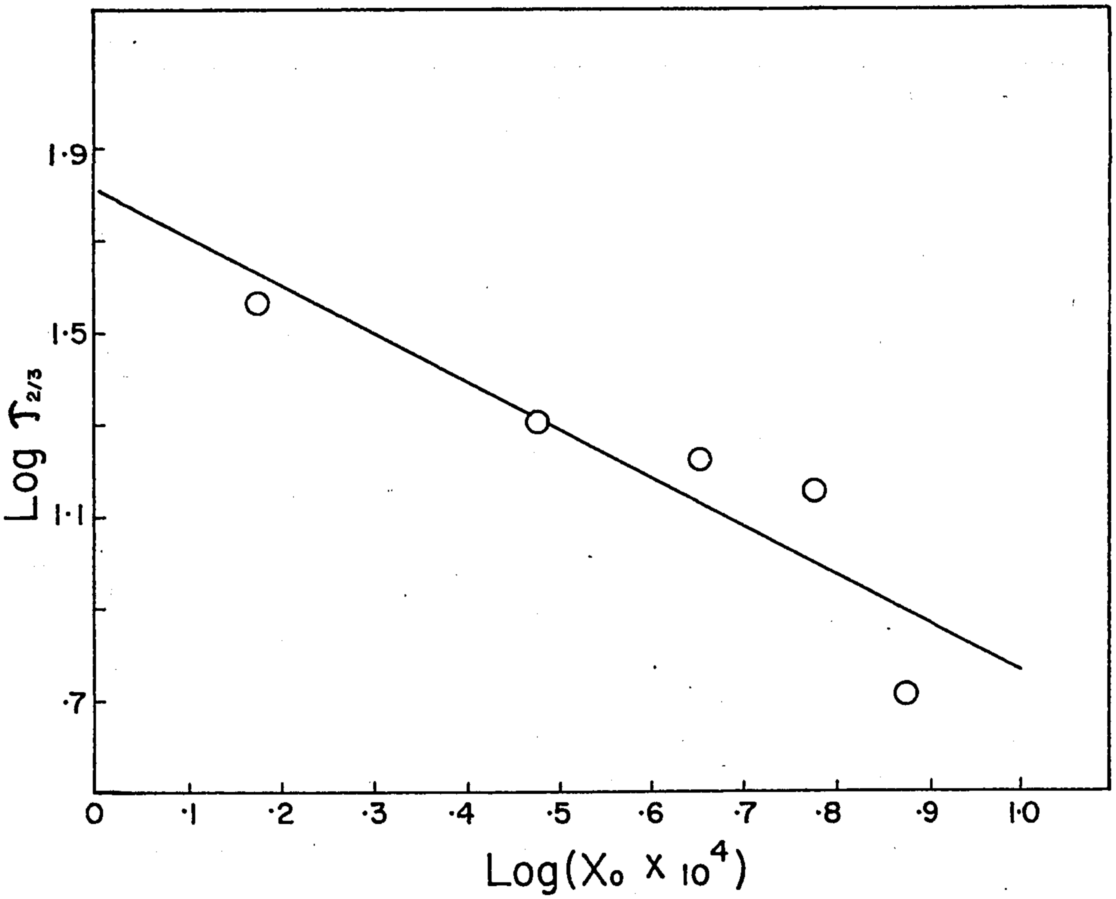


Fig. 17 – Order of the reaction of oleate ion with permanganate at pH 9.5 and 24.8°, determined photometrically using the two-thirds time procedure.

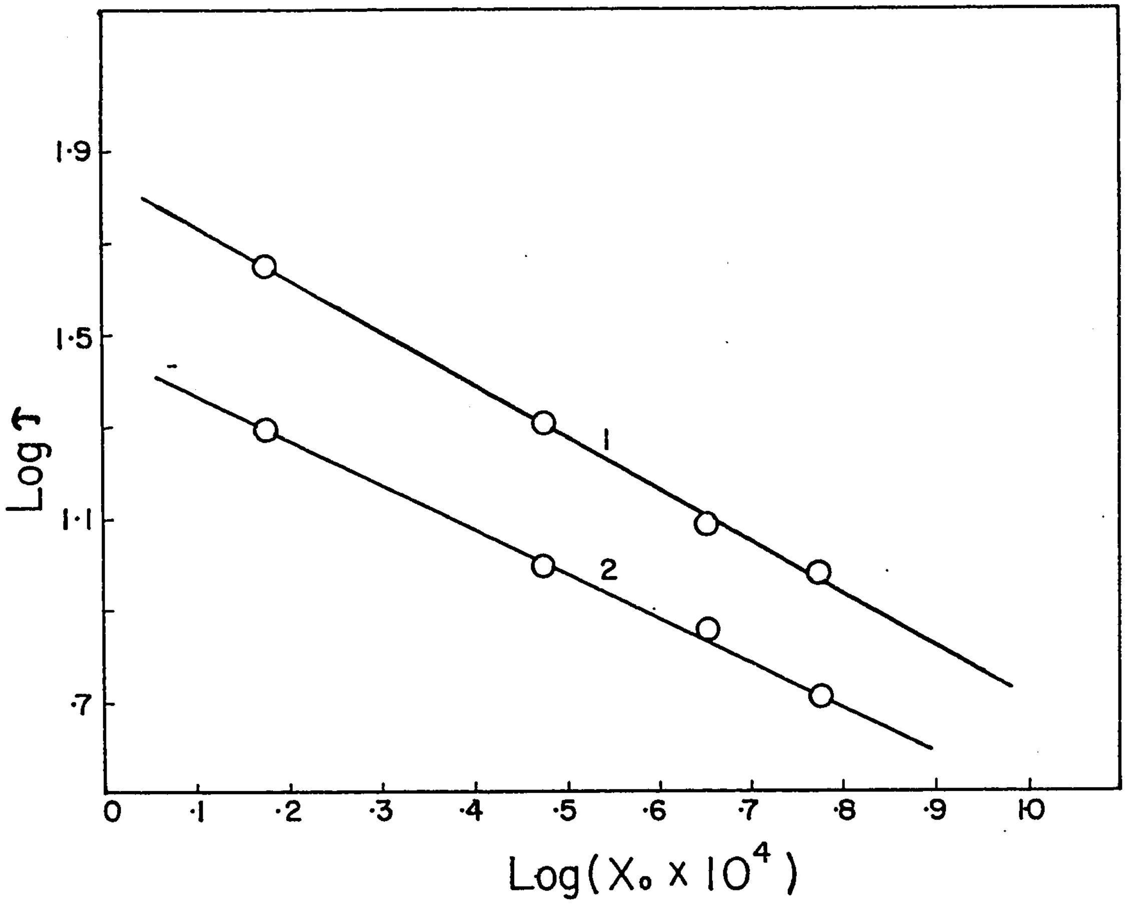


Fig. 18 – Order of the reaction of oleate ion with permanganate at pH 9.5 and 24.8°, determined using the titrimetric procedure. Plot 1, two-thirds time plot. Plot 2, half-time plot.

C. Kinetic Results in the Presence of Tellurate Ion

(i). Effect of Tellurate Ion on the Rate of the Reaction. In the presence of a large excess of tellurate ion, both the rate and the order of the reaction decreased. At constant pH, the time order of the reaction was clearly closer to one than to two. This can be seen from the detailed results of the two typical experiments which are summarized in Table XIX ; the values k_1 and k_2 in the last two columns represent the calculated first order and second order rate constants respectively.

Several methods of analyzing the data were tried, with varying success. The effects of the various concentration variables on the rate of the reaction were determined by the half time or the two-thirds time method. Concentration-time plots were drawn, the two-thirds time was estimated, and the proper functions were then plotted. The most common method of analyzing experimental data from a complex reaction requires a study of the effect of variation of the concentration of each component of the reaction mixture on the initial rate of the reaction. In this work, however, the initial part of the reaction could be obtained only by extrapolation of the concentration-time plots. The uncertainty of this extrapolation and of any subsequent estimate of initial rates precluded an accurate analysis of the results in this way.

TABLE XIX

The Reaction of Permanganate (3.18×10^{-4}M) with Oleate Ion (3×10^{-4}M) at 22.0° in the Presence of Tellurate (5×10^{-3}M)

Time (sec.)	Optical Density	X ($\times 10^{4}$M)	k_1^{*}	k_2^{**}
(a) Initial pH, 10.2				
10	.76	2.46	.0254	89
15	.63	1.93	.0322	126
20	.56	1.65	.0319	131
25	.51	1.44	.0315	131
30	.465	1.26	.0309	135
35	.425	1.09	.0304	146
40	.39	0.95	.0302	145
50	.33	0.70	.0302	159
60	.29	0.60	.0294	167
70	.257	0.40	.0294	182
80	.234	0.31	.0290	189
90	.215	0.23	.0290	199
100	.200	0.17	.0295	
125	.172	0.06		
150	.155			
175	.145			
(b) Initial pH, 8.75				
10	.75	2.42	.0270	97
15	.694	2.20	.0244	89
20	.635	1.95	.0244	92
25	.58	1.73	.0244	96
30	.535	1.54	.0240	99
35	.488	1.35	.0244	105
40	.46	1.24	.0235	108
50	.393	0.96	.0240	115
60	.350	0.79	.0242	118
70	.312	0.63	.0247	126
80	.285	0.52	.0226	130
90	.262	0.43	.0223	134
100	.245	0.36	.0219	137
150	.193	0.14	.0215	156
200	.172			

---

* Calculated from the expression, $k_1 = 2.303/t \log C_o/C$

** Calculated from the Expression, $k_2 = 2.303/t \log [(3X + X_o)/4X]$

The method which seemed to give the most satisfactory results involved extrapolation of the calculated second order rate constant (equation 52) to zero time. Since the variation of k_2 with time was less than the variation of X with time, extrapolation of the former plots could be made with more confidence, and were subject to less error. It was then assumed that the second order rate constant obtained in this way was the rate constant for a true second order reaction between the olefin and the permanganate, and was related to the initial rate by the following expression,

$$(55)\ldots \qquad v_o = -[dX/dt]_o = k_o [X_o][Y_o] ,$$

where k_o is 260 litres $\text{moles}^{-1}\text{sec.}^{-1}$, the second order rate constant in the absence of telluric acid, and X_o and Y_o were assigned from the data (see below). This assumption was considered valid since the telluric acid did not affect the route of the reaction, the yield of the 9,10-ketohydroxystearic acids being unchanged. Therefore, the initial stages of the reaction should involve a strictly second order reaction between the olefin and the permanganate.

The fact that a numerical value for the initial rate could be arrived at, even in this indirect manner, enabled numerical values to be given to some of the constants of the reaction. While the author admits that the data are necessarily rather crude, the effects described are real and the numbers arrived at should be correct at least to an order of magnitude. The author is, moreover, satisfied that these results are of a sufficiently novel character that, with suitable refinement of the experimental techniques, they may lead to a new experimental approach to the field of olefin complexes.

The data plotted in Fig. 19 show the effect of tellurate concentration on k_2^o , the apparent second order rate constant at zero time. K_2^o is related to v_o , the initial rate of the reaction, by the expression,

$$(56)\ldots \qquad v_o = k_2^o [X'_o][Y'_o] \quad ,$$

where $X'_o = Y'_o = 3 \times 10^{-4}M$. Equations 55 and 56 are actually identical. According to the above assumptions, the decrease in v_o with increasing tellurate concentrations was due to the fact that either the initial olefin concentration or the initial concentration of permanganate was lowered as a result of the addition of tellurate. That is,

$$X_o = X'_o \quad \text{and} \quad Y_o = k_2^o Y'_o / k_o \quad ,$$

or

$$X_o = k_2^o X'_o / k_o \quad \text{and} \quad Y_o = Y'_o \quad .$$

The data of Fig. 19 were obtained with a potassium oleate solution freshly-prepared from very pure oleic acid. It was necessary to employ a fresh solution of oleate ion for these determinations, since an aged solution, which had been exposed to the atmosphere to a considerable extent, gave considerable scattering of the experimental points, and the overall effect of tellurate ion was difficult to interpret.

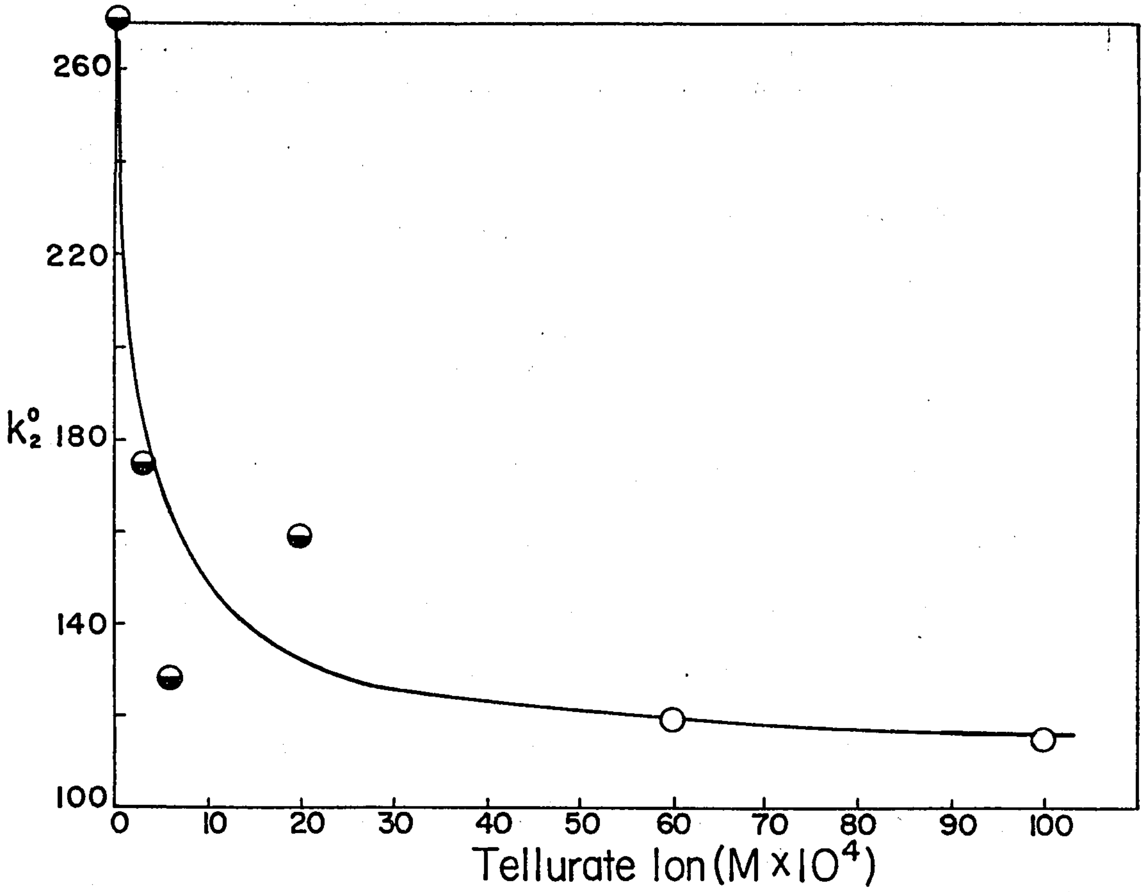


Fig. 19 - Effect of tellurate ions on the reaction of permanganate (3×10^{-4} M) with oleate ion at pH 9.5 and 24.8°. The oleate ion concentration was 3×10^{-4}M. The darkened circles indicate that the reaction followed second order kinetics at these tellurate concentrations.

This effect of tellurate ion was satisfactorily accounted for by the assumption that tellurate ion had complexed with one of the reactants; that is,

$$\text{olefin} + H_4TeO_6^{-2} \rightleftharpoons [\text{olefin} \cdot H_4TeO_6]^{-2}$$

or

$$MnO_4^{-1} + H_4TeO_6^{-2} \rightleftharpoons [MnO_4 \cdot H_4TeO_6]^{-3}. .$$

Formation of the complex would effectively reduce the initial concentration of the reacting species and thereby lower the initial rate of the reaction (equation 55). The equilibrium constant of complex formation was high, since the inflection in Fig. 19 occurred when a twofold excess of tellurate ion had been added, and the limiting rate was reached with a 7- to 10-fold excess of tellurate ion. Since the initial rate of the reaction did not drop to zero with high concentrations of tellurate ions then, under these conditions, either the rate of dissociation of the complex must have been somewhat greater than the rate of the subsequent reaction between permanganate and oleate ion, or the complex itself was entering into the reaction. This will be considered again later on.

A number of facts indicate that the complex formation is associated with the olefin rather than with the permanganate. The spectrum of the tellurate-manganese (IV) complex was distinctly different from that of manganite, while the spectra of solutions containing permanganate or manganate or hypomanganate and an excess of tellurate were quantitatively identical, both in the visible and in the ultraviolet regions, with the spectra shown in Fig. 1 ; the effect of tellurate ions on the spectrum of the olefin could not be readily determined because the tellurate ion shows a cut-off at 280 $m\mu$(150), while the olefin exhibits end absorption near 200 $m\mu$. Secondly (see pages 182 and 208, periodate and borate ions had the same effect on the permanganate-olefin reaction, but again, neither of these ions had an effect on the spectrum of permanganate. Thirdly, when the olefin was replaced by a different kind of reducing agent, e.g. alcohol, the kinetics did not seem to be affected by the tellurate ions, indicating the specificity of the complexing effect. (See page 143). Finally, a mechanism involving an olefin-tellurate complex was in satisfactory agreement with the observed kinetics for high concentrations of tellurate ion, while one involving a permanganate-tellurate complex was not.

(ii) Effect of Tellurate Ions on the Order of the Reaction

While the addition of tellurate ions to reaction mixtures containing initial permanganate and olefin concentrations of $3\times10^{-4}M$ caused a reduction in the rate, even for low concentrations ($3\times10^{-4}M$) of tellurate ion, the order of the reaction, as determined by application of equation 52 to concentration-time plots, remained unchanged, and good second order plots were obtained.

This is evident from the data shown in Table XX. The reduction in the order of the reaction (see Table XIX) became evident at tellurate ion concentrations near the point of inflection of the curve of Fig. 19, and it is apparent that the horizontal portion of Fig. 19 represents a different kind of kinetic effect.

TABLE XX

Effect of Tellurate Ion on the Reaction of Permanganate (3×10^{-4}M) with Oleate Ion (3×10^{-4}M) at pH 9.5 and 24.8°

	$[1/t \log (X_o + 3X)/4X] \times 10^4$		
Time (sec.)	For H_6TeO_6 3×10^{-4}M	For H_6TeO_6 6×10^{-4}M	For H_6TeO_6 20×10^{-4}M
20	5.79	4.46	5.48
30	5.94	4.60	5.50
40	5.94	4.76	5.55
50	5.91	4.91	5.53
60	5.80	5.00	5.55
70	5.86	5.00	5.56
80	5.83	5.02	5.63
90	5.67	5.07	5.52
100	5.59	4.98	5.45

(iii) Effect of Excess Tellurate Ion on the Order of the Reaction with Respect to Permanganate and Oleate Ion. A number of experiments were conducted at pH 9.5 and 24.8° in the presence of excess tellurate ($5\times10^{-3}M$), and the olefin and permanganate concentrations were varied in turn to determine the order of the reaction with respect to these components. These determinations proved unexpectedly difficult. The results were not easily reproducible, and different methods of analyzing the data led to differing results. However, in general, the order with respect to permanganate was always close to zero, and the order with respect to oleate ion was between 0.5 and 1.0.

The results of one series of runs to determine the order with respect to permanganate are shown in Table XXI. For application of the half-time method in this way, it was assumed that

$$\tau \propto 1/v_o \qquad \text{and} \qquad v_o \propto X_o^n \ ,$$

so that $\tau \propto X_o^{-n}$. Application of this relationship to the data of Table XXI gave an apparent order of 0.14±0.07.

The results of another series of runs to determine the order with respect to olefin are given in Table XXII. The order of the reaction, by the two-thirds time method was 0.45, while the order with respect to olefin using the calculated initial rates was 1.0.

TABLE XXI

Order of the Reaction with Respect to Permanganate in the Presence of Excess Tellurate (5×10^{-3}M)

$Y_o = 3.0 \times 10^{-4}$M

Concentration of MnO_4^- ($\times 10^4$M)	Half-life (sec.)	Two-thirds Life (sec.)
1.5	17.4	25.8
3.0	16.7	28.8
6.0	12.7	23.7

TABLE XXII

Order of the Reaction with Respect to Oleate Ion in the Presence of Excess Tellurate (5×10^{-3}M)

$X_o = 3.0 \times 10^{-4}$M

Concentration of Oleate Ion ($\times 10^4$M)	$\tau_{2/3}$ (sec.)	k_2^o	$v_o \times 10^8$
1.0	43.8	37	106
2.0	38.8	34	202
3.0	31.7	56	496
4.0	23.6	34	403
5.0	21.1	38	560

In connection with the mechanism arrived at on the basis of these results, it was of interest to see whether, the fractional dependence on permanganate concentration was in reality a complex dependence,

$$(57)\ldots \qquad v = \frac{A\left[\mathrm{MnO_4^-}\right]}{1 + B\left[\mathrm{MnO_4^-}\right]} \; .$$

The limited range of permanganate concentration used in the determination of the order of the reaction could conceivably lie on a small portion of the curve represented by equation 57, and would lead to a linear logarithmic plot giving a fractional dependence on permanganate concentration. However, the range of permanganate concentrations which could be employed in this work was limited both by the nature of the reaction being studied, and by the experimental techniques used to follow the reaction, and it was not possible to properly evaluate the plausibility of equation 57.

(iv) Effect of Hydroxyl Ion Concentration on the Rate of the Reaction. As the stoichiometric equation of the reaction (equation 49) implies, the pH should increase during a run owing to the liberation of hydroxyl ions during the reaction. Hence, a useful interpretation of the effect of pH on the rate of the reaction can be obtained only by working with buffered solutions. However, an additional complication arose here because the olefin complex discussed on page 176 was not limited to tellurate ion. The most satisfactory buffering agent in the pH region 8-10 is the sodium hydroxide-boric acid system, and a few runs were made in which the permanganate-oleate-tellurate reaction mixtures were buffered with boric acid. A decrease in the rate was obtained, and was greater than that observed with tellurate ion alone. The results of these experiments at pH 9.5 are shown in Table XXIII.

TABLE XXIII

Effect of Boric Acid-Sodium Hydroxide Buffer on the Reaction of Permanganate (3×10^{-4}M) with Oleate Ion (3×10^{-4}M) in the Presence of Tellurate Ions (5×10^{-3}M)

Concentration of Buffer (moles/litre)	k_2^o	v_o
0	120	1.08×10^{-5}
0.05	65	5.85×10^{-6}
0.10	55	4.95×10^{-6}

The effect of the added buffer cannot be an ionic strength effect, since it is in the opposite direction from that expected for a reaction in which ions of the same sign interact in the rate controlling step. The decrease in rate is believed due to complex formation between the olefin and borate ion, analogous to that described above for the tellurate ion.

Since the buffer affected the kinetics of the reaction in an adverse manner, all of the experiments were conducted without addition of added buffer. Hence, in the absence of tellurate ion, only a very cursory study could be made of the effect of hydroxyl ion concentration on the rate of the reaction. Fortunately, the tellurate ion, when it was present in excess (5×10^{-3} M), provided sufficient buffering action to keep the pH change small during a run.

The change in pH during the course of experiments conducted in the presence and absence of tellurate ions is shown in Table XXIV. In these experiments, the electrodes of the pH meter were immersed in a beaker containing 48.5 ml. of potassium oleate (3×10^{-4} M), which was stirred while the permanganate (0.015 mM, 1.50 ml.) was syringed in; the stirring was then stopped and the pH was read.

The effect of variation of the initial pH on the rate of the reaction at 15.3° and 24.8°, using tellurate ions, is shown in Figs 20-24. Since the logarithmic plot of Fig. 22 was not linear, the reaction did not vary with hydroxyl ion concentration according to any simple order. This became apparent when the data were replotted in the form shown in Figs. 23 and 24, demonstrating typical complex order plots, which fit the rate expression,

$$(58)\ldots \qquad v_0 = \frac{M[OH^-]}{1 + N[OH^-]} \quad .$$

TABLE XXIV

pH-Time Studies in the Reaction of Permanganate (3×10^{-4} M) with Potassium Oleate (3×10^{-4} M)

Time (sec.)	pH		
(a) No added tellurate ions			
0	8.82	9.45	9.97
5		9.8	
10	8.88	10.02	10.30
20	9.08	10.18	10.40
30	9.30	10.22	10.43
40	9.52	10.25	10.47
50	9.68	10.30	10.48
60	9.75	10.30	10.49
70	9.81		10.50
80	9.88	10.31	10.50
90	9.89		10.50
(b) Tellurate ion concentration, 5×10^{-3} M			
0	8.70	9.58	10.02
10	8.70	9.64	10.05
20	8.78	9.70	10.10
30	8.80	9.72	10.10
40	8.82	9.74	10.11
50	8.83	9.77	10.12
60	8.86	9.78	10.12
70	8.88	9.78	10.13
80	8.89	9.79	10.13
90	8.90	9.79	
100	8.90	9.80	

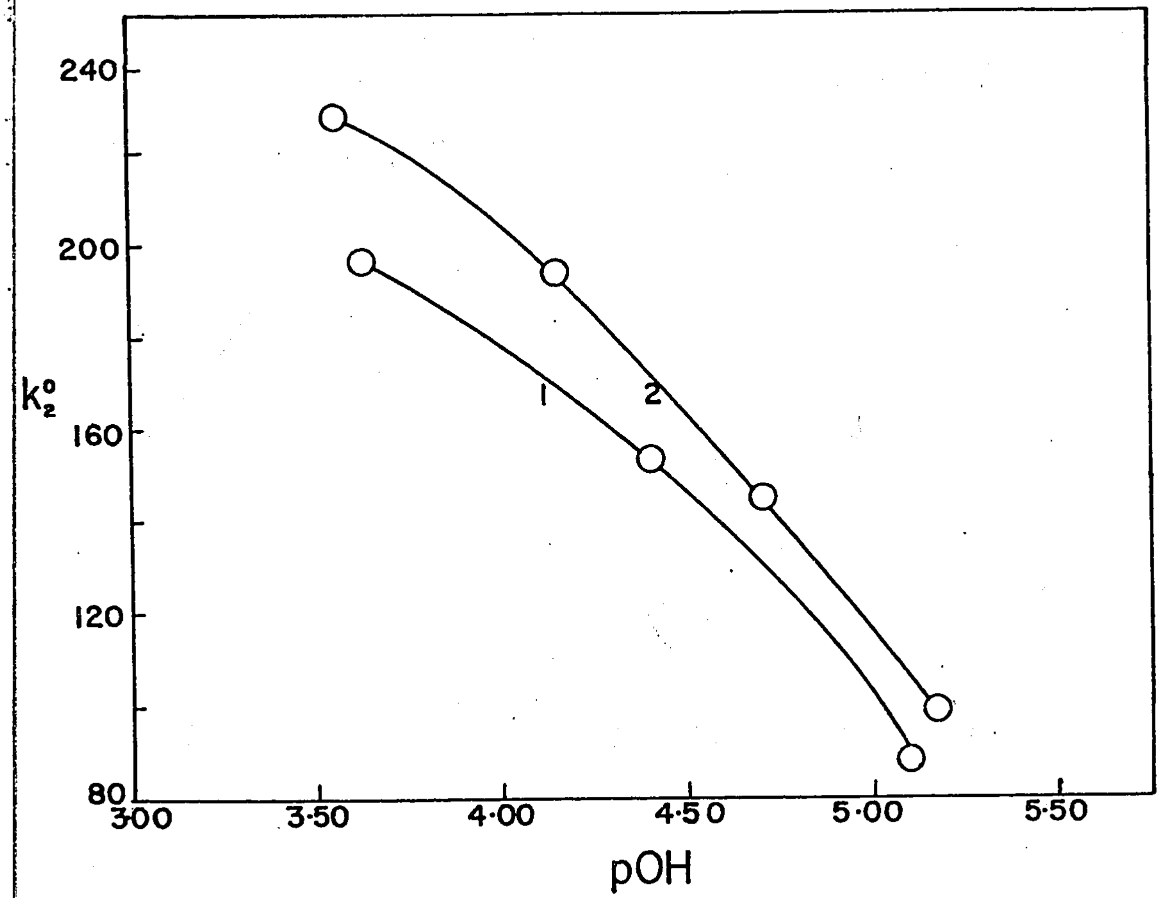


Fig. 20 - Effect of pOH on the reaction of permanganate (3×10^{-4}M) with oleate ion (3×10^{-4}M) at 15.3° (Plot 1) and 24.8° (Plot 2), using a tellurate concentration of 5×10^{-3}M.

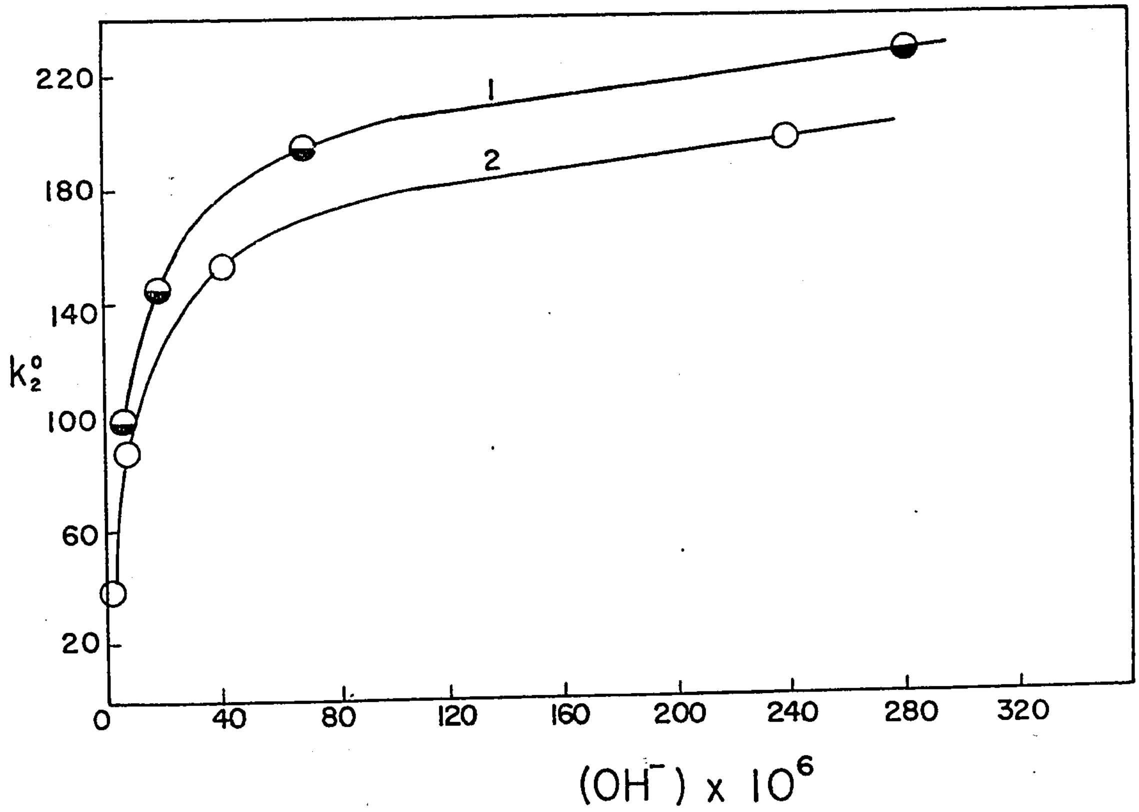


Fig. 21 - Effect of hydroxyl ion concentration on the reaction of permanganate (3×10^{-4}M) with oleate ion (3×10^{-4}M) at 24.8°(Plot 1) and 15.3° (Plot 2), using a concentration of tellurate of 5×10^{-3}M.

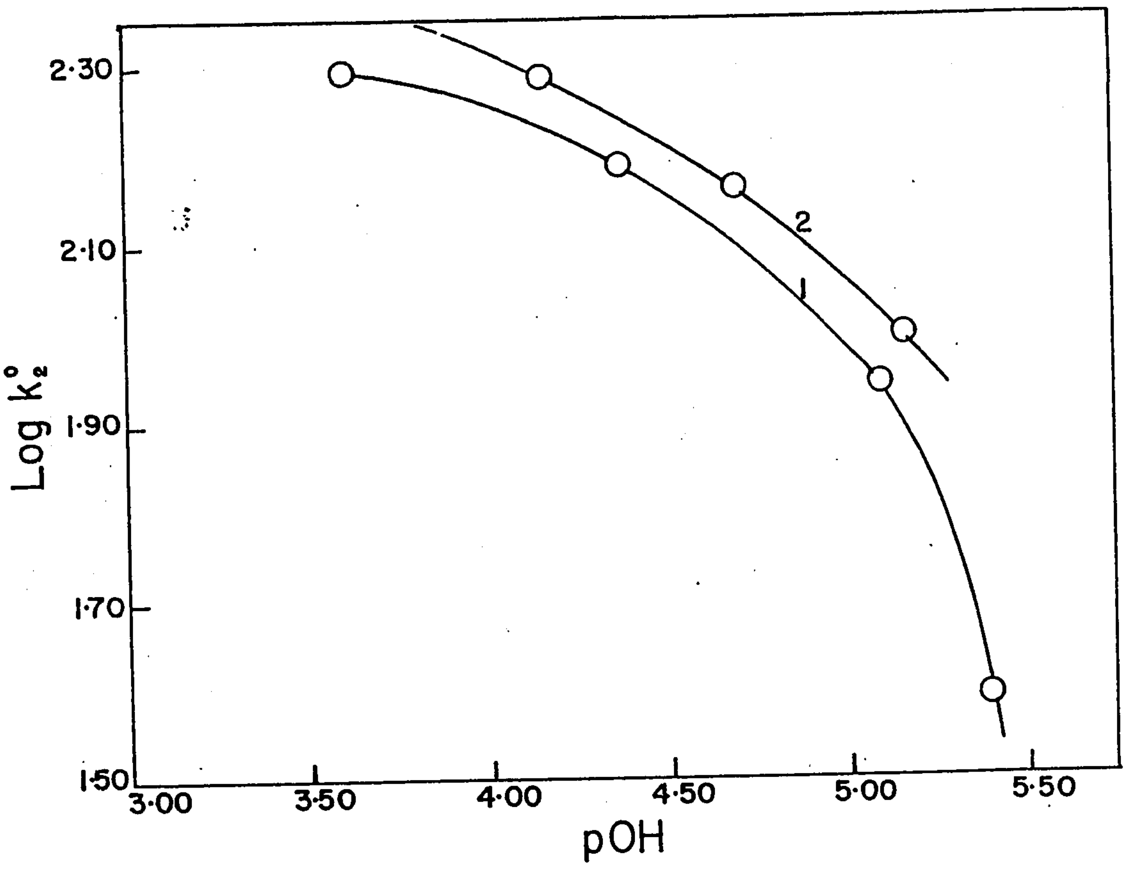


Fig. 22 - Order with respect to hydroxyl ion concentration of the reaction of permanganate (3×10^{-4}M) with oleate ion (3×10^{-4}M) at 15.3° (Plot 1) and 24.8° (Plot 2), using a tellurate concentration of 5×10^{-3}M.

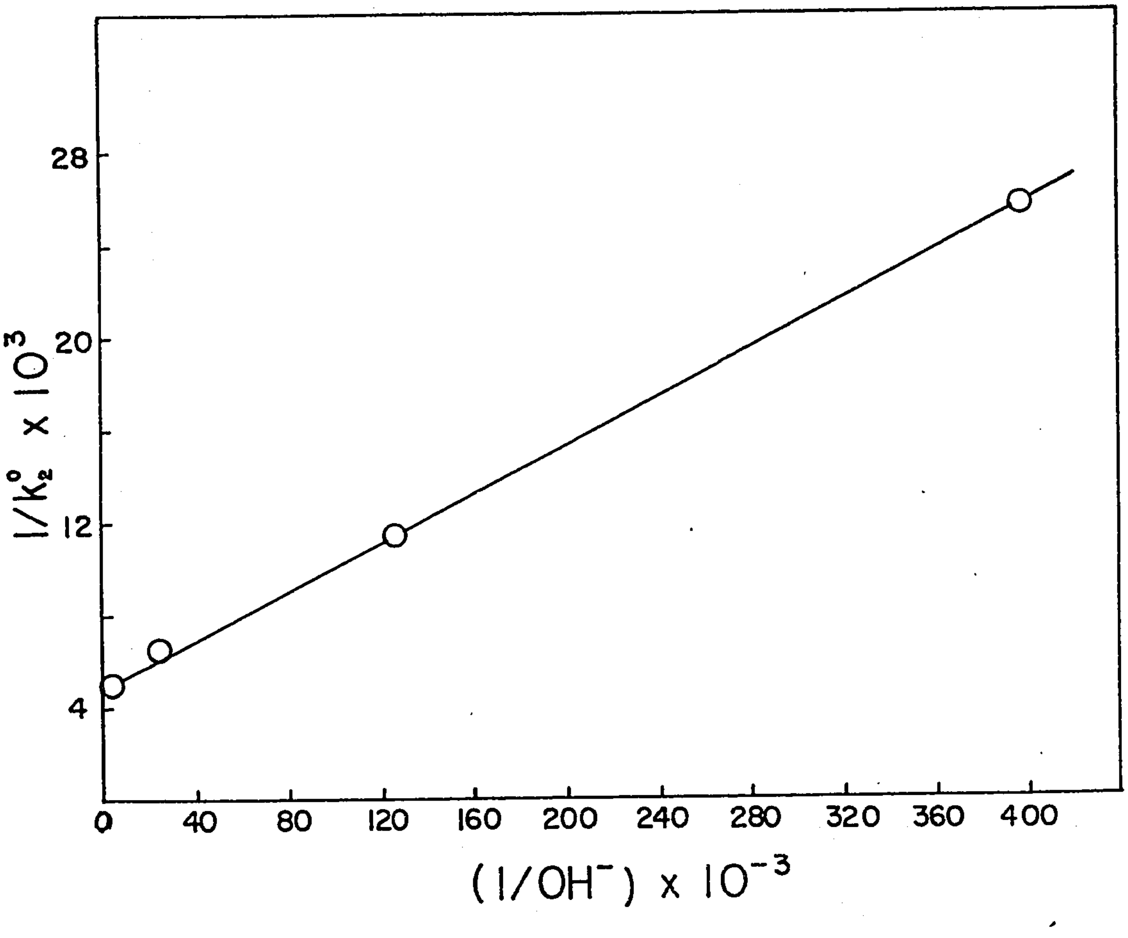


Fig. 23 - Complex order plot for the reaction of oleate ion (3×10^{-4}M) with permanganate (3×10^{-4}M) at 15.3°, using a tellurate concentration of 5×10^{-3}M.

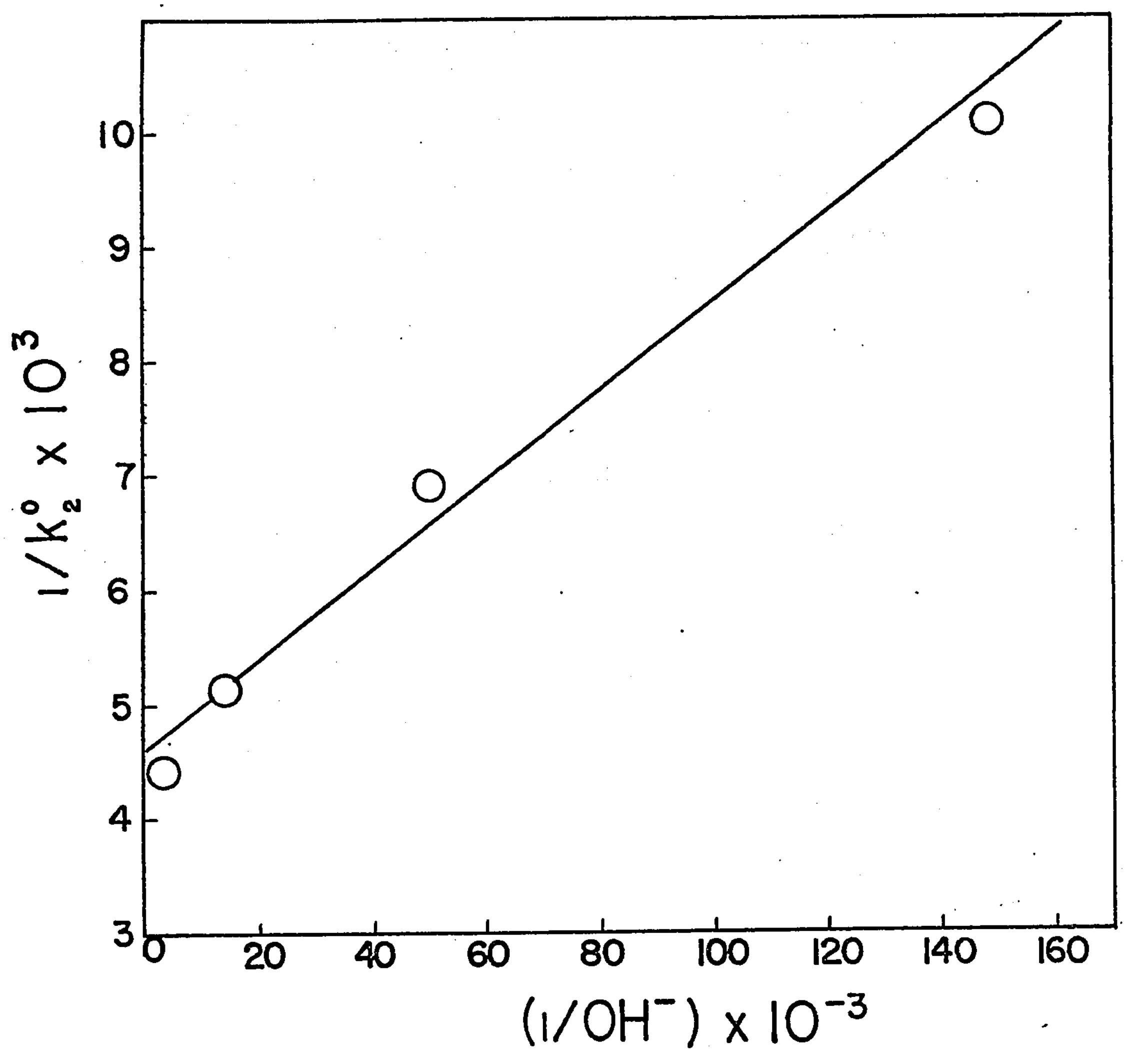


Fig. 24 - Complex order plot for the reaction of permanganate (3×10^{-4}M) with oleate ion (3×10^{-4}M) at 24.8°, using a tellurate concentration of 5×10^{-3}M.

Numerical values for M and N were obtained from the plots of $1/v_o$ versus $1/[OH^-]$ which, as expected, were linear. From equation 58, the slope of these lines is 1/M, and the intercept is N/M. The values obtained for M and N at the two temperatures are given in Table XXV. Both M and N were temperature-dependent.

TABLE XXV

Effect of Hydroxyl Ion Concentration on the Reaction of Permanganate (3×10^{-4}M) with Oleate Ion (3×10^{-4}M) Using Tellurate (5×10^{-3}M)

Temperature (°C)	M	N
15.3	1.87	9.45×10^{4}
24.8	2.12	1.0×10^{5}

This dependence on hydroxyl ion concentration (equation 58) should also hold in the absence of tellurate ions, for two reasons. First, as will be demonstrated below, the kinetic effect of tellurate ions is associated with the formation of an olefin-permanganate complex, but not with its hydrolysis; hence, the mechanism of the hydrolysis should be unchanged in the absence of tellurate ions. Secondly, while conclusions concerning the effect of hydroxyl ion concentration in the absence of added buffer must be rather tenuous, a rough estimate should be possible from the true initial slope of the concentration-time plots. The concentration-time plots for the reaction of permanganate with oleate ion at initial pH values of 9.3 and 10.45, with no added tellurate ions, were extrapolated to zero time, and an estimate was made of the initial rates. The order of the reaction, n , determined from the expression $v_o \propto [OH^-]_o^n$, was 0.22. In the same pH region (9.0-10.5). in the presence of tellurate ions, the order of the reaction, determined from Fig. 22, was also near 0.2, as required by the above assumption that the effect of hydroxyl ion concentration was the same.

(v) Effect of Temperature . Using the data of Fig. 20, the entropy and enthalpy of activation were calculated for the reaction at pH 9.5. While the results represent a rough approximation since only two temperatures were used, this is not a novel occurrence (151). It should be noted, as well, that the experimental procedures which were used in this work precluded the determination of data at temperatures very far from 25°. Above this temperature, the reaction was too fast to follow accurately without resorting to fast reaction techniques; at temperatures much below room temperature, the photometric method could not be employed due to condensation of water vapour onto the photometer tubes.

The equation (152),

(59)... $$k = \mathrm{k}T/h \; \exp(\Delta S^*/R + R) \exp(-E/RT) \; ,$$

where $E = \Delta H^* + RT$,

was employed in making the calculations. The values 146 and 162 for the rate constant were used at 15.3° and 24.8°, respectively. These numbers are somewhat low owing to the effect of tellurate ions on the reaction; however, the proportional decrease should be the same since the tellurate concentration was the same at each temperature. A value of 1.4 kcal. was obtained for ΔH^*, while the entropy of activation at 24.8° was -44 e.u.

D. The Olefin-Permanganate Complex

The results presented so far provide considerable information concerning the olefin-permanganate reaction. Since two permanganate ions enter into the reaction, but the reaction is only first order in permanganate, it is necessary to specify whether the first or the second permanganate ion is involved in the slow step. This question is answered by the non-kinetic evidence. There is considerable evidence that the first molecule of permanganate forms the cyclic ester intermediate and the second molecule effects the oxidation of this intermediate to the ketol. Since the reactions,

$$\mathrm{Mn(V)} + \mathrm{Mn(VII)} \longrightarrow 2\,\mathrm{Mn(VI)} \; , \text{ and}$$

$$\overset{*}{Mn}(VI) + Mn(VII) \longrightarrow Mn(VI) + \overset{*}{Mn}(VII) ,$$

are fast (4, 82), and effectively irreversible owing to the instability of manganate in this pH region, it is reasonable to assume that the same is true for any Mn(V) and Mn(VI)-cyclic ester intermediates. The second stage of the permanganate-olefin reaction must, therefore, be fast and irreversible. The first order in permanganate concentration must, therefore, be associated with the <u>formation</u> of the cyclic ester intermediate.

The rate of the reaction also depends on the hydroxyl ion concentration. This effect can conceivably occur in the formation or the decomposition of the cyclic pentavalent intermediate or possibly both. The order with respect to hydroxyl ion concentration is less than unity. The uncertainty of the experimental data in the <u>absence of tellurate ion</u> permits no distinction between the rate expressions,

(58)... $$v = M[OH^-]/(1 + N[OH^-]) ,$$

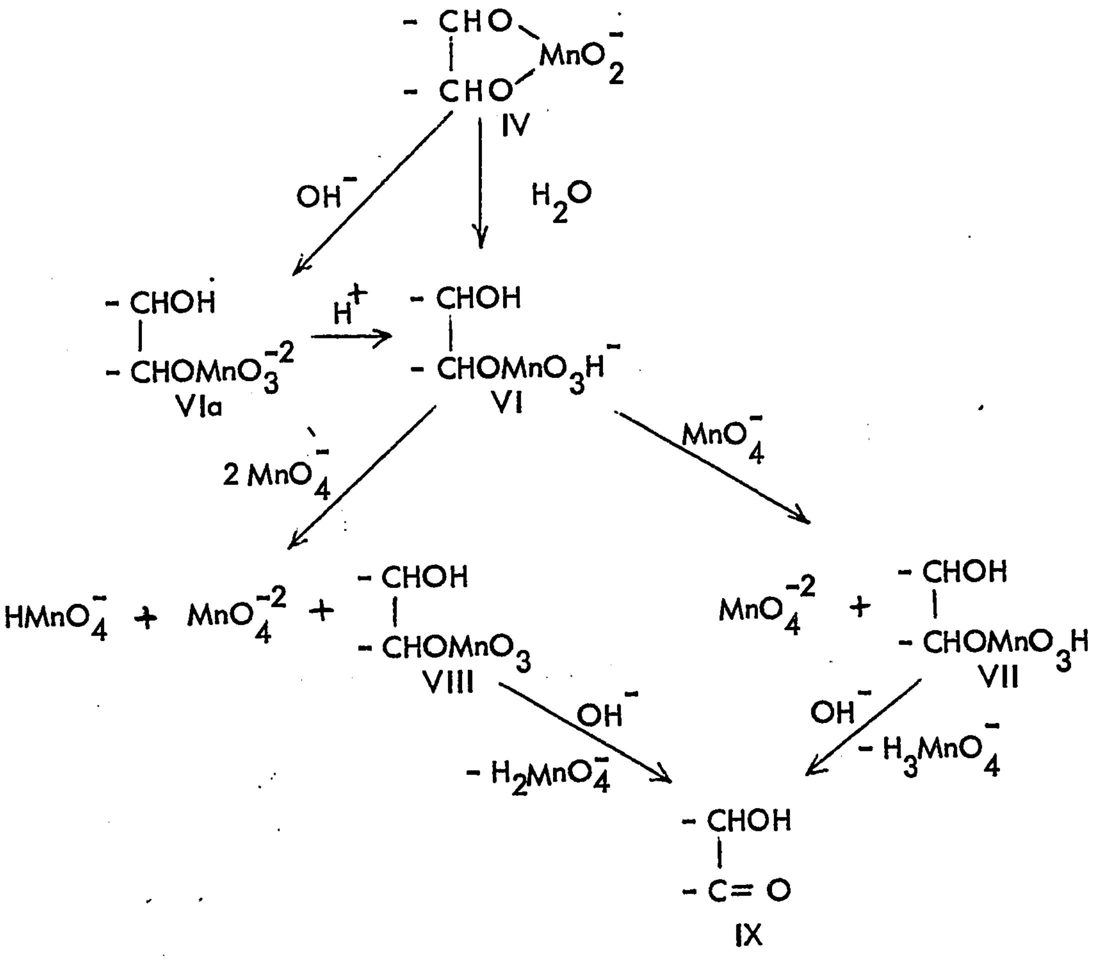
and

(60)... $$v = C + D[OH^-] ,$$

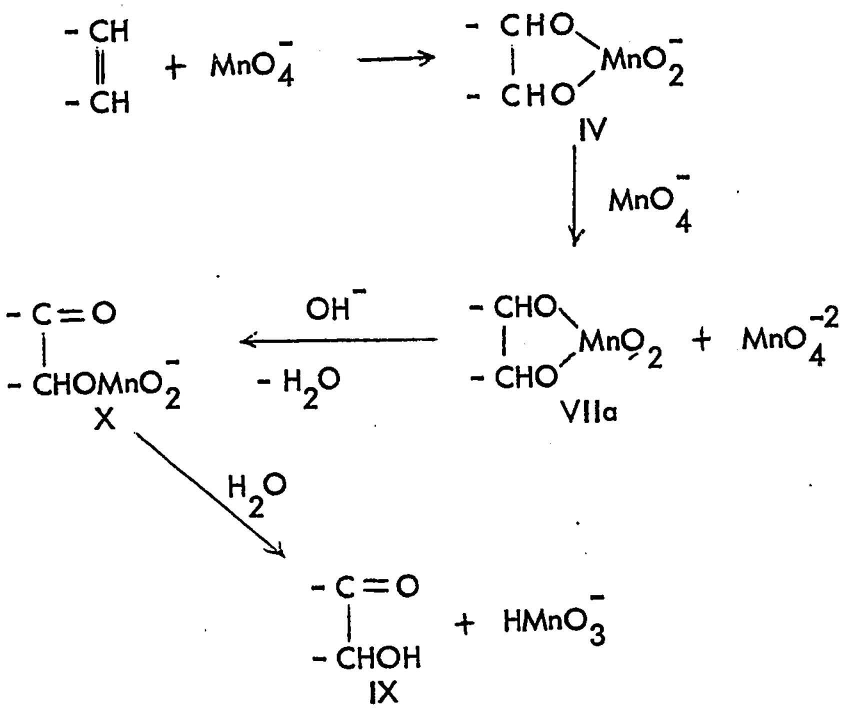
both of which could give a fractional value for n by application of the expression $v_o \propto k [OH^-]_o^n$ to the data. Nevertheless, the fact that the order is fractional permits certain generalizations to be made and definitely rules out some of the plausible mechanisms.

The mechanism of ketol formation may be one of the following two general schemes. The first of these assumes a partial hydrolysis of the intermediate cyclic ester (IV→VI) prior to oxidative decomposition of an ester intermediate (VII or VIII) to ketol (IX). The second mechanism assumes oxidative decomposition of the cyclic ester VIIa before any hydrolysis (X→IX) occurs. These two mechanisms will henceforth be designated as "acyclic mechanism" and "cyclic mechanism" respectively.

Acyclic Mechanism



Cyclic Mechanism



The possibility that the formation of the cyclic intermediate IV is a reversible reaction,

(61)... $$\text{olefin} + MnO_4^- \rightleftharpoons IV ,$$

can be ruled out on the basis that the reverse reaction is not plausible from the thermodynamic point of view. Therefore, the cyclic mechanism can be expressed kinetically as follows,

(i)

(62)... $$\text{olefin} + MnO_4^- \xrightarrow[k_1]{\text{slow}} \text{IV}$$

(63)... $$\text{IV} + MnO_4^- \xrightarrow{\text{fast}} \text{VIIa} + MnO_4^{-2}$$

(64)... $$\text{VIIa} + OH^- \xrightarrow[k_2]{\text{slow}} \text{products}$$

(65)... $$\text{VIIa} + H_2O \xrightarrow[k_3]{\text{slow}} \text{products.}$$

The rate equation for such a scheme would be,

$$v_{(i)} = 2\,k_1k_2\left[\text{olefin}\right]\left[MnO_4^-\right]\left[OH^-\right] + K_1\left[\text{olefin}\right]\left[MnO_4^-\right],$$

where $K_1 = 2\,k_1k_3\left[H_2O\right]$.

In a similar fashion, the acyclic mechanism would be expressed kinetically as follows,

(ii)

(62)... $$\text{olefin} + MnO_4^- \xrightarrow[k_1]{\text{slow}} \text{IV}$$

(66)... $$\text{IV} + OH^- \xrightarrow[k_4]{\text{slow}} \text{VIa}$$

(67)... $$\text{IV} + H_2O \xrightarrow[k_5]{\text{slow}} \text{VI}$$

(68)... $$\text{VIa} + MnO_4^- \xrightarrow{\text{fast}} \text{products}$$

(69)... $$\text{VI} + MnO_4^- \xrightarrow{\text{fast}} \text{products}\ .$$

The rate equation for this scheme would be,

$$v_{(ii)} = 2\,k_1k_4\,[\text{olefin}][\text{MnO}_4^-][\text{OH}^-] + K_2\,[\text{olefin}][\text{MnO}_4^-],$$

where $K_2 = 2\,k_1k_5\,[H_2O]$.

If the cyclic intermediate (IV) is first oxidized and then hydrolyzed as in scheme (i), the occurrence of the substantially irreversible reaction (equation 63) precludes a complex dependence on hydroxyl ion concentration. The observed fractional dependence on hydroxyl ion concentration would, therefore, be ascribed to a true linear dependence (equation 60), which means that the hydrolysis of the ester is effected both by water and by hydroxyl ions. As is evident from $v_{(ii)}$, this kind of formulation of the reaction kinetics predicts that the acyclic mechanism will also require a linear dependence on hydroxyl ion concentration.

Hence, this reasoning does not show whether the acyclic or the cyclic mechanism is the actual route of the oxidation, but it definitely precludes a complex dependence on hydroxyl ion concentration. The experimental facts, however, indicate that the opposite is true, and the complex dependence on hydroxyl ion concentration was proved in the presence of tellurate ions. The formulations (i) and (ii) are, therefore, incorrect.

The inadequacy of these formulations is due to the postulation of the reaction shown in equation 62 as the initial step in the oxidation. The most probable scheme for which a complex dependence on hydroxyl ion concentration would be observed is that which would involve reaction of hydroxyl ions in the rate-controlling step with an intermediate which is being formed in a reversible process. For example,

$$E + F \underset{k_{-e}}{\overset{k_e}{\rightleftharpoons}} EF \text{ , and}$$

$$EF + OH^- \xrightarrow{k} \text{product.}$$

The steady-state rate expression for this reaction is,

$$v = \frac{kk_e[E][F][OH^-]}{k_{-e} + k[OH^-]} \quad .$$

A mechanism for the permanganate-olefin reaction which is in satisfactory agreement with the observed kinetics and with the requirements discussed in the preceding paragraphs is the following,

(70)... $$\text{olefin} + MnO_4^- \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} [\text{olefin} \cdot MnO_4]^{-1},$$

(71)... $$[\text{olefin} \cdot MnO_4]^{-1} + OH^- \xrightarrow{k_R} [\text{olefin} \cdot MnO_4 \cdot OH]^{-2}$$

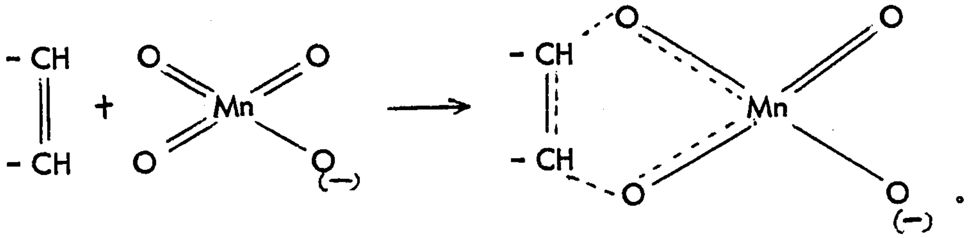
(72)... $$[\text{olefin} \cdot MnO_4 \cdot OH]^{-2} + MnO_4^- \xrightarrow{\text{fast}} \text{products,}$$

wherein the olefin and the permanganate form an intermediate complex which rearranges irreversibly with the participation of hydroxyl ions to a cyclic ester intermediate; the subsequent decomposition of this cyclic intermediate is immeasurably fast. Thus, only equations 70 and 71 need be considered in the formulation of the rate expression,

$$(73)\ldots \qquad v = \frac{2\,k_c k_R\,[\text{olefin}][MnO_4^-][OH^-]}{k_{-c} + k_R\,[OH^-]} \ .$$

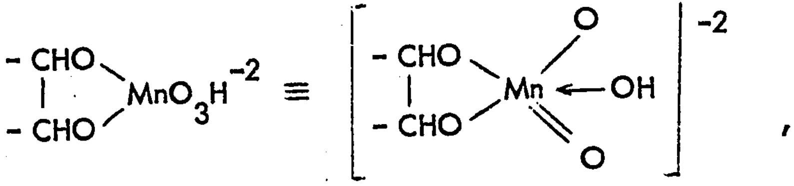
It is concluded, on the basis of the kinetic evidence, that the route of ketol formation proceeds by way of an initially-formed olefin-permanganate complex which is rearranged with the participation of a hydroxyl ion to the cyclic hypomanganate ester (IV). Since the subsequent oxidation of IV to ketol is immeasurably fast, it is clear that the route of this subsequent oxidation cannot be determined by any simple kinetic procedure. Nevertheless, the kinetic evidence for the olefin-permanganate complex seems convincing, and is supported by a variety of other considerations.

First of all, it is unreasonable to suppose that the formation of the cyclic intermediate can occur without some kind of geometrical rearrangement, for the geometry of the reaction is unfavourable. The carbon-carbon distance in an olefin is 1.33 Å, whereas the oxygen-oxygen distance in the permanganate ion, calculated from the manganese-oxygen distance (153) on the basis that the ion is tetrahedral (153, 154), is 2.60 Å. This disparity in bond distance argues against a direct formation of the cyclic intermediate, which would require a simultaneous attack on the double bond by two of the oxygen atoms of the permanganate ion. This, in turn, would require an activated complex resembling that shown below,



The formation of this kind of transition state requires the partial breaking of three double bonds and would, therefore, be expected to require an appreciable activation energy. In fact, the energy of activation was very low (ca. 2 kcal./mole). This suggests that a slow stage in the formation of the cyclic ester involves a different kind of transition state than that mentioned above.

The structure of the cyclic intermediate (XI) which is suggested by the above mechanism (equations 70 and 71),



XI

is supported by the known behaviour of manganate and hypomanganate. Manganate readily exchanges its oxygen atoms with water (55), and on this basis it was suggested previously (page 128) that the disproportionation of manganate includes a step

$$MnO_4^{-2} + H_2O \rightleftharpoons \underset{\text{XII}}{H_2MnO_5^{-2}} \rightleftharpoons H_2O_2 + MnO_3^{-2}.$$

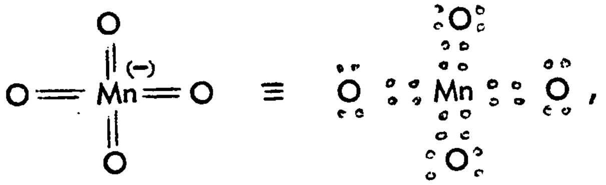
A similar reaction of hypomanganate is thermodynamically feasible and seems indicated by the behaviour of hypomanganate when it disproportionates (see pages 120 and 127),

$$MnO_4^{-3} + OH^- \rightleftharpoons \underset{\text{XIII}}{HMnO_4^{-4}} \rightleftharpoons MnO_4^{-4} + OH \quad .$$

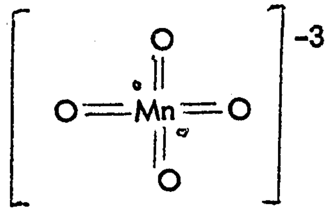
The intermediate stages (XII and XIII) of these two reactions, as well as XI, could be stabilized by the use of vacant inner d-orbitals of the manganese. If this consideration is correct, structures such as XI-XIII should not be limited to manganese but should be common to this part of the Periodic Table. This is well known — such stabilization is so great for periodate and perrhenate ions that hydrated ions such as $H_4IO_6^-$ and ReO_5^{-3} are stable species.

The fact that the hypomanganate ion is stabilized by hydroxyl ions supports this idea, since it is reasonable to assume that a hypomanganate ester will display the same behaviour.

The effect of hydroxyl ions in promoting the rearrangement of the complex to the cyclic intermediate is adequately explained by a consideration of the electronic structures of the manganese oxyanions (154–156). A detailed treatment of the situation is beyond the scope of this thesis, but certain generalizations can, however, be drawn. Each of the three oxyanions is tetrahedral; the permanganate ion contains no unpaired electrons, while manganate contains one and hypomanganate contains two unpaired electrons. These unpaired electrons enter into the t_2 level, which is antibonding. Though the term "double bond" loses much of its meaning when the molecular orbital treatment is applied to the molecule, it is convenient to employ classical "double bonded" structures when considering these oxyanions. Wolfsberg and Helmholz (154), in their treatment of the permanganate ion, postulate that π-bonding between manganese and the four oxygen atoms is complete. This corresponds to the classical structure,

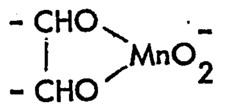


where the negative charge is on the central atom, and the manganese has 16 valence electrons associated with it. Now, reduction of permanganate to hypomanganate leaves the geometric structure of the molecule unchanged, but results in the addition of two electrons to the <u>central</u> atom. Thus, the hypomanganate ion should be represented by the classical structure,



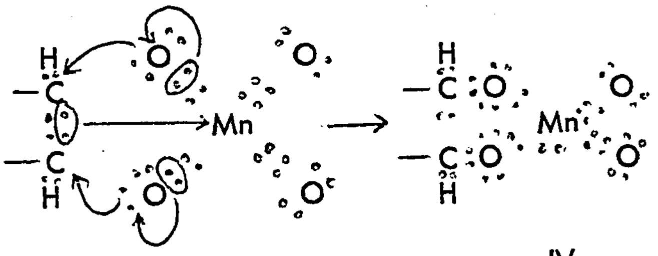
$$\left[\mathrm{O{=}\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{Mn}}{=}O} \right]^{-3}$$

with 18 valence electrons around the manganese. However, as may be readily ascertained by counting electrons, the cyclic (hypomanganate) ester intermediate, when written as the classical organic structure,



IV

has only fourteen electrons around the manganese,



IV

If the structure with eighteen electrons around the manganese is the most stable structure for the ester IV, then it is evident that hydroxyl ion can provide stabilization of IV by supplying two electrons to the manganese. Theoretically, two hydroxyl ions should add to this intermediate. The fact that only one hydion appears to be involved in the rearrangement to the cyclic intermediate may be due either to steric hindrance to the second ion or to the fact that the intermediate is oxidized to the ketols before the second hydroxyl ion can be added.

The effect of tellurate ions on the kinetics of the permanganate-olefin reaction provides independent and conclusive evidence of this intermediate complex formation. The kinetics are explained by the assumption that the tellurate and permanganate ions compete kinetically for the olefin. Since, in these experiments, the permanganate was added to olefin-tellurate solutions, it may be assumed that equilibrium between the olefin and tellurate ion was reached before the permanganate was added.

The data plotted in Fig. 19 indicate that, as long as a finite concentration of free olefin remains, the permanganate reacts with the olefin, and the rate of the second order reaction is governed by the concentration of free olefin, which, in turn, is governed by the equilibrium constant of the olefin-tellurate complex. At constant temperature (24.8°) and pH (9.5), the kinetics are satisfactorily explained by the following mechanism,

$$(74)\ldots \qquad \text{olefin} + H_4TeO_6^{-2} \overset{K}{\rightleftharpoons} \left[\text{olefin} \cdot H_4TeO_6\right]^{-2}$$

$$(70)\ldots \qquad \text{olefin} + MnO_4^- \underset{k_{-c}}{\overset{k_c}{\rightleftharpoons}} \left[\text{olefin} \cdot MnO_4^-\right]$$

(71)... $$\left[\text{olefin} \cdot \text{MnO}_4^-\right] \xrightarrow{k_R} \text{XI}$$

(72)... $$\text{XI} + \text{MnO}_4^- \xrightarrow{\text{fast}} \text{products.}$$

At constant pH, this mechanism leads to the rate expression,

(75)... $$v_o = \frac{k_c k_R \left[\text{olefin}\right]_o \left[\text{MnO}_4^-\right]_o \left[\text{OH}^-\right]_o}{(1 + K\left[\text{H}_4\text{TeO}_6^{-2}\right])(k_{-c} + k_R\left[\text{OH}^-\right]_o)}$$

$$= \frac{Z\left[\text{olefin}\right]_o \left[\text{MnO}_4^-\right]_o}{1 + K\left[\text{H}_4\text{TeO}_6^{-2}\right]} \quad .$$

The equilibrium constant K is readily evaluated from a plot of $1/k_2^o$ against the concentration of tellurate ion. By definition,

$$v_o = k_2^o \left[\text{olefin}\right]_o \left[\text{MnO}_4^-\right]_o$$

or,

$$k_2^o = Z/(1 + K\left[\text{H}_4\text{TeO}_6^{-2}\right]) ,$$

and,

$$1/k_2^o = 1/Z + K/Z \left[\text{H}_4\text{TeO}_6^{-2}\right].$$

A good straight line was obtained from this plot for tellurate concentrations of 0-6x10^{-4}M, and from the slope and intercept of this line, K was determined as 1820. That is,

(76)...
$$\frac{[\text{olefin} \cdot \text{tellurate}]}{[\text{olefin}][\text{tellurate}]} = K_{24.8^{\circ}} = 1820.$$

Regardless of the accuracy of this number, and an experimental error of 25-50% would not be surprising in view of the crude techniques used, the important fact is that this number can be obtained at all. With a suitable refinement of the experimental technique, it is evident that a powerful new tool can be developed for the study of olefin complexes with oxyanions, of which the complex of oleate ion with tellurate is the first to be reported. The procedure is straightforward — the olefin is mixed in varying proportions with the complexing agent at the desired pH and temperature, and the mixture is allowed to react with permanganate. Initial rates are then determined and the reciprocals are plotted against the concentration of the complexing agent. The data are then treated as described on page 205.

At high tellurate ion concentrations, the rate of the oleate ion-permanganate reaction approaches a limiting value approximately 50% of the rate in the absence of tellurate ions. In addition, the order of the reaction becomes complex. The kinetics are best explained by the assumption that the equilibrium between the olefin and the tellurate ion is far to the right, and the permanganate can react with the olefin only by displacing the tellurate ion from the oleate-tellurate complex. This leads to the following scheme, (74)... $$\text{olefin} + \text{H}_4\text{TeO}_6^{-2} \underset{k'_{-c}}{\overset{k'_c}{\rightleftharpoons}} \left[\text{olefin} \cdot \text{H}_4\text{TeO}_6\right]^{-2}$$

(77)... $$\left[\text{olefin} \cdot \text{H}_4\text{TeO}_6\right]^{-2} + \text{MnO}_4^- \underset{k''_{-c}}{\overset{k''_c}{\rightleftharpoons}} \left[\text{olefin} \cdot \text{MnO}_4\right]^- + \text{H}_4\text{TeO}_6^{-2}$$

(71)... $$\left[\text{olefin} \cdot \text{MnO}_4\right]^- + \text{OH}^- \xrightarrow{k_R} \text{XI}$$

(72)... $$\text{XI} + \text{MnO}_4^- \xrightarrow{\text{fast}} \text{products.}$$

Application of the steady-state approximation to this mechanism is made as follows, where C_1 refers to the olefin-tellurate complex, and C_2 to the olefin-permanganate complex,

$$dC_1/dt = 0 = k'_c [\text{olefin}][\text{tellurate}] - k'_{-c}[C_1] - k''_c [C_1][\text{MnO}_4^-]$$
$$+ k''_{-c}[C_2][\text{tellurate}]$$

$$dC_2/dt = 0 = k''_c[C_1][\text{MnO}_4^-] - k''_{-c}[C_2][\text{tellurate}] - k_R[C_2][\text{OH}^-].$$

(78)... $$v = 2k_R[C_2][\text{OH}^-]$$

$$= \frac{2k'_c k''_c k_R [\text{olefin}][\text{MnO}_4^-][\text{tellurate}][\text{OH}^-]}{k'_{-c}k''_{-c}[\text{tellurate}] + k_R[\text{OH}^-](k'_{-c} + k''_c[\text{MnO}_4^-])}$$

The order with respect to tellurate ion was not studied in detail beyond demonstrating the limiting rate effect. At a constant concentration of tellurate ions, equation 78 is in satisfactory agreement with the observed kinetics, namely, a first order in olefin, a complex order in hydroxyl ion, and a fractional order in permanganate.

In connection with this mechanism, the author wishes to report some observations made using excess tellurate ions and excess olefin. The reaction appeared to include an induction period. The present experimental technique does not permit any significance to be attached to these observations. The experiments should, however, be repeated after the experimental technique has been suitably refined.

The present work indicates that an olefin-borate complex can be formed. No detailed study was made of the effect of borate ion, but the effect seems analogous to that described for tellurate. A similar explanation may account for the effect of periodate in the periodate-permanganate oxidation of oleate ion. In their paper (32), Lemieux and von Rudloff observed that an increase in the periodate ion concentration had a retarding effect on the rate of the reaction. Their data (Fig. 6 of reference 32) indicate an order close to -1, for periodate : olefin ratios of 4-16. This is the result expected if an olefin-periodate complex is formed and has an equilibrium constant of the order of 1000.

Further work on these complexes is indicated, not only for theoretical reasons, but because information gained in this way will be of some assistance in the elucidation of the structure and electronic configuration of the olefin-permanganate complex. It seems reasonable to conclude that the occurrence of complex formation by permanganate, tellurate, borate and periodate is due to some common structural feature of these oxyanions, and the fact that only the permanganate complex can undergo rearrangement and an electron transfer must be due to some special structural feature inherent to this ion. Thus, this work might provide an answer to one of the fundamental problems in the field of oxidation reactions, namely, the reason for the specificity of many of the common oxidizing agents.

As a result of the present work, it is now known that permanganate and osmium tetroxide are effective in the hydroxylation of olefins by way of cyclic ester intermediates, while other, apparently similar oxidizing agents are not effective in this way. The effect of the tellurate, borate, and periodate ions on the permanganate-olefin reaction leads the author to the opinion that the complexes formed by the various oxyanions with olefins are charge-transfer (157), or π-complexes (158).

The theoretical and experimental bases for such complexes between olefins and various kinds of electrophilic species have received considerable attention in recent years (159), and it seems generally agreed that the formation of these complexes is due to a kind of acid-base reaction (cf. $R_3N \rightarrow BF_3$) between the π-electrons of the double bond and a vacant p- or d-orbital of the complexing agent. Dewar has presented an interesting summary of the π-complex theory from the molecular orbital point of view (159).

Dewar considers (159) that a molecular bond, μ, is formed by a donation from the π-orbital of the double bond to a vacant p-orbital of the electrophilic species; where such vacant p-orbitals exist, this leads to a very stable situation. Thus, the olefin-silver ion complexes can be isolated and studied per se. When the complexing agent has no vacant p-orbitals, however, only a weak interaction may occur between the π-electrons of the double bond and d- or π-electrons in the complexing agent.

The nature of the periodate, borate or tellurate species which complexes with the olefin was not established in the present study. Each of these ions is known to exist in several forms. Thus, for periodate, the equilibria,

$$H_5IO_6 \rightleftharpoons H^+ + H_4IO_6^-$$

$$H_4IO_6^- \rightleftharpoons H^+ + H_3IO_6^{-2}$$

$$H_4IO_6^- \rightleftharpoons 2\,H_2O + IO_4^- ,$$

all occur in aqueous medium(160), although the IO_4^- ion appears to be the predominant species. Likewise, for telluric acid, possible equilibria are,

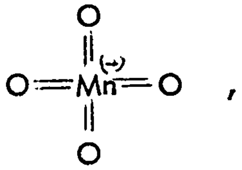
$$H_6TeO_6 \rightleftharpoons H^+ + H_5TeO_6^-$$

$$H_5TeO_6^- \rightleftharpoons H^+ + H_4TeO_6^{-2}$$

$$H_4TeO_6^{-2} \rightleftharpoons 2\,H_2O + TeO_4^{-2} \quad .$$

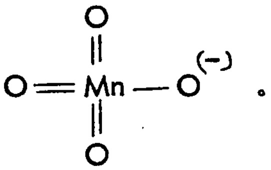
However, the evidence indicates that the TeO_4^{-2} ion is not present under normal circumstances, and the main species in aqueous alkaline solution is the $H_4TeO_6^{-2}$ ion (161). Periodic acid and telluric acid are both octahedral molecules (162, 163), but the IO_4^- ion is tetrahedral (164); the borate ion, BO_3^{-3}, is planar (165).

The permanganate ion was considered previously. The molecular orbital treatment (154) for this ion indicated that it should be written, in a classical structure, as



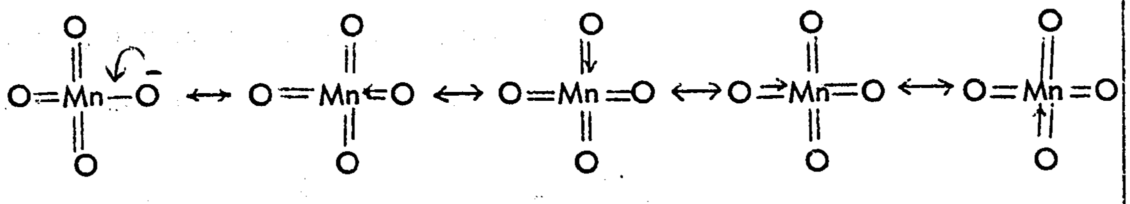
$$O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Mn^{(-)}}}{=}O \quad ,$$

rather than

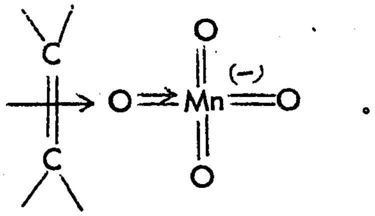


$$O{=}\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{Mn}}{-}O^{(-)} \quad .$$

The accumulation of negative charge on the manganese would leave each of the oxygen atoms with a slight deficit of negative charge, corresponding to a hypothetical reaction,

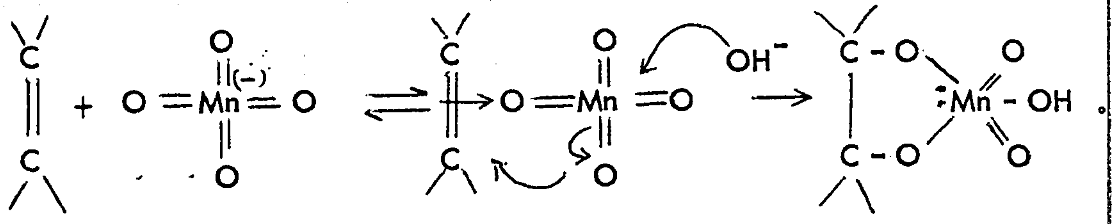


This would have the effect of partially freeing a p-orbital on the oxygen atoms, and a weak p-π complex should then become possible between this p-orbital and the π-orbital of the double bond of an olefin. The π-complex theory, therefore, predicts that the initial reaction between an olefin and the permanganate ion involves the formation of a complex XIV,

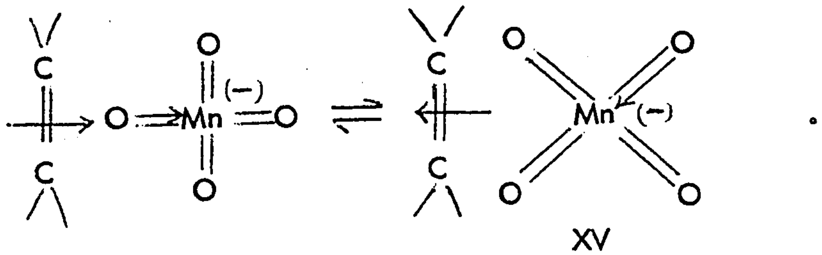


XIV

The subsequent rearrangement of this complex to the cyclic intermediate can occur in two ways. In the first, the electron transfer from the olefin occurs through an oxygen of the permanganate ion, according to a scheme such as the following,

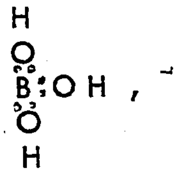


According to the second scheme, the initial complex may rearrange to a d-π complex, XV , formed by a donation from the outer shell d-electrons of the permanganate ion to an antibonding orbital of the olefin (see reference 159 for examples of this kind of d-π interaction),

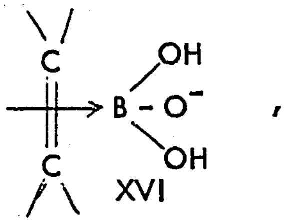


XV

A consideration of the effect of the other oxyanions on the olefin-permanganate reaction leads the author to favour the second of these reaction routes at the present time. Since they effectively remove the π-electrons of the olefin from the reaction, the periodate, tellurate and borate complexes must resemble the initial permanganate complex (XIV) in some way. In the absence of knowledge of the electronic structures of the periodate and tellurate ions, it is not possible to draw any satisfacory conclusions concerning these complexes, although it seems reasonable to suppose that a p-π complex is formed with an oxygen atom of the oxyanions IO_4^- or $Te(OH)_4O_2^{-2}$. In the case of the borate ion, an obvious interpretation of the complex formation exists, since boron is well-known to form "electron-deficient" compounds. Thus, boric acid is usually represented as



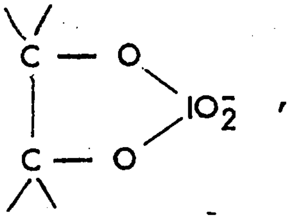
and the boron has only six electrons around it. This accounts for the large variety of coordination compounds formed by this element, and means that, in its compounds (such as BO_3^{-3}, BF_3, etc.), boron contains two vacant p-orbitals. Thus it is entirely reasonable to anticipate that a p-π complex, XVI ,



XVI

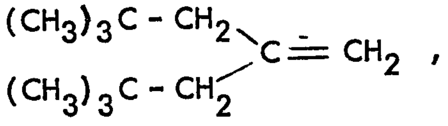
is formed between an olefin and the borate ion (cf. $R_3N \rightarrow BF_3$, or $Et_2O \rightarrow BF_3$), in which there is a donation from the π-orbital of the olefin to a vacant p-orbital of the boron.

It should be sterically possible for an olefin-periodate complex to rearrange to a cyclic ester structure,



since such a structure is presumably formed as an intermediate in the periodate-glycol reaction (42-44). Therefore, the fact that the IO_4^- ion is not capable of oxidizing olefins is not due to any stereochemical reason. Furthermore, the oxidation potential of the $IO_4^- - IO_3^-$ couple, -1.49 V. (163), is even higher than that of the $MnO_4^{-1} - MnO_4^{-3}$ couple, -0.43 V. (see page 56); hence, the difference in the behaviour of the two ions cannot be attributed to this factor either. The common feature of the permanganate ion and the osmium tetroxide molecule is that, from the molecular orbital point of view, both of these species are formed by combination of d, s and p electrons. In the case of the periodate, tellurate and borate ions, only s and p electrons are involved in the formation of the ions. Thus, only permanganate and osmium tetroxide have d-orbitals available for d-π complex formation. These considerations lead the author to believe that, in the hydroxylation of olefins by permanganate or osmium tetroxide, the electron transfer may occur within a complex XV, as shown on page 213.

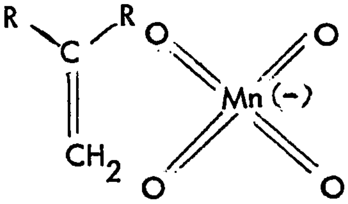
The idea that the initial stage of the olefin-permanganate reaction involves an attack by an oxygen of the permanganate on the double bond is supported by data on the reaction of some hindered olefins with permanganate. Bartlett, Fraser and Woodward (166) have reported that the compound 1,1-dineopentylethylene,



$$\begin{matrix}(CH_3)_3C-CH_2 & \\ & >C=CH_2\;, \\ (CH_3)_3C-CH_2 & \end{matrix}$$

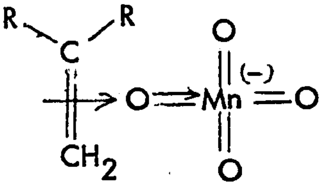
is completely resistant to attack by permanganate, even in hot, excess alkali.

Since one of the carbon atoms of this olefin is completely hindered to any kind of attack, the formation of a cyclic ester complex, XVII , is precluded.



XVII

However, an initial p-π complex,



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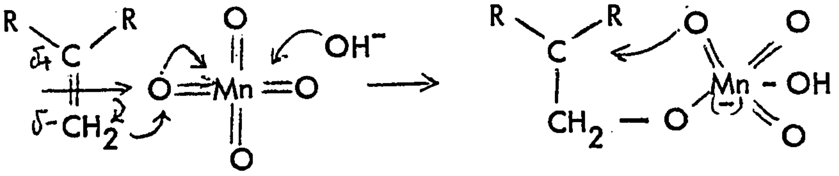
should not encounter any appreciable steric hindrance. If the re-arrangement of this complex occurred by way of a direct electron transfer through an oxygen atom, Markownikoff's rule predicts that the species XVIII would be an intermediat

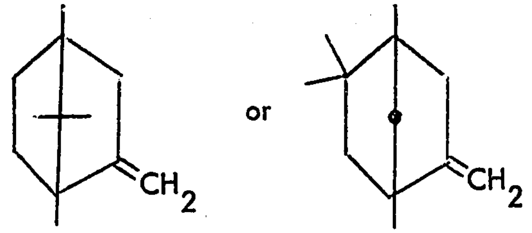


XVIII

,

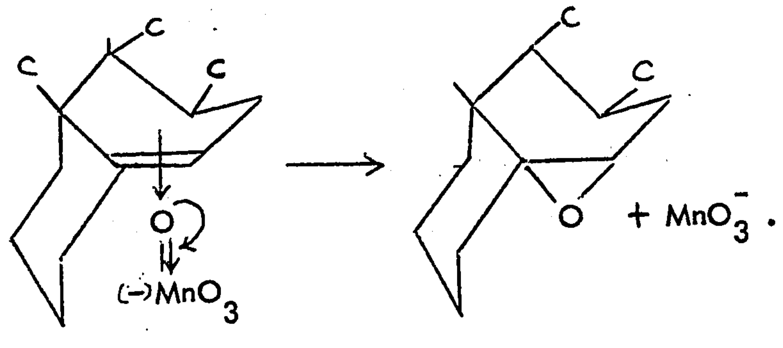
and, as a result of a lessening of the steric hindrance at the penultimate carbon atom, might undergo ring closure to form the cyclic intermediate. The fact that <u>no</u> reaction occurred appears to argue against this kind of reorganization of the initial olefin-permanganate complex.

Farmer and Martin (167) have shown that this hindrance effect is not an isolated one, for a compound believed to have the structure,

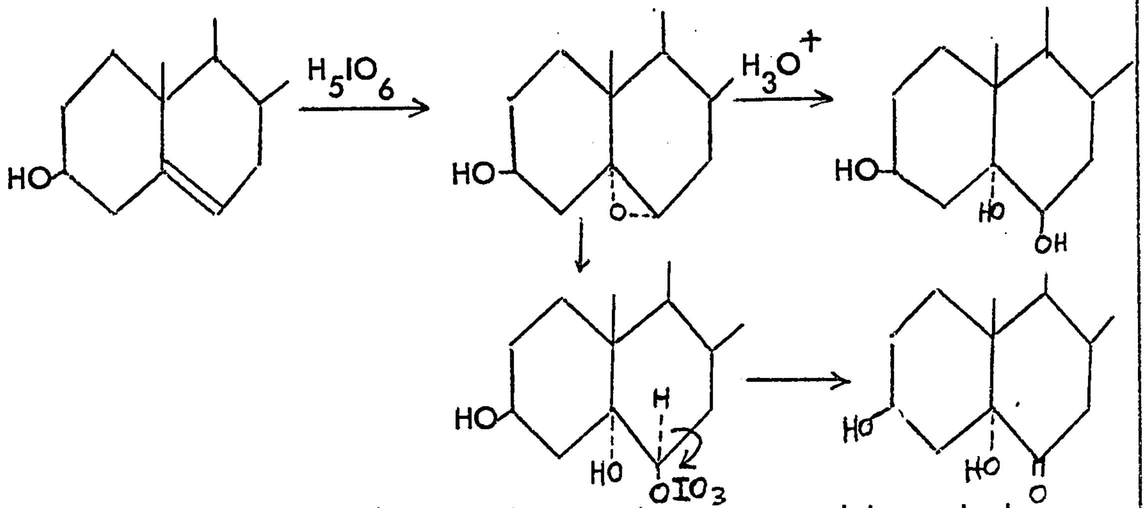


was also resistant to permanganate oxidation.

The results of Marker and Rohrmann (95) and of Ehrenstein and Decker (97) on the oxidation of $\Delta^{5,6}$- unsaturated steroids by permanganate in aqueous acetic acid are satisfactorily explained by the assumption that the initial reaction involves attack by an oxygen atom of the oxidizing agent on the double bond. The isolation of epoxides from these oxidations thus provides some support for the early ideas of Butlerov (65) on the mechanism of permanganate oxidation. Direct transfer of an oxygen atom to the olefin would seem to be due to a combination of the solvent and the hindered double bond,

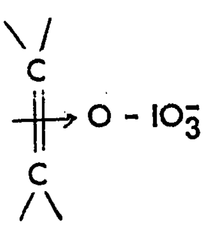


In two recent papers, Chatterjee and Majumdar (168) and Wendler and co-workers (169) have reported that periodic acid, H_5IO_6, unlike sodium meta-periodate, $NaIO_4$, is capable of oxidizing olefins. Thus, Chatterjee and Majumdar (168) have obtained formaldehyde from the oxidation of a number of olefins containing a terminal methylene group, while Wendler and co-workers (169) isolated cholestane-3β, 5α, 6β-triol and 3β, 6α-dihydroxycholestane-6-one from the oxidation of cholesterol in aqueous tetrahydrofuran. The route of this reaction was formulated as

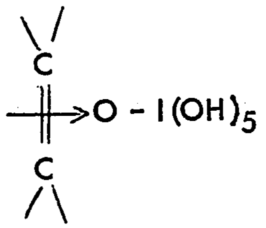


The striking similarity between this reaction and the result obtained with the same compound using permanganate in aqueous acetic acid suggests that the oxidation mechanism may be the same. This would confirm the suggestion that the periodate ion can complex with the olefinic linkage.

The difference in reactivity between the IO_4^- ion and the H_5IO_6 molecule should be further investigated, for it would seem to be related to the differing abilities of complexes such as



and



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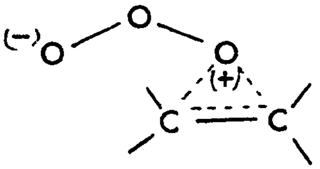
to accept electrons from an olefin.

In view of the results obtained by Wendler and co-workers (169), it should be noted that the oxidation of an olefin to ketol by permanganate does <u>not</u> proceed by way of an intermediate oxide; Lemieux and von Rudloff (32) have shown that 9,10-epoxystearic acid is resistant to the periodate-permanganate reagent under conditions where oleic acid can be converted to the 9,10-ketohydroxystearic acids.

Finally, it is of interest to note that Bailey has recently postulated that the ozonolysis reaction is best explained by the assumption that a π-complex, XIX, is formed (170).



XIX

Hence the oxidation of olefins by permanganate does not appear to be an isolated case of this kind of π-complex formation.

4. The Route of Oxidation of the Cyclic Intermediate to Ketol. The Oxidation of Ethylene and 1,1-Dideuteroethylene

The use of isotope techniques comprises a powerful tool in the study of reaction mechanisms, and the theoretical and experimental bases for the deuterium isotope effect should be well-known to all students of organic chemistry. Only a brief description need be given here(171). The effect is based on the generally lower reactivity of bonds to deuterium as compared to the corresponding bonds to hydrogen. The major factor which contributes to this difference in reactivity is the difference in zero point energy between a bond to deuterium and the corresponding bond to hydrogen. (It is assumed that bonds in the molecule which do not participate in the reaction are not affected during the process). Now, to a reasonable approximation, the zero point stretching vibrational energy for a bond between two atoms is

(79)... $$E_o = h/4\pi \sqrt{k/\mu} ,$$

where h is Planck's constant; k is the bond stretching force constant and μ is the reduced mass.

All of the factors in equation 79 for C-H and C-D bonds will be the same except for $\sqrt{1/\mu}$. Since E_o is directly proportional to $\sqrt{1/\mu}$, the zero-point vibrational energy for C-H bonds is greater than for C-D bonds. Hence, the net energy for breaking a C-H bond should be less than that for a C-D bond (see Fig. 25). On this basis, a reaction in which a C-H bond is broken should proceed more rapidly than the corresponding reaction with a C-D bond. This difference in the rates at which C-H and C-D bonds are broken is the deuterium isotope effect, and is usually expressed as k_H/k_D, where k_H and k_D are the rate constants of the two reactions.

The kinetic isotope effect is helpful in the determination of reaction mechanisms because, wherever such an effect is found, there is a strong supposition that a bond involving the isotope is made or broken in the slow step of the reaction. The isotope effect is usually used to distinguish between the fast and slow steps of a complex reaction mechanism.

The deuterium isotope effect in permanganate oxidations has been summarized by Wiberg (171), and some of the results which have been reported were discussed earlier in this thesis (see pages 11, 13 and 20). In the oxidation of organic compounds by alkaline permanganate, the isotope effect varied from 1.9 in the oxidation of p-chlorobenzaldehyde to p-chlorobenzoic acid (7) to 7.4 in the oxidation of formate ion (14).

The second stage of the oxidation of an olefin to a ketol involves the breaking of a carbon-hydrogen bond. It should, therefore, be possible to determine the route of this second stage of the reaction by a suitable application of the deuterium isotope effect. Since the formation of the

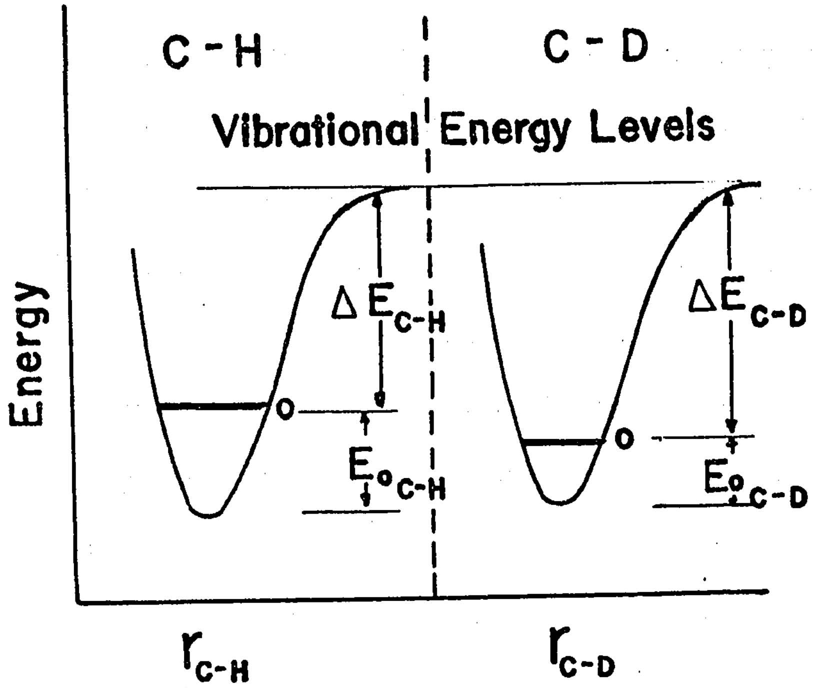
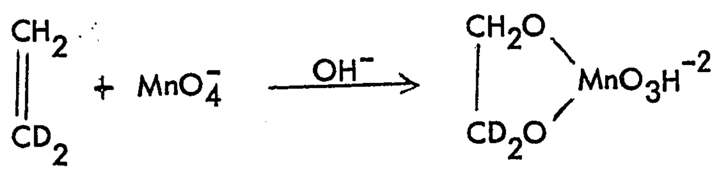


Fig. 25 - Schematic potential energy diagrams for C–H and C–D bonds taken as diatomic molecules. (From D.A. Semenow and J.D. Roberts, J.Chem. Ed., 33, 2 (1956))

cyclic intermediate, and not the subsequent oxidation to ketol has been found to be the slow stage of the reaction, it is clear that application of the kinetic isotope effect in the usual manner should show no rate difference between an olefin $R - CH = CH - R'$ and the corresponding deuterated compound, $R - CD = CD - R'$. The performance of such an experiment is of interest, since it should provide an independent check of the conclusions arrived at from the kinetic study of the reaction. This experiment was not carried out during the present investigation, but will be performed in this laboratory in the near future.

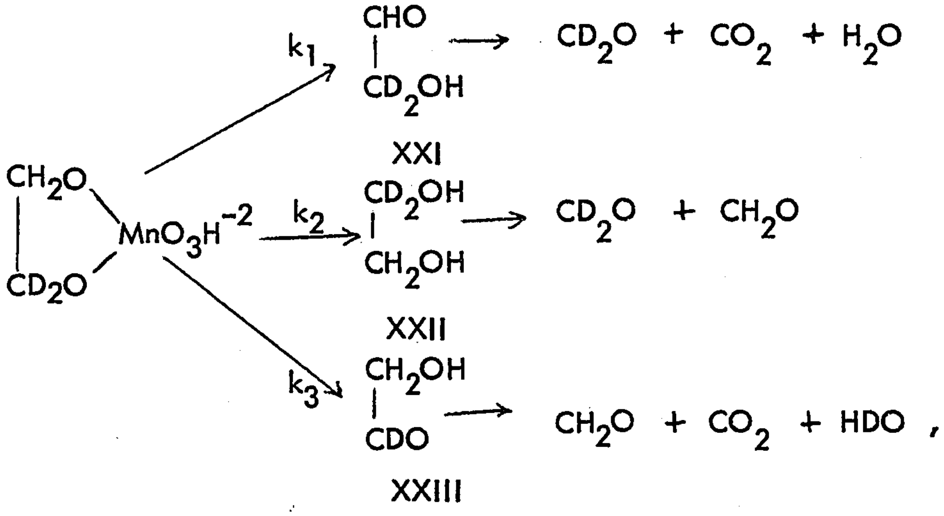
In view of the conclusions arrived at on the basis of the kinetic study of the oxidation of oleate ion by permanganate, it was evident that a more subtle approach would be required in order to determine the extent of a deuterium isotope effect in this reaction. The approach selected effectively represented studying the k_H/k_D ratio within a single molecule. Thus, only the actual step in which the C-H bond or the C-D bond was broken would affect the experimental results. The assumptions on which this approach was based may be illustrated by a consideration of the molecule 1,1-dideuteroethylene. If this molecule is oxidized to "ketol" (glycolaldehyde) by permanganate, the initial intermediate in the reaction should be the species XX.



XX

This will then be oxidized further, either by the acyclic mechanism (page 194), or by the cyclic mechanism (page 195).

Since some glycol is always detected as a product of the oxidation of olefins in the pH region 7–14, even when (as demonstrated for oleate ion in the pH region 7–10) the major product is ketol, it can be concluded that the rates of glycol and ketol formation do not differ greatly, and probably by a factor of less than one hundred even at neutrality. This difference in rate will be even less at a given pH if the olefin RCH ═ CHR' is replaced by the olefin RCD ═ CDR', for the reasons discussed above. Therefore, for the cyclic mechanism, the overall oxidation of 1,1-dideuteroethylene by periodate-permanganate can be formulated as follows (compare reference 32, page 40 of this thesis; see also page 158),



where k_1 , k_2 and k_3 represent the rates of formation of the products XXI, XXII and XXIII, respectively. The total yield of formaldehyde will then be

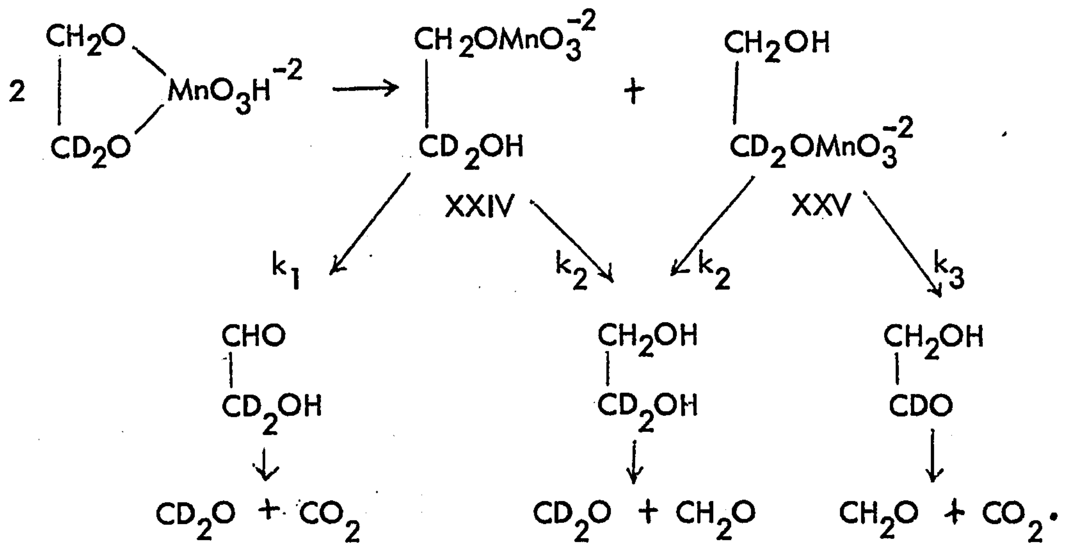
$$\frac{k_1}{k_1 + k_2 + k_3}\ CD_2O + \frac{k_2}{k_1 + k_2 + k_3}\ CD_2O$$

$$+ \frac{k_2}{k_1 + k_2 + k_3}\ CH_2O + \frac{k_3}{k_1 + k_2 + k_3}\ CH_2O,$$

and the percentage of CD_2O in the product would be

$$(80)\ldots \qquad \% \ CD_2O = \frac{(k_1 + k_2)\,100}{k_1 + 2k_2 + k_3} .$$

The following situation would maintain in the case of the α cyclic mechanism, where k_1, k_2 and k_3 have the same meaning as above,



The total yield of formaldehyde from the periodate-permanganate oxidation would be

$$\frac{k_1}{k_1 + k_2} CD_2O + \frac{k_2}{k_1 + k_2} CD_2O + \frac{k_2}{k_1 + k_2} CH_2O + \frac{k_2}{k_2 + k_3} CD_2O$$

$$+ \frac{k_2}{k_2 + k_3} CH_2O + \frac{k_3}{k_2 + k_3} CH_2O \ .$$

The percentage of CD_2O in the formaldehyde product would, therefore, be,

$$(81)\ldots \qquad \% \, CD_2O = \frac{\left(1 + \dfrac{k_2}{k_2 + k_3}\right) 100}{2 + \dfrac{k_2}{k_2 + k_3} + \dfrac{k_2}{k_1 + k_2}} \ .$$

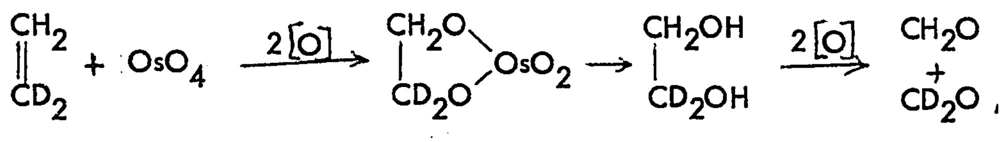
These expressions (equations 80 and 81) show that the yield of CD_2O can be expected to depend greatly on the mechanism of the reaction. Thus, if $k_1 = 3\,k_3$ (a reasonable mass effect, in view of the results reported by Wiberg, reference 171) and $k_1 = 9\,k_2$ (90% yield of ketol; compare the results described for oleate ion, page 158), the cyclic mechanism would result in a 71.5% yield of CD_2O, whereas the yield would be only 53.5% in the case of the acyclic mechanism. In view of these facts, and since a supply of 1,1-dideuteroethylene was available through the courtesy of Dr. L.C.

Leitch of the National Research Council, a study was undertaken of the periodate-permanganate oxidation of this compound.

Since excess periodate was to be used in the reaction mixture, the products XXI-XXIII would be oxidized under the reaction conditions to CH_2O , CD_2O , HCOOH and DCOOH. This provided the experimental basis for the determination of the mass effect. It was anticipated that the formaldehyde could be readily isolated as the 2,4-dinitrophenylhydrazone, and that the infrared spectra of formaldehyde-2,4-dinitrophenylhydrazone and formaldehyde-d_2-2,4-dinitrophenylhydrazone would be sufficiently characteristic to permit the establishment of an analytical method for determining the CD_2O/CH_2O ratio in the product.

A small vacuum line (Fig. 3) was constructed in which to conduct the oxidations. As a check on the experimental work, both with ethylene and dideuteroethylene, the oxidation by the osmium tetroxide-periodate reagent was also examined (33). The periodate-osmium tetroxide oxidation of 1,1-dideuteroethylene can be formulated as

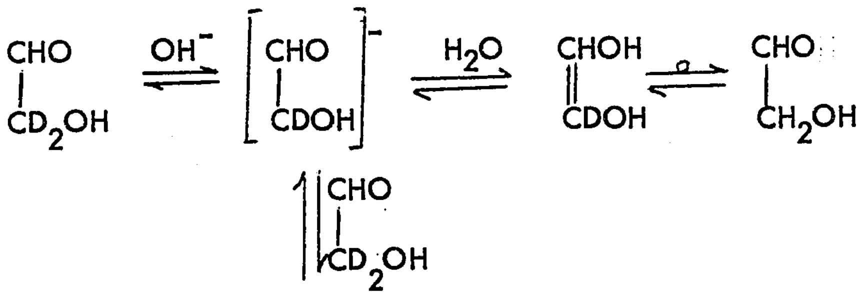
(82)...



where $\boxed{O}$ represents one equivalent of oxidant. Thus, the gas should consume four equivalents of oxidant per mole of olefin, yield two moles of formaldehyde per mole, and the formaldehyde should contain 50% of CD_2O.

Since formaldehyde is oxidized only slowly under the conditions of the periodate-permanganate reaction (84), it was anticipated that the only factor which might obscure the experimental determination of the deuterium isotope effect was the possibility of self-condensation of the glycolaldehyde or formaldehyde products under the mildly alkaline reaction conditions. It is well-known that such reactions occur; glycolaldehyde is the key intermediate in the polymerization of formaldehyde to sugars (172) and, with formaldehyde, will give a 75% yield of glyceraldehyde (173).

The occurrence of such a condensation reaction following the initial stage of the oxidation of 1,1-dideuteroethylene would tend to lower the observed isotope effect, where one existed, because of exchange with the solvent,

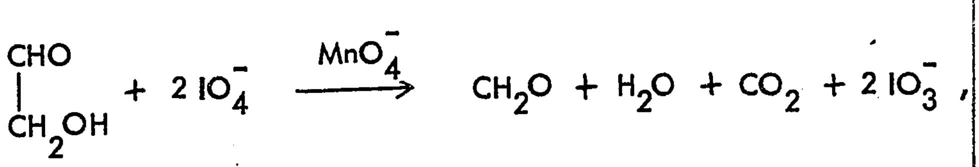


$$CHO - CDOH - CHOH - CD_2OH \ .$$

Indeed, if this reaction were at all rapid under the conditions of the periodate-permanganate oxidation of ethylene, a complete loss of deuterium would result.

The paper chromatographic behaviour of solutions of glycolaldehyde demonstrated this condensation reaction. Solutions in water or in dilute acid were stable and gave only one spot, R_f 0.66, on irrigation with butanol-water. However (see Tables XI and XII), when the pH of the solution was adjusted to 7.5-8.5, and the solution was chromatographed again, a series of spots with R_f 0.05-0.25 was obtained. The R_f values of the spots decreased the longer the glycolaldehyde was maintained in the alkali, indicating that the initial condensation products were undergoing further condensations to yield higher molecular weight materials.

Though the self-condensation of glycolaldehyde in alkaline media alone appeared to be rapid (see below), no condensation occurred when the glycolaldehyde was added to alkaline (pH 8.2) solutions of periodate or periodate-permanganate. The consumption of oxidant and yield of formaldehyde were in quantitative agreement with the formulation,



$$\begin{array}{l} CHO \\ | \\ CH_2OH \end{array} + 2\,IO_4^- \xrightarrow{MnO_4^-} CH_2O + H_2O + CO_2 + 2\,IO_3^- ,$$

and it was possible, in fact, to follow the rate of the condensation of glycolaldehyde by dissolving the compound in potassium carbonate solution, and then removing aliquots at various times for reaction with periodate. The results of one experiment at pH 8.2 are shown in Table XXVI.

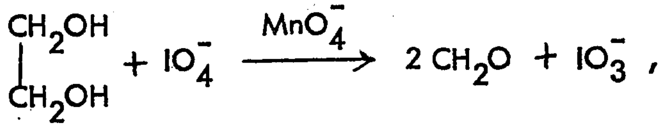
TABLE XXVI

Rate of the Self-condensation of Glycolaldehyde at pH 8.2

Glycolaldehyde, 1mM, was dissolved in 50 ml. of water containing sufficient potassium carbonate to give a pH of 8.2. Aliquots were withdrawn at various times for treatment with excess periodate. The consumption of oxidant and yield of formaldehyde were determined.

Time (hr.)	Equivalents of Oxidant Consumed per Mole of Glycolaldehyde	Moles of Formaldehyde Liberated per Mole of Glycolaldehyde
0.0	2.00	1.00
0.25	2.31	0.99
0.5	2.39	0.88
1.0	2.58	0.83
2.0	2.71	0.73

Experiments with ethylene glycol in mildly alkaline media gave similar results. The oxidation of this compound by periodate-permanganate or by periodate alone was in quantitative agreement with the formulation,



$$\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix} + IO_4^- \xrightarrow{MnO_4^-} 2\,CH_2O + IO_3^- ,$$

and there was no evidence of condensation of the formaldehyde under the conditions of the periodate-permanganate oxidation.

Two different experimental procedures were used for the oxidation of ethylene. In the first, a volume of gas was measured into the reaction flask containing the oxidizing agent, and the flask was then sealed and mechanically shaken. Several runs were made using identical conditions, and the progress of the reaction was followed by opening the reaction flasks at different times and analyzing the contents for consumption of oxidant and yield of formaldehyde. In the second procedure, the oxidizing agent was introduced into the system in an atmosphere of the gas, and the solution was stirred until a sufficient quantity of the gas had been absorbed. The reaction flask was then removed from the ethylene atmosphere and the contents were analyzed as described above. The first of these procedures had the advantage that the consumption of the gas could be measured very accurately, but the reaction required 24 hours for completion and analysis of the reaction mixture indicated that an appreciable yield of ethylene glycol was formed. The use of the second procedure enabled the reaction to be conducted at an increased rate, but it was not possible to measure the consumption of gas. Introduction of the oxidizing agent into the ethylene atmosphere caused a displacement of the mercury level in the manometer owing to the volume change and to the vapour pressure of water. It was not possible to level the manometer to atmospheric pressure, take a reading and then begin stirring the solution, since some gas always dissolved in the solution as the oxidizing agent was introduced into the reaction flask, and this could not be accurately measured since the amount of gas which dissolved in this way was different depending on whether oxidizing agent or blank was used.

All of the experiments with periodate-permanganate were conducted at pH 7.5-8.0, using potassium carbonate to buffer the reaction mixture. No buffer was used in the periodate-osmium tetroxide oxidations.

If the periodate-permanganate oxidations proceeded quantitatively to glycolaldehyde, the stoichiometric equation of the reaction,

$$C_2H_4 + 4\,IO_4^- \xrightarrow{MnO_4^-} CO_2 + CH_2O + H_2O + 4\,IO_3^- ,$$

indicates that a consumption of eight equivalents of oxidant would yield one mole of formaldehyde per mole of olefin. On the other hand, the formation of ethylene glycol as the principal product of the reaction would yield two moles of formaldehyde per mole of olefin from the consumption of only four equivalents of oxidant.

Using Procedure (i), page 96, 0.96 mM of ethylene was oxidized at pH 7.5 by a solution containing 8.0 mM of periodate, 0.125 mM of permanganate and 2.0 mM of potassium carbonate in 250 ml. of water. The reaction was complete in 24 hours and yielded 1.21 mM of formaldehyde from the consumption of 5.69 mE of oxidant. The relative yields of ketol and glycol were determined most conveniently from the ratio of

(mE of oxidant consumed/mM of formaldehyde liberated). The use of this ratio (abbreviated, O/CH_2O) had the advantage that the route of the reaction could be determined under conditions where the consumption of olefin was not known. Thus, using Procedure (i) and 1.02 mM of ethylene, a reaction time of 6 hours resulted in the liberation of only 0.58 mM of formaldehyde from the consumption of 2.62 mE of oxidant, but the O/CH_2O ratio of 4.80 was in good agreement with the value of 4.74 obtained after 24 hours. The yields of glycol and glycolaldehyde could be calculated using the equation,

$$(83)\ldots \qquad O/CH_2O = 4.77 = \frac{4X + 8(1-X)}{2X + (1-X)} ,$$

where X was the proportion of glycol and (1 - X) was then the proportion of glycolaldehyde. Procedure (i), therefore, gave 63% of glycolaldehyde and 37% of ethylene glycol.

This high yield of glycol was unsatisfactory for the proposed oxidation of 1,1-dideuteroethylene, since the resultant lowering of the $\%CD_2O$ in the product could conceivably obscure any mass effect in the formation of glycolaldehyde. For example, if it is assumed that the mass effect is 3 ($k_1 = 3\,k_3$) and that $k_1 = 63/37 k_2$, then substitution of these values into equations 80 and 81 shows that the $\%CD_2O$ for the cyclic mechanism will be lowered to 63.2, while that for the acyclic mechanism would be lowered to 54.5.

The foregoing experimental results were substantiated by the fact that the periodate-osmium tetroxide reagent gave results in close agreement with those expected on the basis of the reaction scheme shown in equation 82.

The oxidation of 0.38 mM of ethylene by a solution containing 1.6 mM of periodate and 0.02 mM of osmium tetroxide in 50 ml. of water resulted in the consumption of 1.51 mE of oxidant* and the formation of 0.75 mM of formaldehyde.

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* The arsenite procedure for the determination of the consumption of periodate could not be employed here. It was observed that, even at pH 8.5, all of the periodate was reduced to iodide ions. Thus, when a slight excess of arsenite, calculated on the basis of the equation,

$$As_2O_3 + 2\,IO_4^- \xrightarrow{pH\ 7.6} As_2O_5 + 2\,IO_3^- ,$$

was added, all of the arsenite was consumed. The total consumption of arsenite was in agreement with the equation

$$2\,As_2O_3 + IO_4^- \longrightarrow 2\,As_2O_5 + I^- .$$

Apparently, the osmium tetroxide was able to catalyze the reaction

$$6\,H^+ + IO_3^- + 5\,I^- \longrightarrow 3\,I_2 + 3\,H_2O ,$$

even when the hydrogen ion concentration was very low.

In order to determine periodate in the presence of osmium tetroxide, it was necessary to employ the iodometric procedure.

The experimental procedure was modified to enable the reaction to be conducted at an increased rate with the idea that, if appreciable yields of glycol were still obtained, it might prove possible to stop the reaction after a short time and either separate the products directly or selectively oxidize one of them to formaldehyde. If either of the glycol or the glycolaldehyde were oxidized to formaldehyde at an appreciably higher rate than the other, then the procedure for the estimation of the mass effect was straightforward. If the two compounds were oxidized at the same rate, it would be necessary to separate the ethylene glycol from the glycolaldehyde chromatographically, and then oxidize the ketol fraction to formaldehyde.

The relative rates of oxidation of ethylene glycol and glycolaldehyde were studied by conducting competitive experiments in which a deficit of periodate was treated at pH 8 with mixtures of ethylene glycol and glycolaldehyde containing varying proportions of the two reductants. The results obtained from the reduction of 0.0198 mM of periodate by 0.075 mM of mixtures containing ethylene glycol and glycolaldehyde are shown in Table XXVII.

TABLE XXVII

Reduction of 0.0198 mM of Periodate at pH 8.0 by Mixtures Containing Excess Ethylene Glycol and Glycolaldehyde

Mole Fraction		mM of CH_2O
Ethylene Glycol	Glycolaldehyde	Liberated
0.67	0.33	0.0222
0.33	0.67	0.0195
0.25	0.75	0.0189
0.10	0.90	0.0189

If it is assumed that the periodate reacted with p moles of the glycol and q moles of glycolaldehyde, then

$$p + q = 0.0198 .$$

Since each mole of ethylene glycol liberated two moles of formaldehyde, and each mole of glycolaldehyde liberated one mole of formaldehyde, then

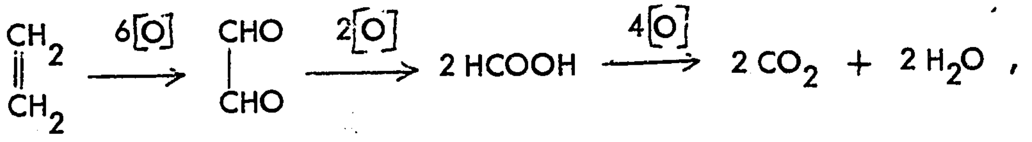
$$2p + q = \text{mM of } CH_2O \text{ liberated.}$$

It is evident that $p = 0$ for a mole fraction of glycolaldehyde $\geqslant 0.67$. An estimate of the relative rates of reaction of the two compounds is possible from the result obtained by the use of 0.33 mole fraction of glycolaldehyde and 0.67 mole fraction of ethylene glycol. The liberation of 0.0222 mM of formaldehyde indicates that $p = 0.0024$ and $q = 0.0174$, or (rate of oxidation of ketol)/(rate of oxidation of glycol) $=$ 0.0174/0.0024. Since the ratio of the concentrations of the two compounds was $C_{glycolaldehyde}/C_{glycol} = 1/2$, the ratio of the rate constants is $k_{glycolaldehyde}/k_{glycol} \doteqdot 14$. Hence, the periodate oxidation of glycolaldehyde is appreciably faster than that of ethylene glycol.

The relative proportions of the ethylene glycol and glycolaldehyde products of the oxidation of ethylene by Procedure (ii), page 97, were determined from the O/CH_2O ratio. For runs conducted using the same concentrations of periodate and permanganate, the O/CH_2O ratio, determined four to six hours after the beginning of the reaction, was reproducible, but varied within a single run during the first part of the reaction and also varied with the periodate to permanganate ratio.

The variation in the O/CH_2O ratio during a run was presumably due to the fact that the initial products of the reaction were still being oxidized during the first part of the run; when the oxidation of these compounds to formaldehyde and carbon dioxide was complete, there was no further variation with time of the O/CH_2O ratio. The progress of this second stage of the reaction was followed either by removing the reaction flask from the ethylene atmosphere before the permanganate colour disappeared and then allowing the reaction to run to completion, or by allowing the reaction to run until the oxidizing agent was completely reduced by the ethylene, and then removing the reaction flask and adding more periodate. The results of several experiments conducted with different periodate to permanganate ratios are shown in Table XXVIII. In all of these experiments, the initial reaction with the gas was carried out with a solution containing 30 ml. of 0.067 M periodate, buffered to pH 8.0 with 0.067 M carbonate solution, and 10 ml. of a permanganate solution of the desired concentration. The reactions were conducted at room temperature (22-27°).

The data of Table XXVIII indicated that, on the assumption that ethylene glycol and glycolaldehyde were the only initial products of the oxidation, the ethylene glycol was formed in the reaction mixture to the extent of 9-20% of the total product, depending on the periodate to permanganate ratio. However, the results of run 4 indicated that some of the olefin had also been oxidized to glyoxal; the high O/CH_2O ratio in the initial part of the reaction would suggest that the subsequent oxidation of this product was more rapid than the subsequent oxidations of ethylene glycol and glycolaldehyde,



$$\begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} \xrightarrow{6[O]} \begin{matrix} CHO \\ | \\ CHO \end{matrix} \xrightarrow{2[O]} 2\,HCOOH \xrightarrow{4[O]} 2\,CO_2 + 2\,H_2O\ ,$$

so that, in the initial stages of the reaction, a considerable amount of the oxidizing agent would be expended in the oxidation of a mole of ethylene to two moles of carbon dioxide. As the reaction proceeds, liberation of formaldehyde from the glycol and glycolaldehyde would lower this ratio to the final value of 6-7. Further evidence that some glyoxal was formed in the

TABLE XXVIII

The Oxidation of Ethylene by Periodate-Permanganate

Run	mM of MnO_4^-	Duration of Initial Reaction with Ethylene	Time of Analysis from Start of Experiment (hr.)	Results of Analysis mE of Oxidant Consumed	mM of CH_2O Liberated	O/CH_2O
1	0.2	0.37 hr.	3.0	2.33		
			6.0	2.70	0.306	9.0
			9.5	3.76		
2	0.2	0.27 hr.	0.5	1.71	0.241	7.1
			1.0	1.91	0.262	7.3
			2.0	2.08	0.300	6.9
			3.0	2.29	0.330	6.9
3	0.02	0.58 hr.	1.0	3.15	0.430	7.3
			5.0	3.45	0.670	5.2
			23.0	3.98	0.782	5.1
			41.0	4.39	0.774	5.7
4	0.02	1.17 hr.	2.0	4.76	0.390	12.2
			4.3	5.26	0.728	7.2
			6.5	5.54	0.822	6.7
			12.0	6.05	1.028	5.9
			27.0	6.78	1.002	6.8

reaction was obtained from a fifth run, which was stopped after 16 minutes and analyzed immediately for consumption of oxidant and yield of formaldehyde. The O/CH_2O ratio was 19.

This conclusion could be further substantiated by the performance of competitive experiments in which mixtures of glyoxal and glycolaldehyde, or glyoxal and ethylene glycol were oxidized under the conditions of the periodate-permanganate reaction; this was not done, but since the glycolaldehyde is oxidized at an appreciably higher rate than the glycol, it would be anticipitated that the second carbonyl group (as in glyoxal) would enhance the rate even further.

The formation of glyoxal as a product of the oxidation of ethylene would interfere with the interpretation of the deuterium isotope effect when 1,1-dideuteroethylene was oxidized, since an exact estimation of the reaction products (and hence, of the relative values of k_1, k_2 and k_3) was more difficult. The effect of the formation of glyoxal on the relative yields of ethylene glycol and glycolaldehyde may be seen in Table XXIX. These numbers were calculated by assuming that the observed O/CH_2O ratio,

$$7.0 = \frac{8X + 4Y + 12Z}{X + 2Y} ,$$

where X was the proportion of glycolaldehyde, Y was the proportion of glycol, and Z, the proportion of glyoxal was (1 - X - Y). By giving various values to

Z, the above equation, along with the equation

$$X + Y = (1 - Z)$$

could be solved for X and Y.

TABLE XXIX

An Estimate of the Yields of the Products of the Oxidation of Ethylene, Based on an Observed O / CH_2O Ratio of 7.0 and Assumed Values for the Proportion of Glyoxal

Mole Fraction of Ketol in the Product	Mole Fraction of Glycol in the Product	Mole Fraction of Glyoxal in the Product	%D in the CH_2O
0.91	0.09	0.0	71.8
0.81	0.14	0.05	70.0
0.71	0.19	0.10	68.0
0.61	0.24	0.15	65.6
0.51	0.29	0.20	63.5
0.41	0.34	0.25	61.1
0.31	0.39	0.30	58.7

The numbers in the last column of Table XXIX show how the observed deuterium isotope effect of the over-all reaction mixture would decrease in the event that the cyclic mechanism were the route of the oxidation to glycolaldehyde, assuming a mass effect of 3 ($k_1 = 3\, k_3$).

The approximate yields of ethylene glycol, glycolaldehyde and glyoxal from the oxidation of ethylene could be estimated from experiments in which periodate-permanganate solutions were reduced as rapidly as possible by stirring them efficiently in the ethylene atmosphere. Rapid reduction of the oxidant should result in mixtures containing ethylene glycol, glycolaldehyde and glyoxal, along with formaldehyde and formate ion from the subsequent oxidation of these products. This subsequent oxidation should be minimized by the rapid reduction of the oxidant. After allowing the reaction mixtures to stand for several hours to enable condensation of the glycolaldehyde to take place, it should prove possible to separate the products by Celite partition chromatography (128).

With this purpose in mind, two experiments were performed at pH 8.0; in the first, the oxidant was 2 millimoles of periodate and 0.2 millimole of permanganate in 40 ml. of solution; in the second, the oxidant was 2 millimoles of periodate and 0.02 millimole of permanganate in 40 ml. of solution. In each experiment, complete reduction of the oxidant was completed in fifteen minutes. The first reaction mixture was left for six hours, and the second was left for one hour; each was then chromatographed. Bands were located on each column at the positions expected for ethylene glycol and the condensation products. These bands were cut out, the products extracted into water, and the composition of the resulting aqueous solutions was examined by treatment with periodate and determination of the yield of formaldehyde and consumption of oxidant. The results are summarized in Table XXX. For each run the fast-moving band (presumably ethylene glycol) is given last.

TABLE XXX

Celite Partition Chromatography of the Reaction Products Obtained by the Oxidation of Ethylene with Periodate-Permanganate

Run	Band No.	mE of Oxidant Consumed on Treatment with Periodate	mM of CH_2O Formed on Treatment with Periodate
1	1	0.025	0.0070
	2	0.013	0.0038
	3	0.014	0.0036
	4	0.140	0.127
2	1	0.025	0.0178
	2	0.039	0.0136
	3	0.339	0.325

The results given in this table permit a number of conclusions to be drawn concerning the course of the reaction. First, in each run, the fast-moving band (band 4 of run 1 and band 3 of run 2) was ethylene glycol, since the O/CH_2O ratio of the material extracted from these bands was unity. Secondly, the increase in the yield of glycol with the decrease in the concentration of permanganate (run 2) appears to be a true observation, since the same effect was noted in another way (compare runs 2 and 3 of Table XXVIII). Thirdly, the slow-moving material isolated from each Celite column gave analytical results near those expected for glyceraldehyde (compare reference 173; see also page 228) ; bands 1,2 and 3 of run 1 and band 2 of run 2 show an average O/CH_2O ratio of 3.5 (calculated for glyceraldehyde, $O/CH_2O = 4$). Finally, since (for run 2) a total of 4.1 milliequivalents of oxidant were consumed in the initial fast reaction, but the material isolated from bands 1 and 2 consumed a total of only 0.064 milliequivalent of oxidant, the majority of the glycolaldehyde product must have been oxidized to formaldehyde and formate ion during the initial fast reaction; conversely, most of the ethylene glycol must have remained in the reaction mixture at the end of this fast initial reaction.

A rough estimate of the consumption of olefin was made for run 2 and it was noted that approximately 0.91 millimole of ethylene was consumed during the reaction. Since the majority of the ethylene glycol appeared to have remained after completion of the initial reaction and 0.17 millimole of this compound was isolated on the Celite column, the yield of this product must have been close to 19%. Interpolation of this value in Table XXIX indicates that the yield of glycolaldehyde was near 71% and the yield of glyoxal was 10%. Thus, for ethylene, using these reaction conditions, the rate of ketol formation is nearly four times the rate of glycol formation.

The conclusions concerning the relative rates of the periodate oxidations of ethylene glycol and glycolaldehyde are supported, as seen earlier, by the results of competitive experiments with these two compounds (see page 236).

The information acquired from the periodate-permanganate oxidations of ethylene described above enabled a procedure to be developed for the oxidation of 1,1-dideuteroethylene which would permit the proper interpretation of any mass effect. The deuterated compound was oxidized by a solution containing 2.0 millimoles of periodate, 2.0 millimoles of potassium carbonate and 0.2 millimole of permanganate in 40 ml. of water. The reaction mixture was vigorously stirred for 10 minutes and was then removed from the vacuum line and immediately poured into a solution prepared from 30 ml. of N arsenite and 15 ml. of 6 N sulphuric acid. The resulting clear, colourless solution was treated with 2,4-dinitrophenylhydrazine reagent, as described in the experimental section, and the percentage deuterium in the formaldehyde-2,4-dinitrophenylhydrazone product was determined.

Oxidation of the olefin in this way should minimize the proportion of formaldehyde from further oxidation of ethylene glycol and thus eliminate a major factor which could obscure the results. The infrared spectrum of the 2,4-dinitrophenylhydrazone obtained from this experiment is shown in Fig. 26. The significant portion of the spectrum is the region 725-715 cm^{-1}, and comparison of this band of Fig. 26 with those of the known mixtures shown in Fig. 7 showed that the deuterium content of this formaldehyde product was

68 ± 2%. A second experiment conducted in the same way gave an identical result (Fig. 27 d).

This result comprises direct evidence that the route of decomposition of the cyclic intermediate XX occurs mainly via the cyclic mechanism. It is inconceivable that this kind of mass effect would have been obtained if the acyclic mechanism were an important route of decomposition of the intermediate XX. For a constant ratio of k_1/k_3, equation 81 passes through a maximum when plotted as a function of k_2. The percentage CD_2O at the maximum can be determined simply by differentiation of this equation with respect to k_2. For a value of k_1/k_3 of 10 (deuterium isotope effect of 10, which is higher than any experimental value which might be envisaged), the maximum of equation 81 occurred at 58.9% of CD_2O. For any "normal" mass effect, the acyclic mechanism would have yielded formaldehyde containing less than this amount of deuterium.

Since the foregoing experiments with 1,1-dideuteroethylene were conducted under conditions where the liberation of formaldehyde from the ethylene glycol product of the reaction was minimized, the magnitude of the deuterium isotope effect is approximately 68/32, or 2.1. The fact that a mass effect was observed indicates that, at some time during the reaction, a symmetrical intermediate must have been formed, which permitted a competition between the breaking of a C-H bond and a C-D bond. This symmetrical intermediate can only be the cyclic intermediate; this result, therefore, provides independent

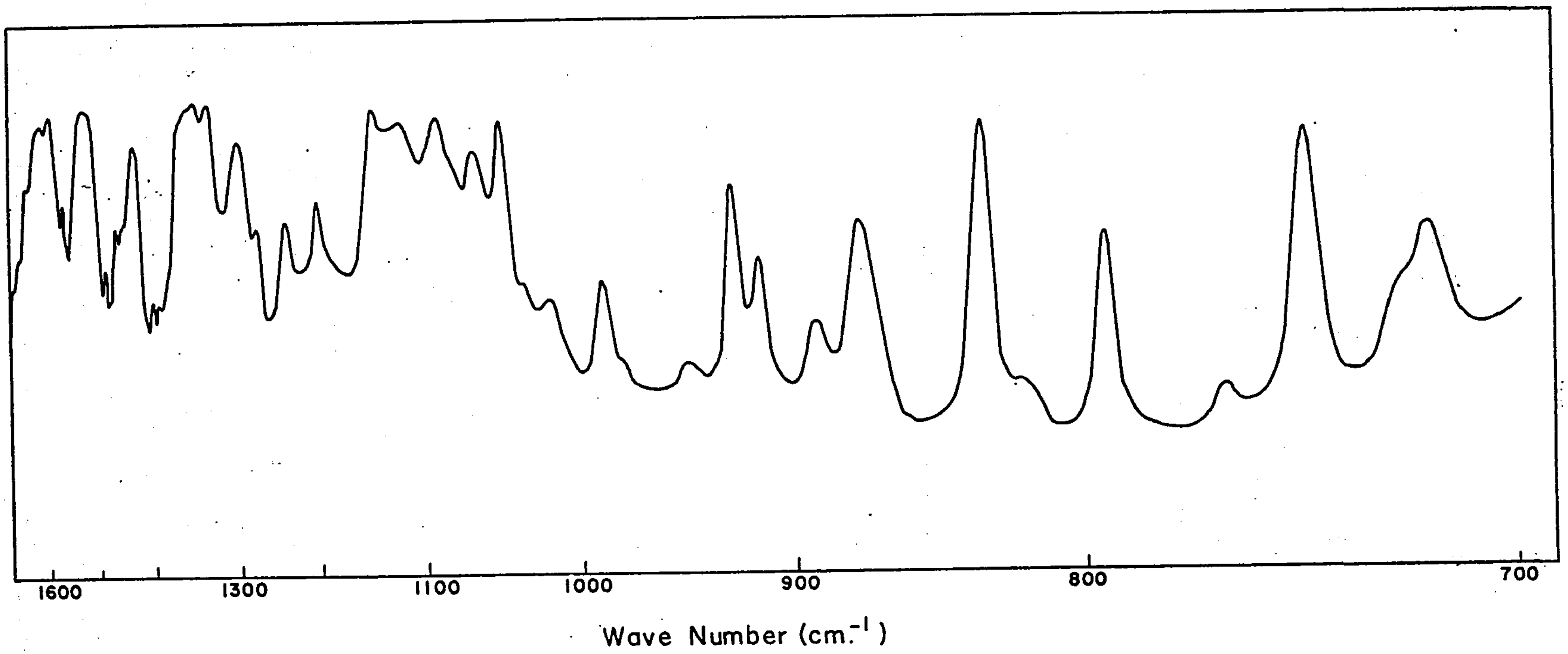


Fig. 26 - Infrared spectrum of the formaldehyde-2,4-dinitrophenylhydrazone obtained by a 10 minute oxidation of 1,1-dideuteroethylene with 2 mM of periodate and 0.2 mM of permanganate.

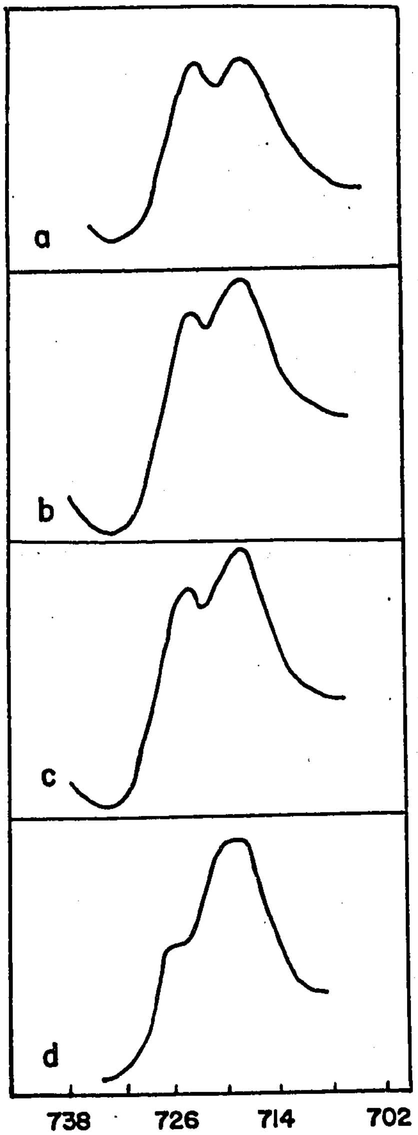


Fig. 27 - Infrared spectra, showing the 725-715 cm.$^{-1}$ region, of the formaldehyde-2,4-dinitrophenylhydrazones obtained by oxidation of 1,1-dideuteroethylene. (a) Oxidation by periodate-osmium tetroxide. (b) Oxidation by periodate-permanganate, 60 min. reaction. (c) Oxidation by periodate-permanganate, 24 hr. reaction. (d) Oxidation by periodate-permanganate, 10 min. reaction.

evidence for the existence of the cyclic intermediate during the conversion of the olefin ethylene to the ketol glycolaldehyde.

The conclusions on page 246 were confirmed by the following additional experimental results: (a) oxidation of 1,1-dideuteroethylene by the osmium tetroxide-periodate reagent yielded a formaldehyde product whose 2,4-dinitrophenylhydrazone had an infrared spectrum identical in every respect with that of the synthetic 50% mixture (the 725-715 $cm.^{-1}$ region of this spectrum is shown in Fig. 27 a), thus demonstrating the reliability of the experimental and analytical procedures; (b) a slow reduction (30-60 minutes) of the periodate-permanganate solution, followed by addition of excess periodate to the reaction mixture to effect complete oxidation of ethylene glycol and glycolaldehyde, yielded formaldehyde containing 58% deuterium (Fig. 27 b,c). This lowering of the observed mass effect owing to the liberation of formaldehyde from the ethylene glycol is discussed in more detail below. (c) There was no exchange of deuterium with the solvent under the mildly alkaline reaction conditions, since the same result was obtained from (b) when the formaldehyde was isolated after 1,6 and 24 hours.

The formation, from the use of an extended reaction time and excess periodate, of formaldehyde containing 58% of deuterium can be employed to calculate the magnitude of the mass effect by a somewhat different method than that used above. It was demonstrated on page 244 that the ratio of ketol formation to glycol formation for the oxidation of ethylene was approximately 4.

This ratio should be nearly the same for 1, 1-dideuteroethylene; the occurrence of the mass effect would tend to decrease the total amount of glycolaldehyde, owing to the formation of the species XXIII (see page 224), but the mass effect would also decrease the yield of glyoxal, with a concomitant increase in the yield of glycolaldehyde. That there is no appreciable change in the proportion of glycolaldehyde to ethylene glycol on going from ethylene to 1, 1-dideuteroethylene was demonstrated by the result of an experiment in which the oxidation of 1, 1-dideuteroethylene was studied under the conditions used in run 4 of Table XXVIII. The variation with time of the O/CH_2O ratios of the two olefins is shown in Table XXXI.

The magnitude of the deuterium isotope effect, y , may then be calculated by substitution of the values

$$k_1 = y k_3$$

$$\text{and} \quad \frac{k_1 + k_3}{k_2} = 4$$

into equation 80, page 225. This leads to the equation,

$$\% \, CD_2O = 58 = \frac{\left(y + \frac{y+1}{4}\right) 100}{y + \frac{y+1}{2} + 1} ,$$

from which y is 1.61.

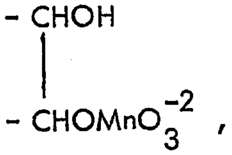
TABLE XXXI

The Oxidation of Ethylene and 1,1-Dideuteroethylene with Periodate-Permanganate

Time of Analysis From Start of Experiment (hr.)	Results of Analysis mE of Oxidant Consumed	mM of CH_2O Liberated	O/CH_2O
(a) oxidation of ethylene with 2 mM of periodate and 0.02 mM of permanganate; the initial reaction with the olefin required 1.17 hr.			
2.0	4.76	0.390	12.2
4.3	5.26	0.728	7.2
6.5	5.54	0.822	6.7
12.0	6.05	1.028	5.9
27.0	6.78	1.002	6.8
(b) oxidation of 1,1-dideuteroethylene with 2 mM of periodate and 0.02 mM of permanganate; the initial reaction with the olefin required 3.5 hr.			
3.8	4.56	0.355	12.8
7.2	5.02	0.625	8.0
10.3	5.25	0.762	7.0
22.0	6.00	0.820	7.3

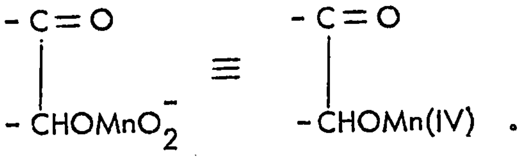
This direct determination of the route of ketol formation was substantiated in a number of indirect ways by results obtained from the permanganate oxidation of various other olefins. In their study of the conversion of oleate ion to the 9,10-ketohydroxystearic acids, Coleman, Ricciuti and Swern (85) isolated significant yields (3-7%) of 9,10-diketostearic acid. They did not prove whether this oxidation occurred directly from the olefin or by a subsequent oxidation of the ketohydroxystearic acids since fast reaction times were not used for the reaction, and since, under the conditions of the oxidation of the olefin, a 25% yield of 9,10-diketostearic acid was obtained after 1.5 hours by permanganate oxidation of the ketohydroxystearic compounds. It was of interest to re-investigate this reaction since the mechanism of the formation of the diketo compound has some bearing on the mechanism of formation of the ketol. Using reaction conditions described on page 158, but high concentrations of permanganate and olefin, a solution of 2 millimoles of oleate ion in 30 ml. of potassium hydroxide at pH 9.6 was cooled to 5° and was oxidized for 60 seconds by a solution of 30 mM of permanganate in 100 ml. of cold water. The insoluble products of this reaction were <u>erythro</u>-9,10-dihydroxystearic acid (24%), 9,10-diketostearic acid (22%), and the 9,10-ketohydroxystearic acids (22%). In the same time interval, and using the same reaction conditions, both the ketols and the glycol were recovered quantitatively. Therefore, the 9,10-diketostearic acid must have been formed by direct oxidation of the olefin and, presumably, by oxidation of the cyclic ester intermediate.

Since the glycol was not attacked under these reaction conditions, a partially-hydrolyzed hypomanganate ester,



$$\begin{array}{l} -\mathrm{CHOH} \\ \quad | \\ -\mathrm{CHOMnO_3^{-2}} \end{array} ,$$

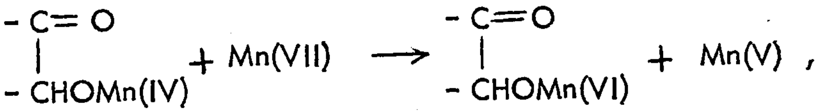
cannot be an intermediate in the reaction. That is, a mechanism analogous to the "acyclic mechanism" (page 194) is precluded for the oxidation of the cyclic ester to the diketo compound. Further oxidation of the cyclic ester should proceed via the cyclic mechanism, yielding XXVI,



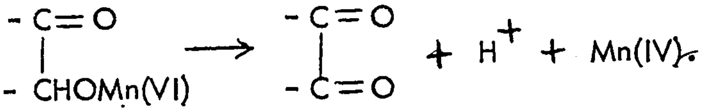
$$\begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{CHOMnO_2^-} \end{array} \equiv \begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{CHOMn(IV)} \end{array} .$$

XXVI

At low permanganate concentrations, this intermediate undergoes hydrolysis, yielding ketol; however, the high concentration of permanganate used in this reaction favours the reactions,



$$\begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{CHOMn(IV)} \end{array} + \mathrm{Mn(VII)} \longrightarrow \begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{CHOMn(VI)} \end{array} + \mathrm{Mn(V)} ,$$



$$\begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{CHOMn(VI)} \end{array} \longrightarrow \begin{array}{l} -\mathrm{C{=}O} \\ \quad | \\ -\mathrm{C{=}O} \end{array} + \mathrm{H^+} + \mathrm{Mn(IV)} .$$

The above scheme seems quite reasonable, and comprises added evidence in favour of the oxidative opening of the cyclic ester intermediate. The formation of glyoxal in the periodate-permanganate oxidation of ethylene is explained in the same way. Periodate must be capable of oxidizing the tetravalent ester ultimately to a carbonyl. Since the glyoxal was formed in low yield, the competition between periodate and hydroxyl ions for this tetravalent intermediate must favour the hydroxyl ions, in contrast to the competition for the pentavalent intermediate.

The oxidation of oleic acid to ketol yields the 9,10-keto-hydroxystearic acids in approximately equal amounts (3), owing to the similar electronegativities of the two R- groups of this olefin. When the two R- groups differ in size or in electronegativity, the amounts of the two ketols should also differ, since opening of the cyclic ester at one of the carbon atoms should be favoured by structural or electronic factors. If the mechanism for the oxidation of the cyclic ester to ketol is correct, the relative amounts of the two ketols should vary in the proper direction as the R- groups are varied.

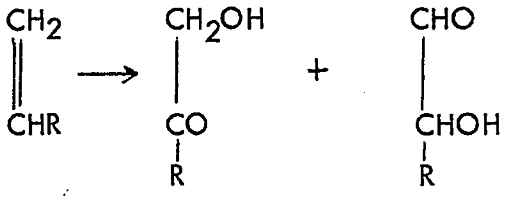
Experimental data concerning this aspect of the reaction can be obtained from the periodate-permanganate oxidation of compounds containing a terminal methylene group (84, 174). It is found that the yield of formaldehyde decreases as the electronegativity of the R- group increases. This is illustrated by the data of Table XXXII ; all of the compounds were oxidized in the same way.

TABLE XXXII

Effect of Substituents on the Periodate-Permanganate Oxidation of $RCH{=}CH_2$

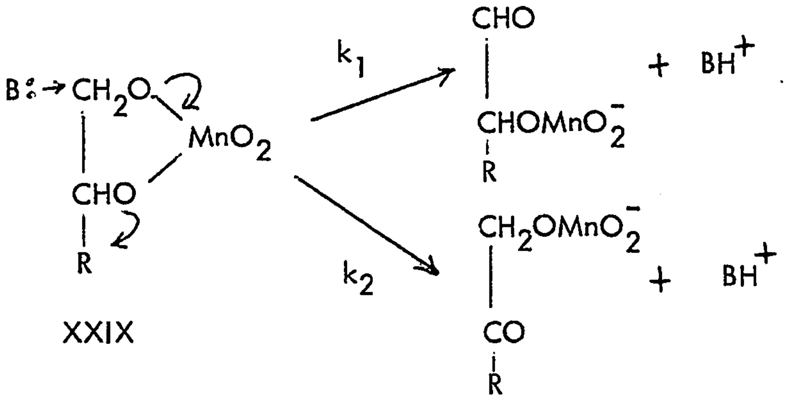
R - group	% Yield of CH_2O	pK_a of RCOOH
$-CH_2COO^-$	82	5.85
$-(CH_2)_8COO^-$	76	5.52
$-C_6H_5$	62	4.17
$-CH_2OEt$	56	----
$-CH_2OAc$	50	----
$-CH_2Br$	45	2.87
$-CH_2CN$	25	2.44
-CN	13	----

The oxidation of these compounds will yield initially a mixture of the two ketols XXVII and XXVIII,



XXVII XXVIII

Since only XXVII can liberate formaldehyde, it is evident that the proportion of this compound decreases as the electronegativity of the R- group increases. On the assumption that the cyclic ester is oxidized by the cyclic mechanism, this means that the proportion of the cyclic ester XXIX which opens at the terminal position is increased by this increase in electronegativity. The diagram below indicates that the trend is in the proper direction.



($k_1 > k_2$ with increasing electronegativity)

This effect of electronegativity on the reaction is thus consistent with the mechanism arrived at in other ways.

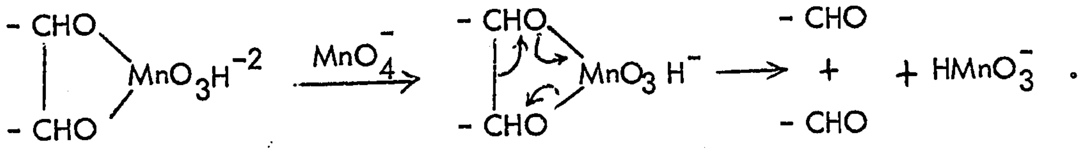
5. Scission of the Carbon-Carbon Bond in the Oxidation of Olefins by Permanganate

Though it is generally believed that the oxidation of olefins by excess permanganate in hot alkali or in non-aqueous media results in scission of the carbon-carbon bond and the formation of acids or ketones (page 7), the low yields and complex nature of the products of such oxidations should be ample evidence that the reaction route is not so simple. The fact that glycol and ketol can be isolated from the oxidation of an olefin in the cold and in weak alkali has suggested that such compounds may be intermediates under other reaction conditions as well, and that scission of the carbon-carbon bond of the olefinic linkage then results from further oxidation of these compounds. In point of fact, this viewpoint is incorrect, for the scission of the carbon-carbon bond of a glycol by permanganate does not occur at the -CHOH - CHOH- linkage. The experimental basis for this assertion lies in two papers published over twenty years ago, which bear important implications on the mechanism of the scission of the olefinic linkage by permanganate.

In 1925, Lapworth and Mottram (5) showed that the oxidation of erythro-9,10-dihydroxystearic acid by permanganate at room temperature and pH 12.5 resulted in the formation of suberic, n-octoic and oxalic acids. The yields were better than 80%. No azelaic acid was obtained at this temperature, but some of this compound, in addition to suberic, n-octoic and oxalic acids was isolated from a reaction conducted at a higher temperature. This work was confirmed and extended by Green and Hilditch (175) to a number of other di- , tetra- and hexahydroxystearic acids. They found that the same type of "lateral" oxidation occurred in all of these compounds. The course of the oxidation was independent of the stereoisomeric form of the hydroxy compound, the length of the chain of carbon atoms or of the position of the hydroxyl groups in the carbon chain. There was in no case evidence of a direct scission of the glycol linkage. Thus, the oxidation of these glycols, at pH 12-13, was represented approximately by the equation,

$$RCH_2 - CHOH - CHOH - CH_2R' \xrightarrow{6\,[O]} RCOOH + R'COOH + H_2C_2O_4$$

Since the oxidation of olefins by excess permanganate in this pH region frequently yields some of the product corresponding to cleavage of the olefinic bond, and the results of Lapworth and Mottram and Green and Hilditch suggested that this scission of the olefinic linkage did not require a glycol intermediate, it, therefore, seemed likely that cleavage of the <u>olefinic</u> linkage by permanganate occurred by decomposition of the cyclic ester intermediate,



(Compare the periodate-glycol reaction, references 42-44). It is apparent that the results obtained by these earlier workers offers a direct experimental approach to the question of whether such a reaction route is of any importance in aqueous medium,for the formulation of the mechanism in this way would be considerably enhanced if it could be demonstrated that, under the conditions used by Lapworth and Mottram, oleic acid gave appreciable yields of azelaic and pelargonic acids. A search of the literature revealed, however, that the cleavage products of the oxidation of oleic acid had not been examined under these reaction conditions. Moreover, it was noted that, in general, no satisfactory data existed concerning the nature of the cleavage products which were formed as by-products when olefins were converted to glycols or ketols.

It was, therefore, considered worthwhile to investigate this aspect of the oxidation of oleic acid by permanganate. Such a study should be of interest for several reasons. First, a demonstration that the olefin is cleaved at the olefinic linkage, while the primary products (glycol and ketol) are not, would show that the carbon-carbon bond was broken by direct oxidation of the olefin. Secondly, it was of interest to study the effects of temperature and pH on the reaction to determine the relative importance of these factors on the various routes of decomposition of the cyclic intermediate, and to see which conditions were most favourable for scission of the olefinic linkage.

The composition of the cleavage products was determined by vapour phase chromatography. Insoluble products of these oxidations were separated by filtration and the filtrates, after extraction with ether, were methylated before chromatographing them. The column used was packed with Celite and silicone grease; this provided an efficient separation of the dicarboxylic esters and the $C_6 - C_9$ monocarboxylic esters. Using nitrogen as carrier gas, the "retention times" of the compounds were constant over a fairly wide range of flow rate, and the composition of unknown mixtures was easily determined by reference to the standard curve (Fig. 28), prepared by the chromatography of mixtures of known compounds. The relative amounts of the various compounds in the product of the oxidations were determined by comparison of the areas under the curves; the ratios of the areas under the curves were taken as a rough measure of the relative amounts of the compounds in the reaction product.

The results obtained from these experiments are summarized in Table XXIII; unless otherwise mentioned, the reaction time refers to the time for complete reduction of the oxidizing agent to the tetravalent stage. The presence of oxalic acid in the reaction mixtures was determined by a test of the aqueous phase remaining after the ether extraction with resorcinol and sulphuric acid, as described in the Merck Index (176). Positive, negative and uncertain tests are designated by +, -, and ? .

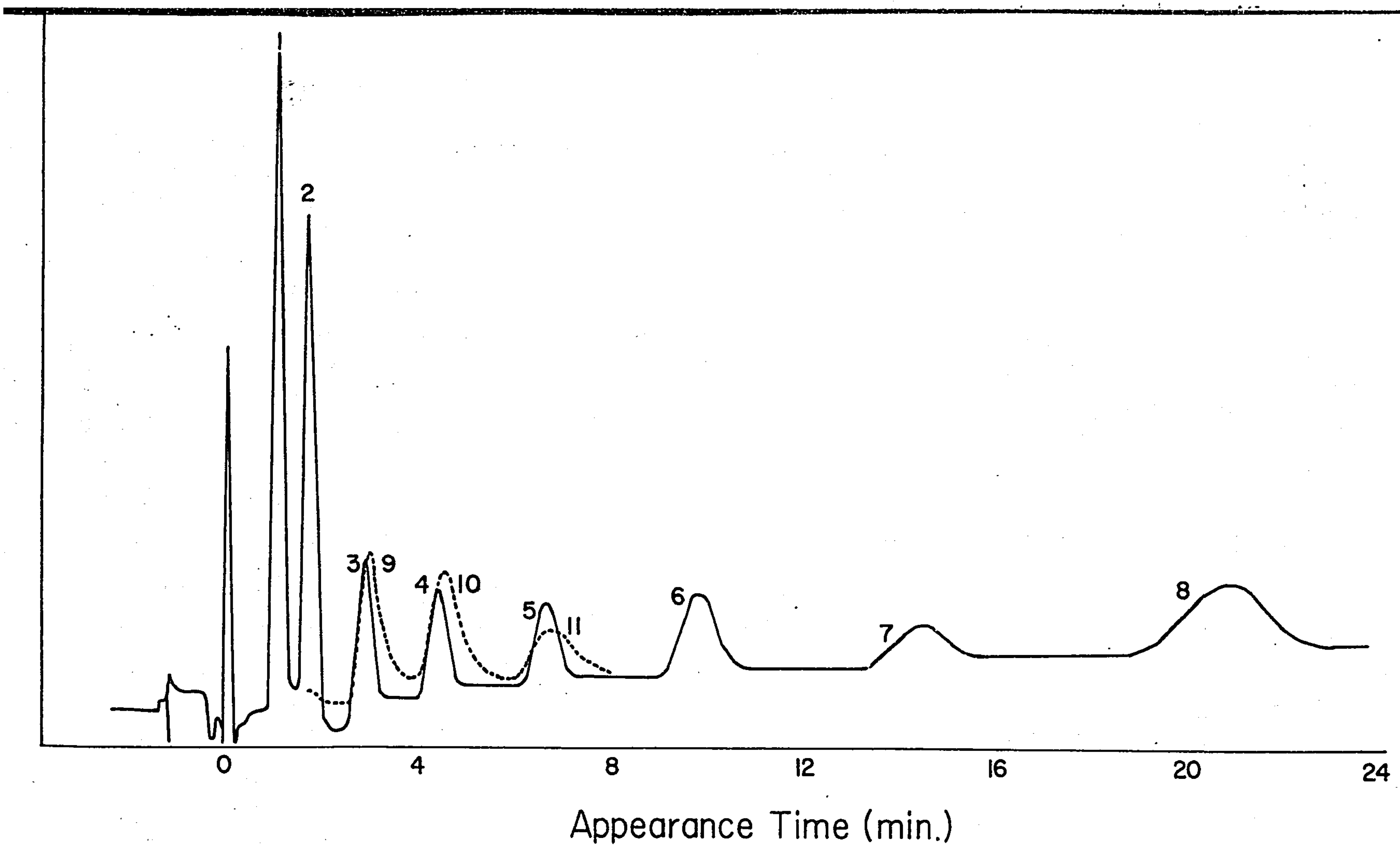


Fig. 28 – Vapour phase chromatogram showing the appearance times of the methyl esters of the saturated C_2 - C_9 dicarboxylic acids (1-8) and the C_7 - C_9 monocarboxylic acids (9-11)

TABLE XXXIII

Scission of the Olefinic Linkage of Oleate Ion, and Related Reactions

Initial Molar Composition of the Reaction Mixture		pH	Temp. °C	Reaction Time, hr.	Percentage Yields of Products			Approximate Relative Amounts of Cleavage Products	
Oxidant	Reductant				Glycol	Ketol	Diketone	Dicarb. Acids $C_2 : C_7 : C_8 : C_9$	Monocarb. Acids $C_6 : C_7 : C_8 : C_9$
1. Oxidations of Oleate Ion									
(a) Permanganate Oxidations									
0.0133	0.0033	9.6	50	stopped (12 hr.)	4	4	0	? : 0 : 88 : 12	0 : 0 : 66 : 34
0.0133	0.0033	9.6	100	0.05	20	4	0	+: 0 : 75 : 25	22 : 5 : 52 : 20
0.0133	0.0033	13.0	50	2.0	47	0	0	only C_8 detected	none detected
0.0133	0.0033	13.0	100	0.05	60	0	0	? : 25 : 64 : 11	0 : 0 : 16 : 84
0.231	0.0154	9.6	0	stopped (1 min.)	24	22	22	0 : * : * : 100	0 : 7 : 32 : 61
(b) Manganate Oxidation									
0.0167	0.0033	13.0	25	3.0	55	0	0	+: 8 : 87 : 5	0 : 7 : 80 : 13
2. Permanganate Oxidation of <u>Erythro</u>-9,10-Dihydroxystearic Acid									
0.0133	0.0033	9.6	100	0.12	24	0	0	+: 3 : 91 : 6	36 : 12 : 43 : 9
3. Permanganate Oxidations of the 9,10-Ketohydroxystearate Ions									
0.0133	0.0033	9.6	100	stopped (.2 hr.)	0	0	0	+: 7 : 89 : 4	0 : 9 : 80 : 11
0.0133	0.0033	13.0	25	0.16	0	0	0	+: 8 : 84 : 8	0 : 8 : 84 : 8
4. Permanganate Oxidations of Azelaate Ion									
0.0150	0.0050	9.6	100	stopped (.25 hr.)				0 : 0 : 0 : 100	--
0.0150	0.0050	13.0	100	stopped (.30 hr.)				the azelaate ion was completely degraded to a complex mixture of lower acids	

---

* Indicates a trace yield of this product.

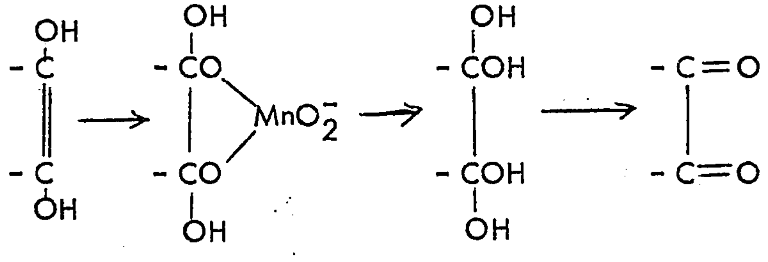
A. Oxidation of the 9, 10-Ketohydroxystearate Ions

The major route of the permanganate oxidation of these compounds at pH 9.6 and pH 13 at both temperatures involved a reaction of the kind described by the earlier workers (5, 175). However, small amounts of azelaic and pelargonic acids were obtained from both oxidations. The mechanism of the reaction was best explained by the assumption that the compounds had reacted via the enols, the enolization being more favourable in the direction remote from the hydroxyl group. Since equal proportions of the two ketols were oxidized (3), the overall effect on both sides of the $C_9 - C_{10}$ bond was the same, and the enolizations may, therefore, be formulated as,

$$CH_3(CH_2)_7CHOH\text{-}CO(CH_2)_7COO^- \longrightarrow \begin{array}{c} CH_3(CH_2)_7COH{=}COH(CH_2)_7COO^-\ (4\%) \\ + \\ CH_3(CH_2)_7CHOHCOH{=}CH(CH_2)_6COO^-\ (96 \end{array}$$

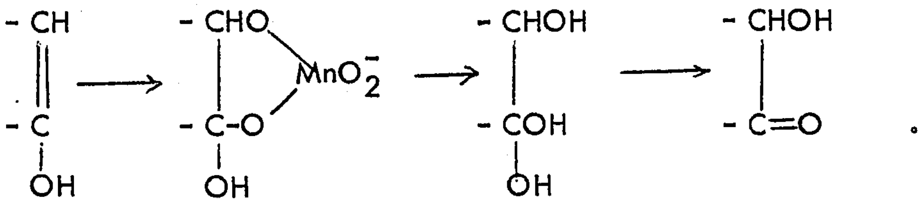
$$CH_3(CH_2)_7CO\text{-}CHOH(CH_2)_7COO^- \longrightarrow \begin{array}{c} CH_3(CH_2)_7COH{=}COH(CH_2)_7COO^-\ (4\%) \\ + \\ CH_3(CH_2)_6CH{=}COHCHOH(CH_2)_7COO^-\ (96\% \end{array}$$

The oxidation of these enols should proceed in the same way as the oxidation of an olefin, yielding initially, intermediates such as XXX and XXXI,



XXX

XXXII



XXXI XXXIII

If hydrolysis of XXX and XXXI to XXXII and XXXIII were the major subsequent reactions of these intermediates, then, by oxidation of the new hydroxyl groups to ketones, followed by further enolization and oxidation along the carbon chain, complete degradation of the molecule would result. Since this did not occur, the scission of the carbon-carbon bonds did not appear to involve the intermediate products XXXII and XXXIII. Thus, if the above interpretation of the results is correct, the oxidation of the ketol is a direct example of the scission of carbon-carbon bonds by further oxidation of a cyclic intermediate.

These considerations and the postulate of XXX and XXXI as intermediates were given strong support by the results of a kinetic study of the reaction. This study, using excess tellurate ions as described in previous sections of this thesis, was conducted at 20°. Plots of the concentration of permanganate against time were linear at each pH studied in the pH region 8-13, indicating that the oxidation was zero order. At pH 8, 9, 10, 11 and 13, the rate constants ($\times 10^4$ moles litre^{-1} sec.$^{-1}$) were 0.00182, 0.00254, 0.00478, 0.0188and 2.25. These results were fit fairly well by the equation,

(84)... $$k = 1.8\times10^{-7} + 2\times10^{-3}[OH^-].$$

At pH 12, the reaction was first order in ketol concentration and zero order in permanganate concentration. This result, along with equation 84, identifies enolization of the ketol as the rate-determining step of the reaction. The enolization of a ketone is well-known to be a base-catalyzed reaction, in agreement with the observed dependence on the hydroxyl ion concentration (equation 84).

At pH 13, the yields of Mn(VI) and Mn(IV) were those which would have been anticipated if the initial reduction of permanganate involved a two-electron exchange (see page 142). This is shown in Fig. 29. The linear concentration-time plots in Fig. 29 demonstrate the zero order nature of the oxidation reaction. The fact that the initial reduction of permanganate involves a two-electron exchange supports the idea that the oxidation was initiated by reaction of permanganate with the enols.

B. Oxidation of Erythro-9,10-Dihydroxystearate Ion

The major route of this reaction, like that of the ketols, involved scission of the $C_8 - C_9$ and $C_{10} - C_{11}$ bonds, although small amounts of azelaic and pelargonic acids ($C_9 - C_{10}$ cleavage) were again obtained. The compound consumed twelve equivalents of oxidant in three minutes, but an appreciable portion remained unreacted, and considerable degradation was observed on the methyl group side of the compound. This suggests that the initial stage of the

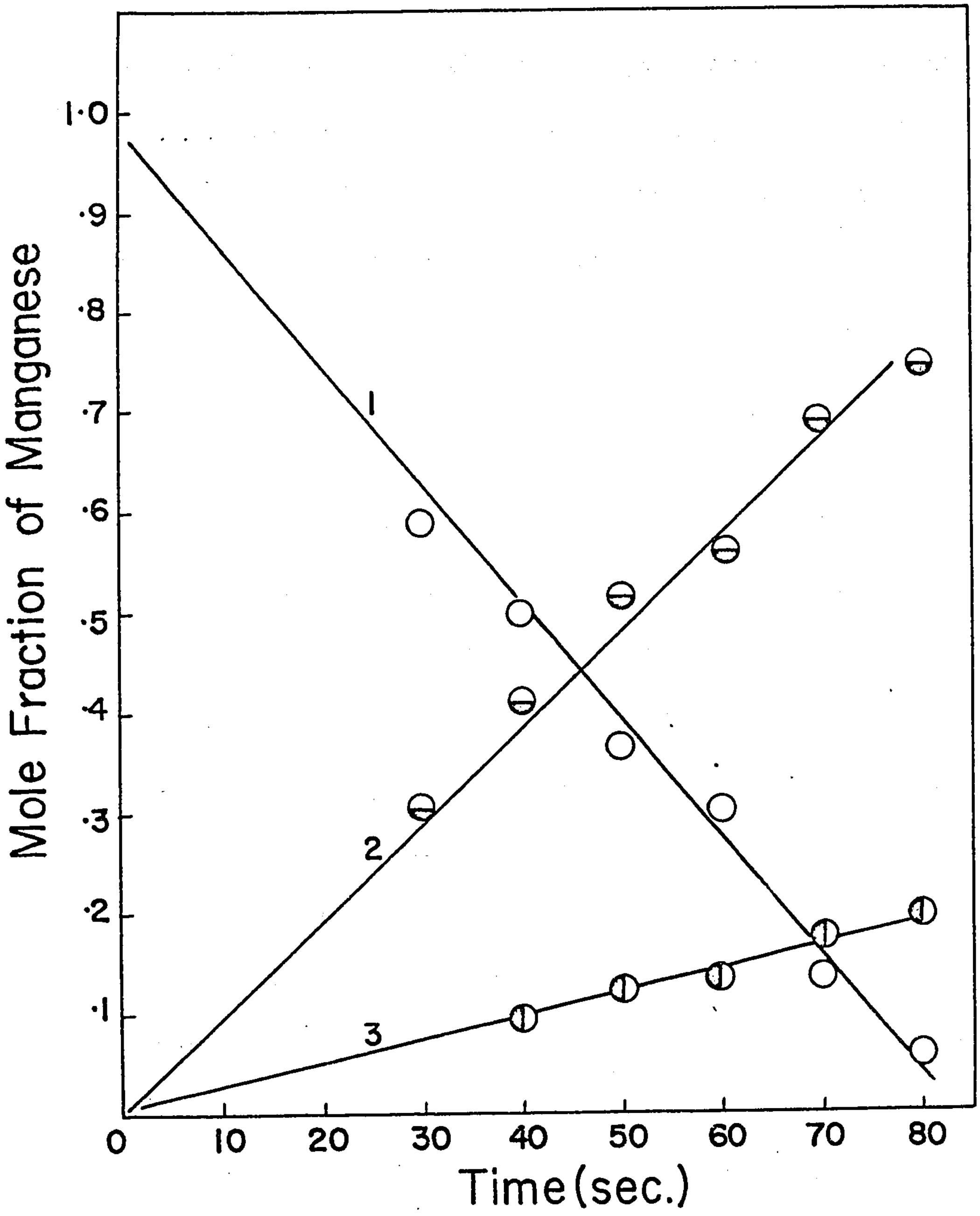


Fig. 29 - The reduction of permanganate (3×10^{-4}M) by the 9, 10-ketohydroxystearic acids at pH 13, using a tellurate concentration of 5×10^{-3}M. The concentration of the ketols was 3×10^{-4}M. Plots 1, 2 and 3 are the concentrations of Mn(VII), Mn(VI) and Mn(IV), respectively.

reaction is oxidation of the C_{10} hydroxyl group (where C_1 is the carboxyl group), followed by enolization towards the methyl group. The low yields of C_9 acids from this oxidation are attributed to the reluctance of the initially-formed ketol to form the ene-diol structure.

C. Oxidation of Oleate Ion by Permanganate

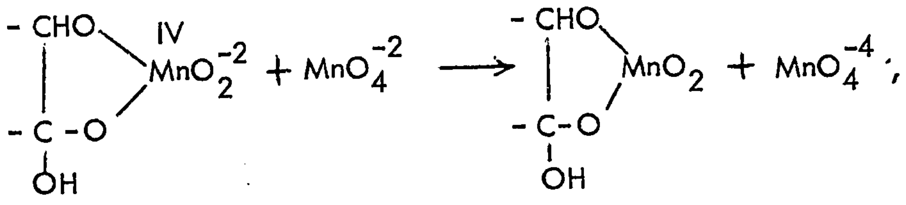
The oxidation of this compound with excess permanganate gave results essentially the same as those obtained from the oxidations of the glycol and the ketols, with one important difference — in all of the experiments, the yield of the C_9 acids was significantly higher than that observed in the oxidations of the glycol and the ketols. This established that, under these reaction conditions, part of the olefin was cleaved at the $C_9 - C_{10}$ bond without intermediate ketol or glycol formation. It is evident, therefore, that with suitable reaction conditions, the oxidation of the olefin by permanganate includes oxidation of some intermediate stage with direct scission of the olefinic linkage. The oxidation of the intermediate in this way is favoured by low pH, high concentrations and excess permanganate, although the reaction seems to have occurred even at pH 13.

The temperature dependence of the various routes of oxidation of the olefin can be ascertained from this work. It is evident that the relative orders for this temperature dependence are, glycol < carbon cleavage < ketol.

Thus, even at 100° and pH 13, a 60% yield of glycol could be isolated from the reaction of excess permanganate with the olefin. The effect of temperature on the route of the reaction was evident at the lower pH as well, since the route of the reaction was apparently changed from predominantly ketol to predominantly glycol by an increase in the temperature.

D. Oxidation of Olefins by Manganate

A fair yield of glycol was obtained from the oxidation of oleate ion by manganate, but the product was not stable, further oxidation to the C_8 acids occurring fairly readily. This secondary oxidation cannot occur in the same way as the oxidation by permanganate, unless a reaction,



can occur first.

A few rate studies were made on the oxidation of oleate ion and 10-undecenoate ion by manganate. The two plots of Fig. 30 are typical of the results which were obtained. Since the rate of oxidation of the glycol

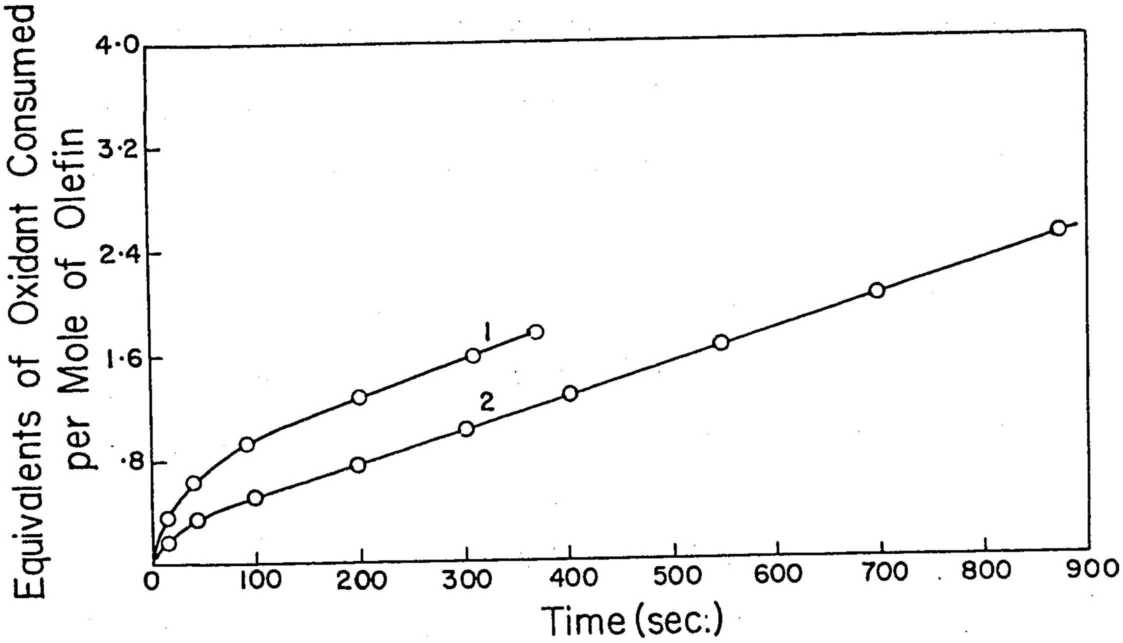


Fig. 30 - The reaction of potassium manganate (0.5 mM) with 10-undecenoic acid (0.26 mM). Plot 1, N/5 alkali. Plot 2, N/1 alkali.

by manganate was of the same order of magnitude as the rate of hydroxylation of the olefin, there was no discontinuity in these plots. Oxidation by manganate is, therefore, rather difficult to study kinetically, since all of the reactions in the overall scheme olefin → glycol → cleaved products would have to be investigated.

The oxidations of oleate ion and dihydroxystearate ion by potassium manganate at pH 12.7 were followed using tellurate ions to solubilize the reaction mixtures. Two typical experiments are summarized in Table XXXIV.

TABLE XXXIV

Oxidations of Oleate Ion (3×10^{-4}M) and Dihydroxystearate Ion (3×10^{-4}M) by Potassium Manganate (3×10^{-4}M) at 25°

Oxidation of the Olefin		Oxidation of the Glycol	
Time (min.)	Conc. of MnO_4^{-2}	Time (min.)	Conc. of MnO_4^{-2}
5.0	2.98×10^{-4}M	2.0	2.86×10^{-4}M
10.0	2.81	4.0	2.77
15.0	2.67	15.0	2.69
20.0	2.52	30.0	2.58
25.0	2.37	47.0	2.50
30.0	2.23	60.0	2.43
35.0	2.13	75.0	2.37
40.0	1.99	90.0	2.27
45.0	1.87	105	2.22
50.0	1.75	120	2.14
55.0	1.66	135	2.08
60.0	1.58	150	2.02
65.0	1.49	165	1.96
70.0	1.42	180	1.88
75.0	1.34	195	1.81
80.0	1.29	213	1.74
85.0	1.19		

E. Oxidation of Azelaate Ion

In order to rule out the possibility that the generally low yields of the C_9 acids which were reported in Table XXXIII were caused by rapid oxidation of these compounds under the reaction conditions, the permanganate oxidation of azelaate ion was also studied. At pH 9.6 and 100°, there was no reaction in fifteen minutes , and no lower acids were isolated from the reaction mixture, the recovery of azelaic acid appearing quantitative. At pH 13, however, though permanganate was only slowly reduced to manganate, complete degradation of the organic compound appeared to have occurred. Since the degradation was more extensive than could be accounted for by the consumption of oxidant, the degradation could have been caused by free radical attack on the organic compound. Since the slow reduction of permanganate to manganate under these conditions appeared to be unaffected by the presence of azelaate ions, this experiment provides confirmation of the suggestion (51) that the initial stage of the decomposition of permanganate in alkaline media results in the formation of a free radical,

$$MnO_4^- + OH^- \longrightarrow MnO_4^{-2} + OH \quad .$$

The fact that azelaic acid could be isolated from the oxidation of oleate ion by manganate and permanganate under conditions where the azelaate ion alone was extensively degraded indicates that the degradation was related to the decomposition of permanganate in alkaline medium.

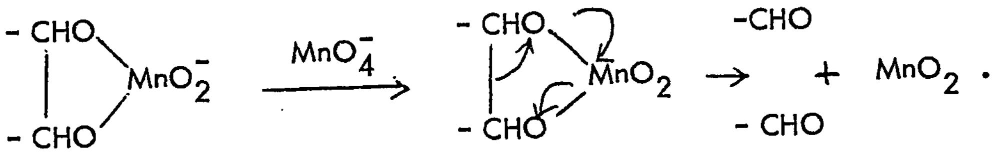
The results discussed in sections A-E are of interest, not only because they permit conclusions concerning the routes by which permanganate will cleave carbon-carbon bonds in the oxidation of olefins, glycols and ketols, but because these conclusions can be extended to include much of the existing data on the scission of carbon-carbon bonds by permanganate under other reaction conditions. It seems clear that, in aqueous medium, the product of the oxidation of the olefin is governed to a considerable extent by the solvent, since the cleavage of carbon-carbon bonds does not require participation of the solvent, and represents only a minor portion of the overall reaction. This is evident from the appreciable yields of glycol which can be isolated using a large variety of reaction conditions, and from the fact that the extent of scission of the olefinic linkage in aqueous medium is generally low.

It is this factor which accounts for the inadequacy of permanganate as a degradative tool in aqueous medium. Since glycol or the ketols are the main products of the reaction, and these are not smoothly cleaved by permanganate, it is evident that the isolation of high yields of cleavage products from the oxidation of an unknown olefin by permanganate in aqueous medium does not necessarily locate the position of the double bond. This emphasizes again the usefulness of the periodate-permanganate reagent for analytical work.

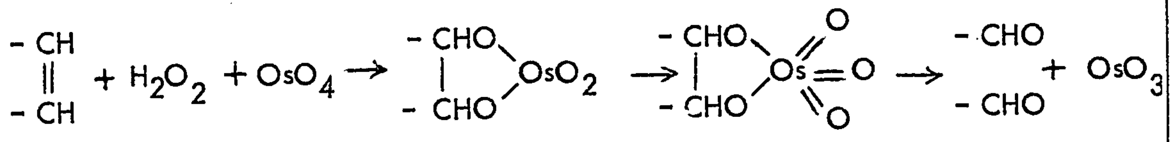
These ideas can be satisfactorily extended to data on the oxidation of olefins by permanganate in non-aqueous media. As indicated on page 46, there are three main differences between the major route of the reaction in aqueous media, and that observed in anhydrous media and in mixed solvents. First, there is no evidence that a ketol can be formed directly from an olefin in mixed solvents or in anhydrous media. In the only reported examples of the isolation of ketols, using 75% acetic acid as solvent, (95, 97; see page 47), the ketols appeared to have resulted from further oxidation of the glycol products. Secondly, the yield of glycol is appreciably decreased on going from aqueous media to mixed solvents, and except for one reaction quoted by Fieser (177), the yield drops to zero in anhydrous media. The example quoted by Fieser appears to be related to some peculiarity of the olefin (Δ^{17}-20-cyanopregnene-21-ol-3,11-dione acetate), since an attempt by the author to extend the reaction to the oxidation of oleic acid failed to yield any glycol. Thirdly, as the yield of glycol decreases in mixed solvents, there is a corresponding increase in the proportion of cleavage products, and the nature of these cleavage products indicates mainly scission of the olefinic linkage. Thus Armstrong and Hilditch (178) found that the oxidation of the methyl and ethyl esters of oleic acid by permanganate in glacial acetic acid yielded 90% of monomethylazelate and 60-80% of pelargonic acid; oxidation in dry acetone gave 80-85% of monomethylazelate and 50% of pelargonic acid. This work was repeated by Haverkamp-Begemann and co-workers (179), who extended the reaction to methyl elaidate and, using an elegant chromatographic procedure, were able to detect smaller amounts of the C_8 and C_7 acids in the reaction product. The proportion of the lower acids was greater in acetone than in glacial acetic acid.

In this Laboratory, Lemieux and Kullnig have isolated, in addition to 30-50% yields of glycol, appreciable amounts of adipic acid from the permanganate oxidation of cyclohexene in aqueous ethanol and aqueous tert-butyl alcohol, using magnesium sulphate as buffer (141).

The effect of change of solvent on the route of the permanganate oxidation of an olefin and, in particular, on the position of the cleavage of carbon-carbon bonds, is satisfactorily explained by the assumption that the cyclic ester is formed first; since the manganese is in an unstable valence state, the ester will decompose as rapidly as possible, provided a mechanism can be found for this decomposition. In aqueous medium, the mechanism is hydrolysis, followed by disproportionation of the liberated hypomanganate. In non-aqueous media, hydrolysis of the ester should be unfavourable, and the decomposition must occur in some other way. This decomposition can occur as the result of cleavage of the carbon-carbon bond of the intermediate ester,



A direct analogy to this kind of reaction exists in the oxidation of olefins by osmium tetroxide. As Criegee's classical work has demonstrated, (41), this reaction results in the formation of a stable ester intermediate containing hexavalent osmium. Since the osmium is in a stable valence state, this ester shows no tendency to hydrolyze, even in hot alkali. However, if an oxidizing or reducing agent is added to the aqueous mixture, the osmium is now in an unstable valence state and must decompose. The decomposition involves hydrolysis of the ester yielding glycol, and osmium in the appropriate valence state. Now, if the cyclic osmium ester is treated with an oxidizing or reducing agent in an anhydrous medium, it again becomes unstable and must decompose, but a hydrolytic decomposition cannot occur. Scission of the carbon-carbon bond must, therefore, result. Thus, treatment of a number of olefins with hydrogen peroxide in a dry ethereal solution to which osmium tetroxide was added gave 60-80% yields of the products expected on the basis of a mechanism (41),



CLAIMS TO ORIGINAL RESEARCH

1. In 10 N alkali, hypomanganate and permanganate react to form a quantitative yield of manganate (88, 108).
2. Hypomanganate does not oxidize olefins (88, 108).
3. The oxidation of an olefin by manganate yields a cis glycol (88,108,109).
4. A mechanism was proposed for the oxidation of an olefin by permanganate to an α-ketol (81, 88).
5. Manganate oxidizes olefins more slowly than permanganate, and the reactions do not stop at the glycol stage (88, 108).
6. A novel synthesis of solid hypomanganate was developed.
7. Hypomanganate was a product of the oxidation of olefins by manganate and permanganate.
8. Hypomanganate was quantitatively oxidized to permanganate by periodate, even at pH 6.8.
9. The oxidation of hypomanganate to manganate by permanganate is quantitative above pH 14.
10. Analytical methods were established for the determination of manganate and hypomanganate.
11. An analytical procedure was developed for following the concentrations of Mn(VII), Mn(VI) and Mn(IV), during a permanganate oxidation.
12. The disproportionation of hypomanganate in acid and alkaline media

was studied.

13. The disproportionation of hypomanganate probably includes an oxidation of the water solvent.

14. A procedure was developed for the determination of the number of electrons transferred in the initial stage of an alkaline permanganate oxidation.

15. Hypomanganate was shown to be the initial reduced stage in the permanganate-olefin reaction.

16. A consideration of all of the experimental facts showed that the cyclic intermediate was formed in the oxidation of an olefin by permanganate.

17. A new compound was prepared by the hydroxylation of cis-4-cyclohexenedioic acid with manganate or permanganate.

18. The configuration of this new compound, m.p. 235°, was established.

19. Two different procedures were developed for the conversion of oleate ion to ketols in near-quantitative yield.

20. Evidence was obtained that ketol is formed by further oxidation of the cyclic ester intermediate.

21. A detailed study was made of the oxidation of ethylene by periodate-permanganate, and the yields of products were determined.

22. It is possible, under certain reaction conditions, to convert ethylene to a mixture of sugars.

23. An analytical procedure was developed for quantitative infrared

spectroscopy of mixtures of CH_2O and CD_2O.

24. The periodate-permanganate oxidation of 1,1-dideuteroethylene was examined. A mass effect was observed.

25. The mass effect provided direct evidence for the route of oxidation of the cyclic ester to ketol.

26. A considerable amount of indirect evidence for the route of ketol formation was also assembled.

27. The direct conversion of an olefin to a diketone (85) by permanganate or periodate-permanganate was observed, and the possible mechanism of this reaction was discussed.

28. A detailed kinetic study of the olefin-permanganate reaction was made.

29. Evidence was obtained for the existence of a π-complex between the olefin and permanganate which rearranges to the cyclic intermediate.

30. The existence of π-complexes between the tellurate, borate and periodate ions and oleate ion was discovered.

31. A procedure, based on permanganate oxidation, was developed for the determination of the equilibrium constant of the oleate - tellurate complex. This procedure can be extended to other systems.

32. The specificity of some of the common oxidizing agents was discussed.

33. A study was made of the cleavage products resulting from the oxidation of an olefin by excess permanganate.

34. Evidence was assembled in support of the postulate that scission of the

olefinic linkage by permanganate occurs by decomposition of the cyclic intermediate.

35. The permanganate oxidations of 9,10-dihydroxystearate ion and the 9,10-ketohydroxystearate ions were studied.

36. Permanganate oxidation of the ketol proceeds by enolization, followed by formation of a cyclic intermediate.

37. Osmium tetroxide catalyzes the iodate-iodide reaction in alkaline medium.

38. A cursory kinetic study was made of the manganate oxidation of olefins.

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