KINETICS AND MECHANISM OF OXIDATION BY PERMANGANATE

J. W. LADBURY[1]

Department of Chemistry, Birkbeck College, London, W.C.1, England

AND (IN PART)

C. F. CULLIS

Department of Chemistry, Imperial College of Science and Technology,
London, S.W.7, England

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I. INTRODUCTION

Ions derived from every valence state of manganese from VII to III, as well as the hydroxyl radical and other oxygenated species (e.g., O^- and HO_2) have been proposed as the active entities responsible for oxidation by permanganate. Almost every conceivable intermediate ion has been suggested as participating at some stage of the reduction of permanganate. It is the purpose of this paper to review the reaction mechanisms put forward to account for the kinetic and other experimental data for oxidation by permanganate. It is not to be expected that a single mechanism will satisfy every reaction; the nature of the substrate and of the medium profoundly affects the course of reaction. However, some advance will be made if it is possible to recognize certain of the more important intermediates and the conditions under which they are produced.

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[1] Present address: Research Laboratories, Imperial Chemical Industries Ltd., (Plastics Division), Welwyn Garden City, Hertfordshire, England.

The amount of oxidation brought about by one permanganate ion varies with the pH of the medium. In alkaline, neutral, and weakly acid solution, the valence change of the manganese is from VII to IV, and the end product is manganese dioxide. In strongly acid solution, the permanganate ion is further reduced, the valence of manganese changing from VII to II.

In oxidation reactions, where the oxidizing species are not only capable of undergoing a series of simple valence changes but also contain oxygen, the substrate may be oxidized by one or more of the following processes:

(i) *Hydrogen-atom abstraction:* This occurs in the oxidation of hydrocarbons and other organic compounds to give free radicals. The hydrogen atom may be removed directly by an oxyanion or by a radical (e.g., OH, HO_2) produced by interaction of the oxidant with the solvent.

(ii) *Electron abstraction (139):* This sometimes takes place with simple ionic oxidizing agents, e.g., $Fe(CN)_6^{3-}$, Fe^{3+}, Ce^{4+}. The permanganate ion is capable of bringing about oxidation by this simple process alone, the MnO_4^{2-} ion being produced.

(iii) *Oxygen-atom transfer:* This occurs in its extreme form in the oxidation of olefins by osmium tetroxide, when a well-defined cyclic intermediate is obtained (32).

In oxidations by permanganate different stages of the reaction often involve different oxidative processes, and the kinetics of the overall reaction may be highly complex. Furthermore, many oxidations by permanganate are carried out under conditions where hydrated manganese dioxide is precipitated, and complications may arise from heterogeneous reactions at the surface of the precipitate. Most of the oxidations by permanganate, studied from a physicochemical viewpoint, have been carried out in acid media, and this review will be concerned mainly with such systems.

Furthermore, the extensive use of permanganate as an oxidant in preparative organic chemistry has resulted in the majority of the kinetic investigations being concerned with the oxidation of organic compounds. Reactions which are of special interest, such as the interaction of permanganate with manganous ions and with oxalic acid, are dealt with in separate sections.

II. OXIDATION BY ALKALINE PERMANGANATE

The manganate ion (MnO_4^{2-}) is quite stable in alkaline solution and the green coloration of the reaction solution during many oxidations by alkaline permanganate is ample evidence of its presence. Holluta (69), who studied the oxidation of formate ions in strongly alkaline solution, suggested that the equilibrium

$$2MnO_4^- + 2OH^- \rightleftharpoons 2MnO_4^{2-} + O + H_2O \qquad (1)$$

is set up, and that subsequent oxidation by oxygen atoms then takes place. This suggestion is similar to that of Stamm (125): namely, that the equilibrium

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

is rapidly established and that hydroxyl radicals are the active oxidizing entities. Duke (47) prefers the equilibrium

$$MnO_4^- + H_2O \rightleftharpoons MnO_4^{2-} + OH + H^+ \tag{3}$$

in which reaction takes place between a water molecule and a permanganate ion rather than between ions of like charge. This equilibrium is, however, intrinsically unlikely, since the back reaction involves a trimolecular reaction between three species present in very low concentration. Even if Duke's scheme is replaced by the more probable sequence

$$\left.\begin{array}{l} MnO_4^- + H_2O \rightarrow MnO_4^{2-} + OH + H^+ \\ MnO_4^{2-} + OH \rightarrow MnO_4^- + OH^- \end{array}\right\} \tag{4}$$

the rate of disappearance of permanganate ions becomes independent of the alkali concentration, and this is contrary to observation (127). However, the existence and rapid establishment of some sort of equilibrium between permanganate and manganate ions in alkaline solution are supported by the results of radiochemical experiments (14, 24, 73, 90, 121).

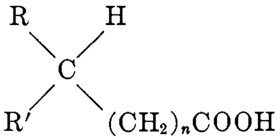
If oxidation by permanganate is carried out in alkaline solution in the presence of a soluble barium salt, it is possible to arrest any further oxidation by the manganate ion, for the latter will be removed as fast as it is formed as insoluble barium manganate; this forms the basis of a quantitative method of estimating formate ions (125).

In the absence of an oxidizable substrate, oxygen gas is evolved from alkaline permanganate solutions according to the equation

$$4MnO_4^- + 4OH^- \rightarrow 4MnO_4^{2-} + 2H_2O + O_2$$

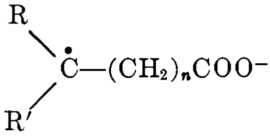
and further reduction of the manganate does not occur. The higher the pH of the solution, the greater is the rate of evolution of oxygen (48). Symons (127) has studied this reaction in the absence of an oxidizable substrate at high alkali concentrations (2.76–7.75 *N*) and proposes the formation of O^-, HO_2^-, and O_2^- radical-ions as well as hydroxyl radicals. Similar schemes involving hydroxyl radicals as the principal intermediates in the decomposition of alkaline permanganate solutions have recently been proposed by other workers (11, 78, 135, 136). Abel (11) has analyzed Symons' results and has discussed an alternative reaction scheme involving the dimerized hydroxyl radical $(OH)_2$. He concludes, however, that the details of the mechanism by which oxygen is evolved from alkaline permanganate solutions have yet to be elucidated. The mechanisms suggested by other workers have recently been reconsidered by Carrington and Symons (29).

Drummond and Waters (40) have observed the behavior of a number of organic compounds towards moderately alkaline solutions of permanganate. They find no evidence for participation by hydroxyl radicals. Thus, diethyl ether and dioxane, which are known to be rapidly oxidized by hydroxyl radicals (100), are unaffected by alkaline permanganate. The observations of Symons (128) and of Kenyon and Symons (80) are relevant in this connection. Symons (128) has observed the formation of acrylonitrile polymer after the addition of dilute potassium permanganate solution to acrylonitrile in 3 *N* potassium hydroxide solution. Polymerization does not occur either when potassium manganate is used instead of potassium permanganate or when the alkali concentration is appreciably less than 3 *N*. Symons (128) has suggested that initiation of polymerization by hydroxyl radicals occurs concurrently with direct oxidation of the acrylonitrile. In neutral solution, only direct oxidation occurs. Furthermore, reactions between branched-chain carboxylic acids and dilute alkaline permanganate solutions are slow even at high temperatures and result in extensive degradation of the acid, but with optically active carboxylic acids of the type

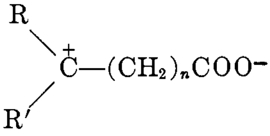


$n = 0,2$; R = alkyl or aryl.

oxidation by permanganate in *strongly* alkaline solution is rapid even at room temperature and good yields of optically *inactive* hydroxy acids are obtained. Although it is possible that the change in mode of reaction is due to stabilization of the manganate ion by the alkali (84) (and consequent decrease in amount of oxidation performed by this ion), this can hardly account for the marked change in oxidation rate. According to Kenyon and Symons (80), the enhanced rate is probably due to the production, at high pH values, of hydroxyl radicals, which are responsible for the oxidation. The optically active forms of both reactants and products are stable in hot concentrated alkali, and the loss of optical activity is attributed to hydrogen-atom abstraction by hydroxyl radicals or O^- radical-ions with the formation of a radical:



Subsequent reaction with another hydroxyl radical produces the inactive hydroxy acid. The alternative process involving the carbonium ion,



is very unlikely, since retention of configuration is likely to occur as a result of intramolecular electrostatic attraction between charges of opposite sign; such retention has been demonstrated in the ionization of optically active halogenocarboxylic acids (75).

When, therefore, the hydroxyl ion is present in large excess compared with the oxidizable substrate, electron abstraction from that ion by permanganate ion probably occurs in preference to reaction with the substrate; as the hydroxyl-ion concentration is reduced, however, some other mechanism comes into operation. Drummond and Waters (40) suggest that this is electron abstraction from the substrate to produce a free radical. It is significant that no organic compound has been found which reduces alkaline permanganate *directly* beyond the manganate stage; such a one-electron transfer from the organic compound must result in the formation of a free radical. Both the mechanism of Symons (128) and that of Drummond and Waters (40) involve the production of free radicals. The scheme

$$\left.\begin{aligned} &MnO_4^- + OH^- \rightarrow MnO_4^{2-} + OH \\ &AH + OH \rightarrow A + H_2O \end{aligned}\right\} \qquad (5)$$

is due to Symons (128), whereas the scheme

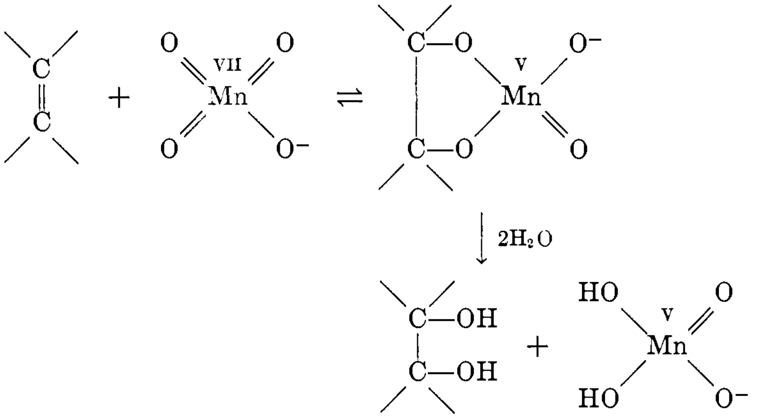
$$\left.\begin{aligned} &AH + MnO_4^- \rightarrow AH^+ + MnO_4^{2-} \\ \text{or}\qquad & \\ &AH + OH^- \rightarrow A^- + H_2O \\ &A^- + MnO_4^- \rightarrow A + MnO_4^{2-} \end{aligned}\right\} \qquad (6)$$

is proposed by Drummond and Waters (40). The argument against scheme 6 is that, if AH were acrylonitrile, polymerization would be expected to occur. Symons (128) has shown that this does not take place in the range of alkali concentration in which the experiments of Drummond and Waters (40) were carried out. Hydrogen-atom abstraction from the organic compound by the permanganate ion, with auxiliary oxidation by the magnanate ion, could account for the observations with acrylonitrile at high pH values (128). However, such a mechanism would not account for the sharp distinction between the modes and rates of oxidation at high and low concentrations of alkali. Furthermore, experiments (127) in the absence of oxidizable substrate strongly suggest the presence of hydroxyl or similar radicals. Drummond and Waters (40) reject the two-electron transition $MnO_4^- \rightarrow MnO_4^{3-}$, since, in order to satisfy the experimental observation that no organic compound directly reduces permanganate beyond the manganate stage, the disproportionation

$$MnO_4^- + MnO_4^{3-} \rightarrow 2MnO_4^{2-} \qquad (7)$$

would have to be extremely rapid; this is said to be too stringent a requirement. Carrington and Symons (29) and Symons (127) point out, however, that reaction 7 is fast and that pentavalent manganese compounds are not unknown. For example, the bright blue compound which is formed when manganate solutions are heated with a large excess of alkali is said to contain the ion MnO_4^{3-} (94). The two-electron change Mn(VII) → Mn(V), followed by the very rapid disproportionation Mn(VII) + Mn(V) → Mn(VI), may well therefore constitute the first stage of oxidation by alkaline permanganate. Symons (127), however, rejects the possibility of a transient pentavalent state of manganese in the decomposition of alkaline permanganate in the *absence* of organic substrate, even though he advocates a mode of oxidation of organic compounds which involves it.

The occurrence of a two-electron transition with a concurrent rapid disproportionation of the heptavalent and pentavalent states to the hexavalent state would invalidate the objection of Drummond and Waters (40) to the scheme first proposed by Böeseken (23). According to this, a cyclic intermediate is formed when olefins are oxidized in dilute, weakly alkaline solutions of permanganate; subsequent hydrolysis of this intermediate produces a *cis*-glycol.



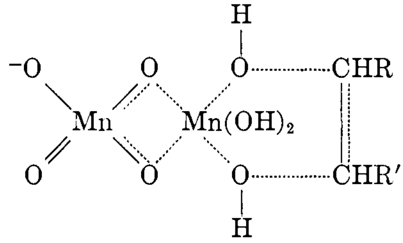
(8)

This scheme is particularly attractive because it accounts for cis addition across the double bond. It is analogous to the mechanism proposed by Criegee (32) for the oxidation of olefins by osmium tetroxide.

A case can be made out, then, for two oxidation mechanisms in the first stages of the decomposition of alkaline permanganate. At high alkali concentrations (> ca. 3 *N*), permanganate ions react with hydroxyl ions in preference to the organic substrate thereby producing hydroxyl radicals; these radicals are then the principal oxidizing entities. At lower alkali concentrations, there is possibly a two-electron transfer from the organic substrate to the permanganate ion, followed by the rapid disproportionation (reaction 7) to give an apparent one-electron transfer reaction.

In the oxidation in strongly alkaline solution of a number of unsaturated carboxylic acids by the one-electron transfer $MnO_4^- \rightarrow MnO_4^{2-}$ (further oxidation being prevented by removal of the manganate as barium manganate), the amount of permanganate consumed is very much in excess of that required for oxidation to the glycol only (40). This suggests that *cis*-glycol formation occurs only in the two-electron transfer Mn(VI) → Mn(IV), while the prior reaction Mn(VII) → Mn(VI) merely produces highly oxidized side products. Rigby (113) has carried out experiments designed to test this point, but finds that although potassium manganate is an effective hydroxylating agent, his results do not provide any conclusive evidence in favor of the above hypothesis.

These reactions are complicated by the marked catalytic activity of precipitated manganese dioxide, and the possible contribution of heterogeneous processes must not be overlooked. This would provide an alternative explanation, in some cases, for the cis hydroxylation of olefins. A transition state involving the surface of hydrated manganese dioxide, a molecule of olefin, and a permanganate ion, e.g.,



can be envisaged, in which the addition of the hydroxyl groups will occur in cis positions.

Tompkins (133) and his coworkers (62, 63, 97) have made detailed studies of the oxidation of benzaldehyde and formate ions by potassium permanganate in dilute alkaline solution and have suggested that the pentavalent manganese ion, MnO_3^-, is formed as an intermediate. Tompkins postulates subsequent reaction of this ion with water to produce the hexavalent ion $HMnO_4^-$ and tetravalent, hydrated manganese dioxide. The $HMnO_4^-$ ion then undergoes a two-electron transfer to the organic ion [benzaldehydate ion, $C_6H_5CH(OH)O^-$, or formate ion], e.g.:

$$HCOO^- + MnO_4^- \rightarrow MnO_3^- + CO_2 + OH^- \quad (9)$$

$$2MnO_3^- + H_2O \rightarrow MnO_2 + HMnO_4^- + OH^- \quad (10)$$

$$HMnO_4^- + HCOO^- \rightarrow MnO_2 + CO_2 + 2OH^- \quad (11)$$

The first reaction is assumed to be rate-controlling and accounts for the first-order dependence of rate on each of the reactant concentrations. There is, however, little other evidence in support of this mechanism.

In a later study of the oxidation of formate ions by alkaline permanganate, Wiberg and Stewart (145) find a value of 7.4 for the ratio of the rate constants (k_H/k_D) of the oxidation when deuterium replaces hydrogen in the formate ion. Such a difference in rate constants is indicative of a reaction where a C—H bond is ruptured in the rate-controlling step and is due to the greater mass of the deuterium atom. Although the force between the carbon and hydrogen atoms does not change on isotopic replacement, the frequency of the vibration is lowered owing to the difference in the "reduced mass" of the bonded atoms. Hence the C—H bond has a higher zero-point energy than the C—D bond. Although a similar difference exists in the transition-state complex, it is smaller because the bonds are weaker and the frequency of vibration itself is smaller. The activation energy is thus smaller and the rate constant greater for the hydrogen than for the deuterium compound. On the basis of further work with isotopically labelled reagents, these authors estimate that 40–50 per cent of the oxygen in the product (carbon dioxide) comes from the permanganate ion. Various possible reaction schemes are suggested, but the most satisfactory mechanism is the following:

(*a*) A two-electron transfer from the formate ion to the permanganate ion:

$$HCOO^- + MnO_4^- \rightarrow H^+ + CO_2 + MnO_4^{3-}$$

(*b*) A rapid reaction between heptavalent and pentavalent manganese oxyanions to produce the manganate ion:

$$MnO_4^- + MnO_4^{3-} \rightarrow 2MnO_4^{2-}$$

(*c*) The reaction of the latter ion with the formate ion to form the bicarbonate ion directly:

$$MnO_4^{2-} + HCOO^- \rightarrow HCO_3^- + MnO_3^{2-}$$

(*d*) The reaction of the tetravalent manganese ion MnO_3^{2-} with water to produce hydrated manganese dioxide:

$$MnO_3^{2-} + 3H_2O \rightarrow Mn(OH)_4 + 2OH^-$$

The electrophilic nature of the permanganate ion, in spite of its negative charge, accounts for the preferential attack of the oxidizing ion on the formate ion rather than on formic acid molecules. (This same electrophilic character is shown in the reaction with hydroxyl ions discussed previously.) The above mechanism accounts for the deuterium isotope effect and is also consistent with the observation that the rate is independent of pH when formate *ions* are taken as the reducing species. Furthermore, the reaction scheme requires a positive salt effect, which is indeed found, and also predicts oxygen transfer from the permanganate ion to the carbon dioxide product owing to reaction (*c*). The observed rate equation is also satisfied by this mechanism, and the decrease of the second-order rate constants with time arises because, as Wiberg and Stewart have shown, the formate ion reacts with the manganate ion about seven times more slowly than the permanganate ion.

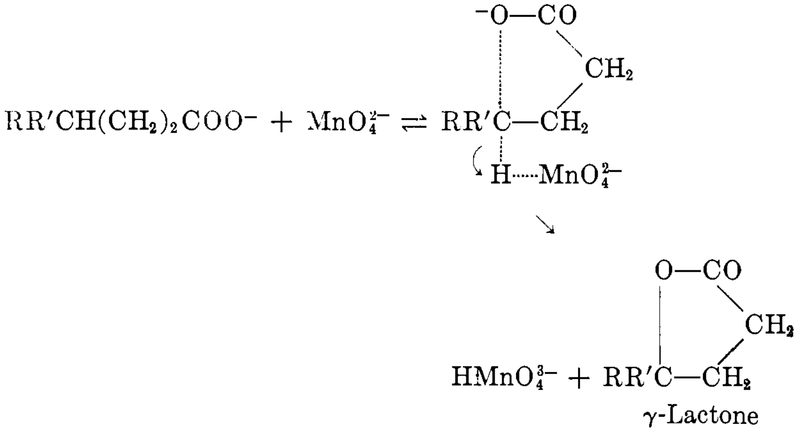
Wiberg and Stewart (144) have also reinvestigated the oxidation by alkaline permanganate of benzaldehyde and of substituted benzaldehydes to the corresponding benzoic acids. In their studies, they have used information from isotopic exchange experiments and have also found that the reaction obeys Hammett's "linear free energy" equation. They have thus been able to supplement the findings of earlier workers. With substituted benzaldehydes, the reaction is accelerated by hydroxyl ions according to the equation:

$$\text{Rate} = k[\text{Ph}'\text{CHO}][MnO_4^-][OH^-]^{1/2}$$

Furthermore, the decrease in rate which accompanies the replacement of hydrogen by deuterium in the aldehyde group becomes much smaller as the pH of the solution increases. Thus, at higher pH values the rate-determining cleavage of the C—H bond to yield a proton becomes less important. Another contrast between the reactions in acid and alkaline media is that, while at low pH values the oxygen introduced into the resulting benzoic acid is derived mainly from the oxidant, at higher pH values this oxygen comes largely from the solvent (water). The rate constants obey Hammett's equation, but while the reaction constant (ρ) for neutral solution is positive, its value for alkaline solution is large and negative, indicating that as the pH increases, the oxidation is facilitated to a great extent by a high electron density at the reaction site (77). Wiberg and Stewart (144) reject the suggestion (133) that the reaction occurs between the permanganate and aldehydate [$Ph'CH(OH)O^-$] ions on the grounds that this would imply first-order dependence of rate on hydroxyl-ion concentration and would also require the rate to increase with ionic strength, an effect which is not found in practice.

Wiberg and Stewart (144) favor a mechanism involving hydroxyl radicals, although the concentration of alkali in which they carried out their experiments was much lower than that at which Symons (128) evinces evidence for such radicals. Wiberg and Stewart (144) were unable to devise a mechanism which involves hydroxyl radicals and at the same time allows a first-order dependence of rate on permanganate concentration. The intervention of hydroxyl radicals is, however, not at variance with the other experimental facts. Thus a small isotope effect would be expected when deuterium replaces hydrogen (20); secondly, the hydroxyl radical is electrophilic and therefore the reaction would have a negative value of ρ; and finally, this radical would be produced from the solvent (water) and hence the source of the oxygen content of the benzoic acid would also be the solvent.

The subsequent stages of the reduction of the permanganate ion ($MnO_4^{2-} \rightarrow MnO_2$) are even less well understood than the first stage. Since Symons (128) finds no evidence for radical formation, the two electrons may be transferred in a single stage. Kenyon and Symons (80) have shown that the action of potassium *manganate* in *dilute* alkaline solution on optically active, branched-chain carboxylic acids of the type $RR'CH(CH_2)_nCOOH$ is quite different from that of potassium *permanganate* in *concentrated* alkaline solution. Whereas the former leads to retention of optical activity, the latter causes complete loss of activity. It has already been seen that the second situation probably arises through the intervention of a free radical; to account for the first observation, Kenyon and Symons (80) invoke the two-electron transfer mechanism shown on page 412. They have shown that oxidation of 4-methylhexanoic acid ($R = C_2H_5$, $R' = CH_3$) by potassium permanganate in dilute alkaline solution gives a small yield of 4-hydroxy-4-methylhexanoic acid, with a rotatory power considerably smaller than that required for complete retention of optical activity. Both types of oxidation, i.e., hydroxyl-radical attack and two-electron transfer, probably contribute to the formation of this hydroxy acid. The main reaction, however, involves further oxidation, and neither of the above two processes contributes greatly towards it.



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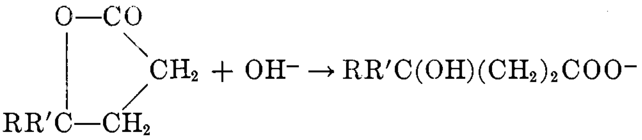


(13)

$$HMnO_4^{3-} + H_2O \rightarrow 3OH^- + MnO_2 \qquad (14)$$

III. Oxidation by Acid Permanganate

A. INTRODUCTION

There is considerable evidence that, with many reactions of permanganate in acid media, some oxidation is performed by ions derived from the tri- and tetravalent states of manganese. These ions are formed by reaction between di- and heptavalent ions. Divalent ions are always present in solutions of permanganate, albeit in minute concentration, as a result of the equilibrium (96)

$$4MnO_4^- + 12H^+ \rightleftharpoons 4Mn^{2+} + 5O_2 + 6H_2O$$

but the concentration may be augmented either by direct reduction of the permanganate by an oxidizable substrate or by deliberate addition of a manganous salt. Ions involving an intermediate valence state of manganese are produced by the Guyard reaction (55), which may be written:

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

In certain reactions, ions produced from the tri- and tetravalent states may be more effective oxidizing agents than the permanganate ion, and part of the oxidation may be performed by them.

There is, then, the possibility of several simultaneous oxidative reactions in acid (and neutral) solutions of permanganate. Direct oxidation by permanganate ions is one possibility, but several ions derived from either or both of the Mn(III) and Mn(IV) states, such as MnO^{2+}, MnO^+, MnO_3^{2-}, etc., may also oxidize the substrate. Abel (2) proposes that several such intermediates are always formed in the various stages of reduction of permanganate and shows how they may be assumed to intervene in the reaction of permanganate with hydrogen peroxide, ferrous ions, oxalate ions, and in the Guyard reaction itself.

A characteristic feature of reactions in which intermediate manganese ions are important oxidizing entities is the sigmoid form of the reaction–time curves, for the production of intermediates increases autocatalytically, as manganous ions are formed and react with further permanganate ions.

Since reduction of the permanganate ion by manganous ions is often preliminary to the main oxidation, a study of the Guyard reaction becomes important in elucidating the stages by which permanganate is reduced by the oxidizable substrate. The reaction will therefore be discussed in the following section.

B. THE PERMANGANATE-MANGANOUS ION REACTION (GUYARD REACTION)

This reaction has been investigated by many workers since the early studies by Gorgeau (54) and Guyard (55). The recent work of Adamson (14) in particular has thrown considerable light on the problem.

The mechanism accepted must be consistent with observations on the radiochemical exchange between the species present. According to Polissar (111), no exchange occurs between *manganous* and *permanganate* ions in acid solution. Adamson (14), on the other hand, detected a slow exchange which is, however, prevented by adding manganese dioxide. The situation with regard to exchange between *manganous* ions and colloidal *manganese dioxide* is less clear. Polissar (111) and Libby (90) found no exchange, while Pullman and Haissinsky (112) noted a fairly fast exchange. Adamson (14) observed a rapid but measurable exchange between *manganous* and *manganic* ions, but Polissar (111) found a considerably faster exchange. Polissar's measurements were, however, carried out in the presence of a large excess of oxalic acid, so that the two reactions are different. The reaction studied by Adamson is essentially

$$\mathrm{Mn^{3+} + {}^*Mn^{2+} \rightleftharpoons {}^*Mn^{3+} + Mn^{2+}}$$

while that investigated by Polissar is either

$$\mathrm{Mn(C_2O_4)_2^- + {}^*Mn(C_2O_4) \rightleftharpoons {}^*Mn(C_2O_4)_2^- + Mn(C_2O_4)}$$

or

$$\mathrm{Mn(C_2O_4)^+ + {}^*Mn(C_2O_4)_2^{2-} \rightleftharpoons {}^*Mn(C_2O_4)^+ + Mn(C_2O_4)_2^{2-}}$$

(see references 96, 101, and 102) or some similar process. Polissar (111) also found no exchange between *permanganate* ions and colloidal *manganese dioxide*.

Polissar (109, 110) found that the Guyard reaction is catalyzed by the manganese dioxide formed, and the work of Tompkins (132) and of Bradley and Van Praagh (25) supports this. When manganese dioxide or a finely divided solid is added initially, the induction period is eliminated. According to Tompkins (132), the induction period (defined as the time required to attain the maximum rate) varies inversely with the amount of manganese dioxide present. Using a turbidimetric method, Tompkins (132) has shown that the maximum rate of production of manganese dioxide ($v_{\max}$) obeys the equation

$$v_{\max} = \frac{k'[\mathrm{MnO_4^-}]\{[\mathrm{Mn^{2+}}] - k''\}}{1 + k[\mathrm{H^+}]}\{[\mathrm{MnO_2}] + k'''\}$$

and the reciprocal of the induction period (t_i) is given by the equation:

$$\frac{1}{t_i} = \frac{k_1\{[\mathrm{MnO_4^-}] - k_2\}\{[\mathrm{Mn^{2+}}] + k_3\}[\mathrm{MnO_2}]}{[\mathrm{H^+}]}$$

The addition of anions which form complexes with manganic ions—e.g., sulfate ion, which forms $[\mathrm{Mn(SO_4)_2 \cdot 2H_2O}]^-$ (134), and fluoride ion, which forms $(\mathrm{MnF_4})^-$ (85)—increases the induction period. The induction periods with sulfate ion and fluoride ion, corrected for the presence of hydrogen ions produced from the sulfuric and hydrofluoric acids used, vary as the square of the sulfate-ion concentration and as the fourth power of the fluoride-ion concentration. The catalytic action of the precipitated manganese dioxide is attributed to a specific surface effect which is diminished by enveloping the surface of the manganese dioxide with gum arabic. When only a small amount of gum arabic is added initially, two distinct portions of the reaction–time curves are observed. In the first part, the velocity decreases continuously owing to the prevention of the heterogeneous reaction by the colloid; in the second stage, the normal acceleration is apparent because all the gum arabic has been used up, and any fresh manganese dioxide formed can catalyze the reaction. As more of the surface of the manganese dioxide is enveloped by increasing the amount of gum arabic added initially, the maximum rate decreases in such a way that $1/v_{\max}$ is proportional to the surface area of the precipitate covered.

On the basis of these experiments, Tompkins (132) proposes the following mechanism for the Guyard reaction:

$$\mathrm{Mn^{2+} + MnO_4^- + H_2O \rightleftharpoons Mn^{3+} + HMnO_4^- + OH^-} \tag{1}$$

$$\mathrm{HMnO_4^- + Mn^{2+} + OH^- \xrightarrow{slow} 2MnO_2 + H_2O} \tag{2}$$

$$\mathrm{2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}} \tag{3}$$

$$\mathrm{Mn^{4+} + H_2O \rightarrow Mn^{3+} + OH + H^+} \tag{4}$$

$$\mathrm{Mn^{2+} + OH \rightarrow Mn^{3+} + OH^-} \tag{5}$$

$$\mathrm{Mn^{4+} + OH^- \rightarrow Mn(OH)^{3+} \dashrightarrow MnO_2} \tag{6}$$

In reaction 6 the addition of the first hydroxyl ion is assumed to be the rate-controlling stage in the hydrolysis of the tetravalent ion; the final product of this hydrolysis we have written as $\mathrm{MnO_2}$, but it could equally well be written $\mathrm{Mn(OH)_4}$. Reaction 6 is assumed to be responsible for the production of the major part of the manganese dioxide, since reaction 2 is believed to be slow. The above mechanism accounts for the effect of complexing anions on the maximum rate, since these react with Mn^{3+} ions and inhibit reaction 3. Thus the rate of production of Mn^{4+} ions is small, and formation of manganese dioxide is consequently retarded. Acceleration due to precipitated manganese dioxide is therefore less in evidence, and it takes a proportionately longer time to reach the maximum rate. The length of the induction period is proportional to the amount of complex that can be formed, which in turn is proportional to the square of the sulfate-ion concentration and to the fourth power of the fluoride-ion concentration. The mechanism also agrees with the results of the radiochemical experiments, provided no exchange occurs between Mn^{3+} and $HMnO_4^-$ ions. No definite processes are postulated for the heterogeneous reaction.

The above mechanism accounts for the observed influence of reactant concentrations on the *maximum* rate. However, the equation for v_{max} refers to the rates measured at a stage where the reaction is largely heterogeneous and may not represent the behavior in the early stages when no manganese dioxide is present.

Adamson (14), using a radiochemical method, has studied the influence of the hydrogen-, permanganate-, and manganous-ion concentrations on the velocity of the rate-controlling step in the exchange reaction between manganous and permanganate ions before any manganese dioxide has been formed. Under these conditions, the exchange reaction obeys a first-order kinetic law (53, 98). The velocity, v, of the rate-controlling step may be expressed by the equation:

$$v = k[H^+]^x[Mn^{2+}]^y[MnO_4^-]^z$$

where $x = 1.0\text{–}1.6$, $y = 1.0\text{–}1.6$, and $z = 0.0\text{–}0.6$. On the basis of these experiments, the following reaction mechanism is advanced to account for the early stages of the reaction between permanganate and manganous ions:

(*a*) Rapid reversible equilibria:

$$6H^+ + 3Mn^{2+} + MnO_4^- \overset{K_1}{\rightleftharpoons} 3Mn^{3+} + MnO^{2+} + 3H_2O \quad (7)$$

$$Mn^{3+} + H_2O \overset{K_2}{\rightleftharpoons} MnO^+ + 2H^+ \quad (8)$$

$$MnO^{2+} + 2H^+ \overset{K_3}{\rightleftharpoons} Mn^{4+} + H_2O \quad (9)$$

(*b*) Rate-determining exchange:

$$MnO^+ + MnO^{2+} \rightleftharpoons MnO^{2+} + MnO^+ \quad (10)$$

(*c*) Competing reactions:

$$MnO^{2+} + H_2O \rightarrow MnO_2(s) + 2H^+ \quad (11)$$

(negligible in the absence of solid manganese dioxide)

$$2H^+ + Mn^{2+} + MnO^{2+} \rightleftharpoons 2Mn^{3+} + H_2O \quad (12)$$

or

$$Mn^{2+} + Mn^{4+} \rightleftharpoons 2Mn^{3+} \quad (12a)$$

If it is assumed that K_2 and K_3 are small, so that in acid solution the principal forms of Mn(III) and Mn(IV) are Mn^{3+} and MnO^{2+}, respectively, then from equilibrium 7,

$$\frac{[MnO^{2+}]}{[Mn^{3+}]} = \frac{1}{3}$$

and the rate of the exchange reaction, which is given by

$$k[\mathrm{MnO}^+][\mathrm{MnO}^{2+}]$$

becomes

$$\left(\frac{k^2K_1K_2^{-2}}{3}\right)^{1/2}[\mathrm{H}^+]\,[\mathrm{Mn}^{2+}]^{3/2}\,[\mathrm{MnO}_4^-]^{1/2}$$

in broad agreement with observed behavior.

Adamson (14) explains the inhibitory effect of solid manganese dioxide on the assumption that an equilibrium concentration of MnO^{2+} is established by reaction 7, which, although small, represents a considerable supersaturation of the solution. When solid manganese dioxide appears, the Mn(IV) concentration drops to a much lower value; furthermore, the reverse of reaction 12 or 12a proceeds rapidly to completion, perhaps as a surface-catalyzed reaction. The result is that the concentration of both MnO^+ and MnO^{2+} is reduced and thus the exchange rate is low.

C. THE PERMANGANATE-OXALATE ION REACTION

This reaction was among the first to be subjected to a detailed mechanistic analysis (57). The overall change is represented by the equation:

$$2\mathrm{MnO}_4^- + 5\mathrm{C}_2\mathrm{O}_4^{2-} + 16\mathrm{H}^+ = 2\mathrm{Mn}^{2+} + 10\mathrm{CO}_2 + 8\mathrm{H}_2\mathrm{O}$$

and the reaction is characterized by two interesting features. Firstly, the amount of oxidation performed in a given time can be decreased by increasing the oxalate concentration (57). Launer (85) showed that the decrease in rate is indeed due to an increase in oxalate concentration and not to a concomitant removal of hydrogen ions. Secondly, manganous ions exert a profound accelerating effect on the reaction. Harcourt and Esson (57) attributed the induction period preceding reaction to the occurrence of two consecutive reactions of comparable rate. The first, and faster, reaction is given as:

$$2\mathrm{KMnO}_4 + 3\mathrm{MnSO}_4 + 2\mathrm{H}_2\mathrm{O} = \mathrm{K}_2\mathrm{SO}_4 + 2\mathrm{H}_2\mathrm{SO}_4 + 5\mathrm{MnO}_2$$

and the second as:

$$\mathrm{MnO}_2 + \mathrm{H}_2\mathrm{SO}_4 + \mathrm{H}_2\mathrm{C}_2\mathrm{O}_4 = \mathrm{MnSO}_4 + 2\mathrm{H}_2\mathrm{O} + 2\mathrm{CO}_2$$

This was a sound analysis of the data, considering the youth of reaction kinetics at that time.

When dilute solutions of potassium permanganate, oxalic acid, and sulfuric acid are mixed, the rate of reaction shows a sigmoid dependence on time. In the presence of added manganous ions, the initial slow reaction is eliminated. If oxalate ions are present in large excess and if manganous ions are also added initially, the reaction obeys a first-order law and the rate is largely independent of the manganous-ion concentration (46, 91). The color of acidified solutions of permanganate and oxalate changes through cherry-red, brown, and yellow to colorless. The different colors are associated with the red $[\mathrm{Mn(C_2O_4)_3}]^{3-}$ and yellow $[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]^-$ complexes (30). In order to account for the first-order kinetic equation, it is necessary to postulate a unimolecular decomposition of one or more of the intermediate complexes. Skrabal (122) attributed the slow initial reaction in the absence of added manganous ions to the reaction of permanganate with oxalic acid molecules and ascribed the first-order relationship to the unimolecular breakdown of a complex of unspecified formula. The principal oxidizing entity was assumed to be the manganic ion; thus when such ions are removed as the mangani-fluoride complex, the purple permanganate color is retained almost indefinitely.

Launer (85) found that the rate of evolution of carbon dioxide, which is normally inversely proportional to the oxalate concentration, becomes directly proportional to it in the presence of fluoride ions. He therefore proposed the mechanism:

$$\mathrm{Mn^{3+}} + 2\mathrm{C_2O_4^{2-}} \overset{K}{\rightleftharpoons} \mathrm{Mn(C_2O_4)_2^-} \tag{1}$$

$$\mathrm{Mn^{3+}} + \mathrm{C_2O_4^{2-}} \xrightarrow{k_1} \mathrm{Mn^{2+}} + \mathrm{CO_2^-} + \mathrm{CO_2} \tag{2}$$

$$\mathrm{Mn^{3+}} + \mathrm{CO_2^-} \xrightarrow{k_2} \mathrm{Mn^{2+}} + \mathrm{CO_2} \tag{3}$$

in which the second stage is rate-controlling. The first equilibrium lies largely in favor of the complex, and both it and the last stage involve rapid reactions. In the absence of fluoride ions, the manganic-ion concentration is controlled by reaction 1. Hence the rate of carbon dioxide evolution becomes:

$$\frac{\mathrm{d}p_{\mathrm{CO_2}}}{\mathrm{d}t} = \frac{2k_1[\mathrm{Mn(C_2O_4)_2^-}]}{K[\mathrm{C_2O_4^{2-}}]}$$

In the presence of fluoride, the equilibrium

$$\mathrm{Mn^{3+}} + 4\mathrm{F^-} \rightleftharpoons \mathrm{MnF_4^-}$$

may predominate over reaction 1 and the concentration of manganic ions becomes independent of the oxalate concentration. Thus:

$$\frac{\mathrm{d}p_{\mathrm{CO_2}}}{\mathrm{d}t} = 2k_1[\mathrm{Mn^{3+}}][\mathrm{C_2O_4^{2-}}]$$

Launer (85) originally assumed, as did Skrabal (122), that $\mathrm{Mn^{3+}}$ ions are formed by the reaction

$$\mathrm{MnO_4^-} + 4\mathrm{Mn^{2+}} + 8\mathrm{H^+} \rightleftharpoons 5\mathrm{Mn^{3+}} + 4\mathrm{H_2O}$$

but Launer and Yost (87) later concluded that oxidation is performed both by $\mathrm{Mn^{4+}}$ and $\mathrm{Mn^{3+}}$ ions, the former being produced by the rapid process:

$$2\mathrm{MnO_4^-} + 3\mathrm{Mn^{2+}} + 16\mathrm{H^+} \rightleftharpoons 5\mathrm{Mn^{4+}} + 8\mathrm{H_2O} \tag{4}$$

The relative amount of oxidation done by the two species depends on their concentrations, which are governed by the disproportionation:

$$\mathrm{Mn^{4+}} + \mathrm{Mn^{2+}} \overset{\text{rapid}}{\rightleftharpoons} 2\mathrm{Mn^{3+}} \tag{5}$$

They were led to this revision in order to account for the preferential oxidation of manganous ions when these are added initially. (Incidentally, the rate of oxidation of manganous ions in the presence of oxalate ions is faster than in their absence (96).) Launer and Yost's (87) subsequent mechanism is:

$$Mn^{4+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{3+} + CO_2 + CO_2^- \quad (6)$$

$$Mn^{4+} + CO_2^- \xrightarrow{\text{rapid}} Mn^{3+} + CO_2 \quad (7)$$

$$Mn^{3+} + 2C_2O_4^{2-} \overset{\text{rapid}}{\rightleftharpoons} Mn(C_2O_4)_2^- \quad (8)$$

$$Mn^{3+} + C_2O_4^{2-} \xrightarrow{\text{measurable}} Mn^{2+} + CO_2 + CO_2^- \quad (9)$$

$$Mn^{3+} + CO_2^- \xrightarrow{\text{rapid}} Mn^{2+} + CO_2 \quad (10)$$

In the presence of manganous ions, the Mn^{4+} ions produced by reaction 4 are rapidly converted to Mn^{3+} ions by reaction 5 and thence to complexes by reaction 8. The decomposition of the latter then occurs in a slow unimolecular stage. In the absence, however, of added manganous ions, the Mn^{4+} ions produced by reaction 4 react rapidly according to reactions 6 and 7 rather than reaction 5. When the oxalate concentration is high, reactions 8, 9, and 10 occur slowly; when it is low, reaction 9 produces a relatively high concentration of manganous ions, which react according to reaction 5 to give further Mn^{3+} ions. Although some alterations are necessary on account of the radiochemical work of Adamson (14) and Polissar (111), the mechanism of Launer and Yost provides a valuable basis for discussion. Bassett and Sanderson (21) consider, however, that Mn^{4+} ions are unlikely to be formed in the direct reduction of permanganate in acid solution.

Many formulas have been proposed for the manganic-oxalate complexes formed. Lidwell and Bell (91) investigated the permanganate-oxalate reaction with only a small oxalate concentration and with manganous ions present. The reaction is fast initially but is followed by a slow first-order reaction. They consider that the manganic ions first react rapidly with oxalate and that, as a result, there is a decrease in the concentrations of both species; the subsequent reaction consists in the unimolecular decomposition of a manganic-oxalato complex. From the composition of the solution at the transition from the fast to the slow reaction, the composition of the complex was deduced to be $[Mn(C_2O_4)_3]^{3-}$, a conclusion which is supported by Fessenden and Redmon (49). Launer and Yost (87) suggested the formula $[Mn(C_2O_4)_2]^-$, and Bradley and Van Praagh (25) attributed the yellow color of the reaction solution to the presence of the dihydrated form of this ion. Cartledge and Ericks (30) prepared certain manganioxalates, such as the red compound $K_3[Mn(C_2O_4)_3]$ and the green compound $K[Mn(C_2O_4)_2(H_2O)_2]$, which gives a golden-yellow solution. The former compound, which only exists at pH $\sim$ 5 and at high oxalate concentrations, is converted on acidification into the latter.

Duke (46) showed that the pseudo-first-order velocity constant, k_1, for the reaction of manganic ions with oxalic acid decreases with the increasing concentration of the latter according to the equation:

$$k_1 = k' + \frac{k''\,[\mathrm{H^+}]^2}{[\mathrm{H_2C_2O_4}]} \tag{11}$$

where k' and k'' are constants. Since

$$\frac{[\mathrm{H_2C_2O_4}]}{[\mathrm{H^+}]^2} = \text{constant} \times [\mathrm{C_2O_4^{2-}}]$$

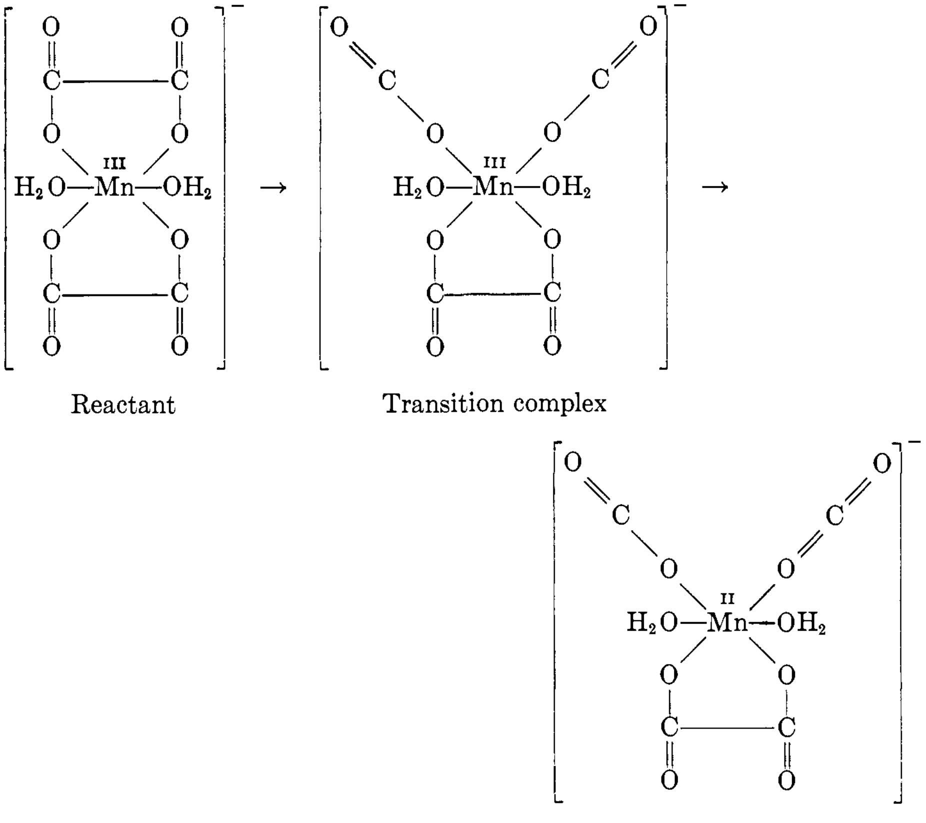
the equation can be written:

$$k_1 = k' + k'''/[\mathrm{C_2O_4^{2-}}]$$

On the basis of this equation, Duke suggests that both the complexes $[\mathrm{Mn(C_2O_4)(H_2O)_4}]^+$ and $[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]^-$ are involved in the slow first-order part of the reaction and that the former is more reactive than the latter. The two species are related by the equilibrium:

$$[\mathrm{Mn(C_2O_4)_2(H_2O)_2}]^- + 2\mathrm{H_2O} + 2\mathrm{H^+} \rightleftharpoons [\mathrm{Mn(C_2O_4)(H_2O)_4}]^+ + \mathrm{H_2C_2O_4}$$

The sequence of the decomposition envisaged is thus:



Reactant

Transition complex

Product

The activated complex is considered to have a disrupted C—C bond, with odd electrons remaining paired to allow resonance with ionic structures as well as with long-covalently-bonded forms; this resonance will result in lowering of the activation energy of the above reaction. The product, which is an unstable radical-ion, is then rapidly attacked by Mn^{3+} to give two molecules of carbon dioxide.

Bradley and Van Praagh (25) have studied the variation with pH and oxalic acid concentration of the first-order velocity constant for the decomposition of yellow potassium mangani-oxalate in acid solution. The rate of loss of oxidizing power at 16°C. is given by equation 12

$$\text{Rate} = [\text{C}]\,[\text{H}^+]\left\{\frac{1.13 \times 10^{-3}}{[\text{H}_2\text{C}_2\text{O}_4]} + 1.67\right\} \tag{12}$$

where [C] is the concentration of the mangani-oxalate complex. A rate equation of the same form is obtained from the following reaction scheme:

$$H^+ + [Mn(C_2O_4)_2(H_2O)_2]^- \rightarrow Mn^{3+} + HC_2O_4^- + C_2O_4^{2-} + 2H_2O$$

$$2Mn^{3+} \rightarrow Mn^{2+} + Mn^{4+}$$

$$Mn^{4+} + H_2C_2O_4 \rightarrow Mn^{3+} + 2H^+ + CO_2^- + CO_2$$

$$Mn^{4+} + CO_2^- \rightarrow Mn^{3+} + CO_2$$

$$2Mn^{3+} + H_2C_2O_4 \rightarrow 2Mn^{2+} + 2H^+ + 2CO_2$$

in which the third and fifth reactions are the rate-determining stages.

The form of the rate equation obtained by Bradley and Van Praagh (i.e., equation 12) is not the same as that found by Duke (i.e., equation 11). The former prepared the complex before starting the reaction, while the latter started with permanganate, manganous ions, and oxalic acid. This difference in experimental procedure should not, however, be the source of the above discrepancy, which is more likely to be due to the widely different ranges of concentration in which the two sets of measurements were made.

Taube (129, 130), from a study of the catalytic effect of manganic ions on the reaction

$$Cl_2 + H_2C_2O_4 = 2H^+ + 2Cl^- + 2CO_2$$

finds that the rate of oxidation of oxalic acid by manganic ions takes place according to either

$$MnC_2O_4^+ \rightarrow Mn^{2+} + C_2O_4^- \tag{13}$$

or

$$MnC_2O_4^+ \rightarrow Mn^+ + 2CO_2$$

with the intervention of

$$Mn(C_2O_4)_2^- \rightarrow Mn^{2+} + C_2O_4^{2-} + C_2O_4^- \tag{14}$$

at high concentrations of oxalic acid.

Reaction 14 is believed to be slower than reaction 13 for the following reason. It is known that $Mn(C_2O_4)^+$ interacts strongly with $C_2O_4^{2-}$, but no such interaction occurs between Mn^{2+} and $C_2O_4^{2-}$. Since the activated complex must be intermediate between $Mn(C_2O_4)^+$ and the two separate entities Mn^{2+} and $C_2O_4^-$, the initial state is stabilized to a greater extent than the transition state by excess oxalate ions. The activation energy of the decomposition of $Mn(C_2O_4)_2^-$ will therefore be larger and the rate will be lower than for the decomposition of the $MnC_2O_4^+$ complex. The validity of this reasoning is doubtful in the light of the work of Schölder and Linström (118) and Money and Davies (102), who find evidence for the existence of the $[Mn(C_2O_4)_2]^{2-}$ ion, and of Brintzinger and Eckardt (26), whose work suggests the existence of the dimeric manganous-oxalato complex $[Mn_2(C_2O_4)_4]^{4-}$.

Taube (131) deduces from kinetic experiments that the first-order reaction can follow three separate reaction paths involving the rate-controlling decompositions of the complexes $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, and $Mn(C_2O_4)_3^{3-}$ and presumably occurring in single stages, i.e., not involving previous decomposition to oxalate ions and MnC_2O_4.

$$MnC_2O_4^+ \xrightarrow{k_1} Mn^{2+} + C_2O_4^- \text{ (or } CO_2 + CO_2^-\text{)}$$
$$\text{or } Mn^+ + 2CO_2$$

$$Mn(C_2O_4)_2^- \xrightarrow{k_2} Mn^{2+} + C_2O_4^{2-} + C_2O_4^- \text{ (or } CO_2 + CO_2^-\text{)}$$
$$\text{or } Mn^+ + C_2O_4^{2-} + 2CO_2$$

$$Mn(C_2O_4)_3^{3-} \xrightarrow{k_3} Mn^{2+} + 2C_2O_4^{2-} + C_2O_4^- \text{ (or } CO_2 + CO_2^-\text{)}$$
$$\text{or } Mn^+ + 2C_2O_4^{2-} + 2CO_2$$

Taube finds that at 25.2°C. $k_1 = 11.8$ min.$^{-1}$, $k_2 = 0.046$ min.$^{-1}$, and $k_3 = 0.021$ min.$^{-1}$, in agreement with his view that those complexes with the highest proportion of oxalate have the least tendency to decomposition.

In his formulation of the mechanism for the second stage of the permanganate-oxalate reaction, Taube allows the possibility that the univalent Mn^+ ion intervenes. Although the univalent state of manganese is known in the complex ion $[Mn(CN)_6]^{5-}$ (105), it is preferable to formulate the transient reducing entity as the radical-ion $C_2O_4^-$. This formulation is consistent with the behavior of oxalic acid toward other oxidizing agents and with the observation (15, 86) that oxygen is absorbed by a reacting mixture of manganic and oxalate ions; such behavior is characteristic of free radicals. It has long been known (1, 39, 119) that oxalic acid, when treated with an insufficient amount of oxidizing agent, such as permanganate or persulfate, acquires an increased reducing power which is easily demonstrated by the rapid appearance of calomel when mercuric chloride is added to such solutions. This enhanced reactivity is attributed to a species which has been called "active oxalic acid." Abel (1) suggested that this species was the radical-ion $C_2O_4^-$, and Malaprade and Coulombeau (95) have recently reiterated this suggestion. Weiss (142) also concurs with this view and points out that when permanganate is the oxidant, the decomposition of the complexes, e.g., $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, and $Mn(C_2O_4)_3^{3-}$, will continually reproduce this radical-ion which will thus appear to have a long life. The nature of the $C_2O_4^-$ or CO_2^- entity and its participation in the reaction between manganic and oxalate ions have been discussed by Abel (7, 10).

The radiochemical work of Polissar (111) and of Adamson (14) demonstrates that the scheme suggested by Launer and Yost (87) is not adequate as a complete explanation of the course of the reaction. As mentioned earlier, both workers found no exchange between manganous and permanganate ions; thus any equilibrium between these ions must involve at least two intermediate valence states of manganese which do not exchange with each other. Adamson (14) has overcome this difficulty by postulating a rapid series of reactions which can be represented by the overall equilibrium:

$$6H^+ + 3Mn^{2+} + MnO_4^- \overset{K_1}{\rightleftharpoons} 3Mn^{3+} + MnO^{2+} + 3H_2O$$

in which no exchange between MnO^{2+} and Mn^{3+} occurs. In the presence of fluoride ions the equilibrium

$$Mn^{3+} + 4F^- \overset{K_2}{\rightleftharpoons} MnF_4^-$$

is rapidly established. The rate-determining step is given as:

$$2H^+ + MnO^{2+} + C_2O_4^{2-} \xrightarrow{k_1} Mn^{3+} + C_2O_4^- \text{ (or } CO_2 + CO_2^-\text{)}$$

Since the principal forms of Mn(III) and Mn(IV) are Mn^{3+} and MnO^{2+}, respectively,

$$3[MnO^{2+}] = [MnF_4^-] + [Mn^{3+}]$$

which gives for the rate of carbon dioxide formation:

$$\frac{dp_{CO_2}}{dt} = k_1 K_1^{1/4} \left\{\frac{1 + K_2[F^-]^4}{3}\right\}^{3/4} [Mn^{2+}]^{3/4} [MnO_4^-]^{1/4} [H^+]^{7/2} [C_2O_4^{2-}]$$

This equation differs from that derived by Adamson (14) by the factor $[H^+][C_2O_4^{2-}]$. It may be compared with that given by Launer and Yost (87):

$$\frac{dp_{CO_2}}{dt} = k [MnO_4^-]^{2/5} [Mn^{2+}]^{3/5} [C_2O_4^{2-}]$$

While the differences in the exponents of the permanganate- and manganous-ion concentrations may reasonably be neglected, the dependence of rate on hydrogen-ion concentration is in disagreement with the experiments of Launer (85), Launer and Yost (87), and Duke (46).

Fessenden and Redmon (49) have proposed another mechanism, but their scheme is in conflict with the radiochemical work, for although the scheme involves both Mn^{4+} and Mn^{3+} ions, the reaction

$$Mn^{4+} + Mn^{2+} \rightleftharpoons 2Mn^{3+}$$

would permit the spread of radioactivity from Mn^{2+} to MnO_4^-. Their scheme is very similar to that proposed by Launer and Yost (87). Fessenden and Redmon (49) have also studied the effect of various salts on the rate of the permanganate-oxalate reaction. In the oxalate-concentration range in which their studies were made, they find the maximum rate of oxidation to be approximately inversely proportional to the oxalate concentration. While sodium, potassium, and magnesium sulfates reduce the rate, the sulfates of zinc, cadmium, and aluminum increase it. The cations of the latter group of salts form complexes with oxalate ions and will reduce the effective concentration of those ions and therefore increase the rate of carbon dioxide evolution.

Recently, Noyes (104) has pointed out that the color of permanganate may persist for 30 sec. or more in solutions containing small quantities of both manganous and oxalate ions. This indicates that the reaction between permanganate and manganous ions in the presence of oxalate ions is not instantaneous. A very rapid reaction between permanganate and manganous ions is an essential requirement of the mechanisms put forward by Launer and Yost (87) and Fessenden and Redmon (49). Malcolm and Noyes (96) propose the following mechanism, which obviates the requirement of a rapid reaction between manganous and permanganate ions:

$$Mn^{2+} + C_2O_4^{2-} \rightleftharpoons MnC_2O_4 \quad \text{(rapid equilibrium)} \tag{15}$$

$$MnC_2O_4 + MnO_4^- \rightarrow Mn(III) + MnO_4^{2-} \quad \text{(fast relative to reaction 19)} \tag{16}$$

$$MnO_4^{2-} + 3Mn(II) + 8H^+ \rightarrow 4Mn(III) + 4H_2O \quad \text{(very fast series of steps)} \tag{17}$$

$$MnO_4^{2-} + \tfrac{3}{2}C_2O_4^{2-} + 8H^+ \rightarrow Mn(III) + 3CO_2 + 4H_2O \quad \text{(fast series of steps)} \tag{18}$$

$$Mn(III) \rightarrow Mn(II) + C_2O_4^- \quad \text{(measurable)} \tag{19}$$

$$Mn(III) + C_2O_4^- \rightarrow Mn(II) + 2CO_2 \text{ (very fast)} \tag{20}$$

Mn(II) and Mn(III) refer to any divalent and trivalent species, respectively. The intervention of manganous oxalate in the permanganate-oxalate reaction had been previously suggested by Fessenden and Redmon (49) and is in accord with the work of Money and Davies (101, 102). Participation of the manganate ion, which will have a very short life in acid media, had previously been proposed by Waterbury, Hayes, and Martin (138) to allow for the radiochemical restrictions and to account for their results in the reaction between periodate and manganous ions. Although reaction 16 is assumed to be fast, Malcolm and Noyes (96) believe that it is not excessively so, and on this basis explain the persistence of the purple permanganate color after mixing solutions of permanganate, manganous, and oxalate ions. The above scheme is a reasonable alternative to that of Launer and Yost. It differs in attributing the first stage of the reaction to process 16, which is fast compared with the second stage, viz., reaction 19, but is slow enough to account for the induction period observed at low manganous-ion concentrations. The scheme will also explain why the reaction between permanganate and either manganous or oxalate ions alone is slow compared with the rate when both ions are present together; the rate of oxidation of manganous oxalate is supposed to be much greater than that of either manganous ions or oxalate ions.

Adler and Noyes (15) have continued this research and have extended the earlier views. They point out that the reaction can be considered to involve the two processes:

$$MnO_4^- + 4Mn^{2+} + 5nC_2O_4^{2-} + 8H^+ \rightarrow 5Mn(C_2O_4)_n^{3-2n} + 4H_2O \qquad (21)$$

$$2Mn(C_2O_4)_n^{3-2n} \rightarrow 2Mn^{2+} + (2n - 1)C_2O_4^{2-} + 2CO_2 \qquad (22)$$

where $n = 1, 2$, or 3. They accept the view of Taube (131) concerning the formulas of the decomposing complexes and obtain similar rate constants for the unimolecular decomposition of the three complexes $MnC_2O_4^+$, $Mn(C_2O_4)_2^-$, and $Mn(C_2O_4)_3^{3-}$. Adler and Noyes (15) suggest the two following generalized stages for the second process:

$$Mn(C_2O_4)_n^{3-2n} \rightarrow Mn^{2+} + (n - 1)C_2O_4^{2-} + CO_2 + CO_2^- \qquad (23)$$

$$Mn(C_2O_4)_n^{3-2n} + CO_2^- \rightarrow Mn^{2+} + nC_2O_4^{2-} + CO_2 \qquad (24)$$

The radical produced in stage 23 may be either neutral HCO_2 or HC_2O_4 or the radical-ions CO_2^- or $C_2O_4^-$ depending on the acidity of the solution. They favor the CO_2^- formulation because they believe that the peroxy compound $O_2CO_2^-$ is more able to account for the diminution in rate of loss of oxidizing power when the partial pressure of oxygen above a reacting solution of permanganate, manganous, and oxalate ions is increased. The experiments of Adler and Noyes (15) further support the view that permanganate ions react with manganous oxalate molecules in the first stages of the reaction. These authors prefer to formulate the reactive species as the neutral manganous oxalate molecule rather than as a negatively charged ion, because the electrostatic repulsion between ions of like charge would lead to a slow reaction. In order to account for the small decrease in oxidizing titer immediately after mixing solutions of acid permanganate, manganous, and oxalate iont, Adler and Noyes (15) find it necessary to postulate an alternative reaction to reaction 21, namely:

$$MnO_4^- + Mn^{2+} + (2n + \tfrac{3}{2})C_2O_4^{2-} + 8H^+ \rightarrow 2Mn(C_2O_4)_n^{3-2n} + 3CO_2 + 4H_2O \qquad (25)$$

This path is less favored than reaction 21 except when the manganous-ion concentration is low and the oxalate concentration high. They presume that the first step can be written:

$$MnO_4^- + MnC_2O_4 \rightarrow MnO_4^{2-} + MnC_2O_4^+$$

The MnO_4^{2-} can then react with the excess manganous ions thus:

$$8H^+ + MnO_4^{2-} + Mn^{2+} \rightarrow 2Mn^{4+} + 4H_2O$$

or

$$\mathrm{Mn(VI)} + \mathrm{Mn(II)} \rightarrow 2\mathrm{Mn(IV)}$$

and

$$\mathrm{Mn^{4+}} + \mathrm{Mn^{2+}} \rightarrow 2\mathrm{Mn^{3+}}$$

or

$$\mathrm{Mn(IV)} + \mathrm{Mn(II)} \rightarrow \mathrm{Mn(III)}$$

or it may react with oxalate ions to produce carbon dioxide. The manganate ion is believed to react with the oxalate ion by the two two-electron transfers

$$\mathrm{Mn(VI)} + \mathrm{C_2O_4^{2-}} \rightarrow \mathrm{Mn(IV)} + 2\mathrm{CO_2}$$

and

$$\mathrm{Mn(IV)} + \mathrm{C_2O_4^{2-}} \rightarrow \mathrm{Mn(II)} + 2\mathrm{CO_2}$$

rather than by way of the $\mathrm{CO_2^-}$ radical since, in the view of these authors, a "mechanistic catastrophe" in the form of a branched-chain explosion type of reaction would result if the latter radical-ions were produced. Adler and Noyes (15) also find it necessary to postulate the increased intervention of the reaction

$$\mathrm{MnO_4^-} + \mathrm{MnC_2O_4^+} \rightarrow \mathrm{MnO_4^{2-}} + \mathrm{Mn(IV)}$$

when the oxalate concentration is low, in order to account for the autocatalytic nature of the reaction at such concentrations.

Summarizing then, it is evident that the reaction between acid permanganate and oxalate proceeds by a number of processes which can be grouped into two stages. The first involves a complex series of steps which have not been completely elucidated but which lead to the accumulation of one or more manganic-oxalate complexes. These decompose by a unimolecular mechanism in the second stage, which may occur as envisaged by Duke (46); this stage has been studied by Taube (131). The autocatalysis in the reaction is to be attributed to the steps in the first stage and an important step may be the reaction between permanganate ion and manganous oxalate which produces a manganic-oxalate complex and a manganate ion. Noyes, Malcolm, and Adler, the originators of this suggestion, then suppose that the manganate ion may react either with manganous ions or, to a smaller extent, with oxalate ions. The existence of a radical in the reaction, which may be any one of the following, $\mathrm{CO_2^-}$, $\mathrm{C_2O_4^-}$, $\mathrm{HCO_2}$, $\mathrm{HC_2O_4}$, and possibly the radical containing manganese postulated by Duke (46), is accepted by most workers and is consistent with the fact that the reaction solution absorbs oxygen.

D. REACTIONS BETWEEN ACID PERMANGANATE AND ORGANIC COMPOUNDS

1. *Introduction*

One of the principal aims of many workers in the field of acid permanganate oxidations has been the attempt to formulate modes of oxidation and to classify reactions between permanganate and organic compounds by the mechanism according to which the oxidation proceeds. Tompkins and his collaborators (16, 17, 62, 64, 97, 132, 133) have attempted to show that there are two principal mechanisms by which organic compounds are oxidized by acid permanganate; one mechanism proceeds by direct oxidation by the permanganate ion, and the second involves the prior formation of the Mn^{4+} ion and subsequent oxidation by hydroxyl radicals produced from this ion and water. It is postulated that the radical mechanism is characterized by an initial induction period, while the direct oxidation by the permanganate ion is of the second order throughout. Also, when the reaction involves the prior formation of Mn^{4+} ions, the activation energy for the reaction is greater than when permanganate ions are directly involved. Further, according to Tompkins and his coworkers, the organic compound should possess a labile hydrogen atom for the reaction to proceed by direct attack of the permanganate ions. Tompkins gives examples of the two mechanisms. Oxidation involving permanganate ions directly is exemplified by the oxidation of formic acid (97; see also 145) thus:

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

$$2MnO_3^- + H_2O \rightarrow MnO_2 + HMnO_4^- + OH^- \quad \text{faster than reaction 1}$$

$$HMnO_4^- + HCOO^- \rightarrow MnO_2 + CO_2 + 2OH^- \quad \text{faster than reaction 1}$$

The rate-determining stage is the bimolecular reaction between the formate and permanganate ions.

The second mechanism is exhibited by the oxidation of 2,6-dinitrophenol (17). In order to overcome the radiochemical restrictions mentioned previously, Alexander and Tompkins (17) propose the following sequence to account for the formation of Mn^{3+} ions which subsequently disproportionate to produce Mn^{4+} ions:

$$Mn^{2+} + MnO_4^- \rightleftharpoons Mn^{3+} + MnO_4^{2-}$$

$$Mn^{2+} + MnO_4^{2-} \rightleftharpoons Mn^{3+} + MnO_3^- + OH^-$$

$$Mn^{2+} + MnO_3^- \rightleftharpoons Mn^{3+} + MnO_2 + OH^-$$

Oxidation of 2,6-dinitrophenol then follows the course:

$$2Mn^{3+} \rightarrow Mn^{4+} + Mn^{2+}$$

$$Mn^{4+} + H_2O \rightarrow Mn^{3+} + OH + H^+$$

$$Mn^{2+} + OH \rightarrow Mn^{3+} + OH^-$$

$$Mn^{4+} + 2H_2O \rightarrow MnO_2 + 4H^+$$

$$MnO_2 + 2H^+ \rightarrow Mn^{4+} + 2OH^-$$

$$C_6H_3(NO_2)_2OH \rightleftharpoons C_6H_3(NO_2)_2O^- + H^+$$

$$C_6H_3(NO_2)_2OH + OH \rightarrow C_6H_3(NO_2)_2(OH)_2$$

$$C_6H_3(NO_2)_2(OH)_2 \rightarrow A$$

$$A + OH \rightarrow B$$

$$B + OH \rightarrow C, \text{ etc.}$$

The activation energy for the oxidation of formic acid is 11.2 kcal. per mole, while that for the oxidation of 2,6-dinitrophenol is found to be 14.4 kcal. per mole, in accordance with Tompkins' criterion. However, in view of the fact that a number of equilibria might be involved in the reaction, such as the ionization of the organic substrate, and the consequent involvement of the energy changes for those reactions in the activation energy for the overall process, it is doubtful whether any diagnostic significance can be placed on the value of the activation energy.

In view of the variety of oxidizing species which are undoubtedly present in a reaction mixture of organic substrate, acid, and permanganate, it is too much to expect that the reaction will follow one reaction path exclusively. Rather, it would seem necessary to allow for oxidation along several courses associated with the several oxidizing species.

Certain general observations concerning the oxidation of organic compounds by permanganate in acid and alkaline solution, and by manganic sulfate and manganic pyrophosphate in acid solutions, have been noted by Drummond and Waters (40). It seems probable that in oxidations by manganic sulfate and manganic pyrophosphate, the anions $[Mn(SO_4)_2H_2O]^-$ (134) and $[Mn(H_2P_2O_7)_3]^{3-}$ (140), respectively, and not the manganic cation, are responsible for the oxidation. Drummond and Waters (40) associate the occurrence of an induction period with the slow initial reduction of the permanganate ion and subsequent production by the Guyard reaction of more reactive ions belonging to lower valence states. They point out that, on one hand, permanganate ions will attack olefinic bonds while the trivalent manganic state does not, and on the other, permanganate ions are inactive towards oxalic acid while the trivalent state is very active.

Drummond, Levesley, and Waters, in a series of papers (40, 41, 42, 43, 44, 45, 89), have reported attempts to isolate the various stages in the reduction of permanganate ions by organic substrates. The first paper deals with the $MnO_4^- \rightarrow MnO_4^{2-}$ stages which occur in alkaline solution in the presence of barium salts which remove the manganate ions as insoluble barium manganate. The subsequent papers deal with the oxidation of organic compounds by the complex manganic pyrophosphate ion. In the oxidations of pinacol (43), malonic acid (44), α-hydroxy acids (89), and pyruvic acid (45), complexes with the manganic pyrophosphate anion are formed which break down to give free radicals which have been detected by their ability to initiate vinyl polymerization. Malonate complexes of trivalent manganese have also been described by Cartledge and Nichols (31).

Merz, Stafford, and Waters (99) have pointed out the probable existence of the valence change $Mn^{4+} \rightarrow Mn^{2+}$ in the oxidation of alcohols by permanganate in the presence of ferrous sulfate or hydrogen peroxide. It is believed that the ferrous sulfate or hydrogen peroxide first reduces the permanganate to Mn^{4+}

and that this then undergoes a two-electron transfer to the alcohol to give manganous ions. That two electrons are involved is suggested by the inability to detect free radicals in the reaction.

2. Oxidation of particular groups of organic compounds

a. Hydrocarbons

The oxidation of the side chain in toluene and substituted toluenes, and of ethylbenzene, isopropylbenzene, and *n*-propylbenzene in aqueous acetic acid, has been the subject of a series of papers by Cullis and Ladbury (33, 34, 35, 36). In 50 per cent by volume acetic acid, the permanganate is reduced only to the manganese dioxide stage, and the oxidation occurs in a stepwise manner. Concurrently with side-chain oxidation, the aromatic ring is attacked, producing carbon dioxide. The observation that ring oxidation occurs with chlorotoluenes is in disagreement with the work of Speroni and Barchielli (124), who state that no carbon dioxide is evolved when aqueous acetic acid is the solvent. However, the present authors found that chloride ions are also produced in the oxidation of the chlorotoluenes, and this clearly suggests that some of the aromatic nuclei undergo complete rupture. The extent of ring oxidation diminishes as the size of the alkyl group in the monoalkylbenzenes increases. With the xylenes, the ring suffers considerable oxidation and most of this occurs during the oxidation of the first methyl group, since the toluic acids suffer less total oxidation than the corresponding xylenes. With toluene, the evidence suggests that ring rupture occurs after the prior oxidation to benzyl alcohol. In general, the effect on the rate of oxidation of substituted toluenes is as would be expected for an electrophilic (ionic) attack. The effect of added salts which have anions capable of complexing with manganic ions, e.g., potassium fluoride and pyrophosphate, is to decrease the rate to a limiting value, but this depends largely on the organic substrate. Evidently the manganic ion is not the sole attacking species and probably the permanganate ion plays some part. The initial reaction is generally of the first order with respect to both the permanganate and the organic compound, but this simple kinetic relationship is never maintained beyond the initial stages of the reaction; indeed, second-order kinetics are frequently found for the initial stages of acid permanganate oxidations (*cf.* 16, 65, 103, 124).

The Arrhenius parameters are given for a number of the reactions studied by Cullis and Ladbury (33, 34, 36), but no functional correlation exists between the velocity constant for the initial reaction and the activation energy, and the considerable changes in reactivity which occur with changes in structure are therefore not primarily dependent on either of the Arrhenius parameters. A similar conclusion was reached by Hinshelwood and Winkler (66, 67) as a result of an analysis of the kinetic data on the oxidation of a number of phenols.

Sigmoid forms of the reaction–time curves are found for several of the compounds studied and this is particularly pronounced in the slow oxidations of substituted benzoic acids. The form of the curves is attributed to the decomposition of the aromatic ring and the consequent formation of labile open-chain fragments.

Finally, from product analyses on the reactions with various monoalkylbenzenes, it is concluded that the α-carbon atom is the initial point of attack.

b. Phenols and aromatic alcohols

An early kinetic investigation into the permanganate oxidation of substituted phenols, e.g., salicylic acid, *p*-nitrophenol, picric acid, trinitrocresol, etc., was made by Hinshelwood (65). The reaction–time curve for *p*-nitrophenol is interesting in that it shows an initial high rate followed by a quiescent period and a sigmoid-shaped curve. Similar curves were obtained by Cullis and Ladbury for the oxidation of *n*-propylbenzene (36).

Alexander and Tompkins have studied the oxidation of 2,6-dinitrophenol (16), and their views on the mechanism have been presented earlier in this section of the present review. It will be recalled that these authors attributed the oxidation of 2,6-dinitrophenol to attack by hydroxyl radicals produced by the interaction of tetravalent manganese cations with water. In the earlier work of Hinshelwood and Winkler (66) the kinetics were explained by assuming collisions between a phenol molecule and a permanganate ion. Musgrave and Moelwyn-Hughes (103) in a study of the oxidation of picric acid found that the phenoxide ion rather than the undissociated molecule was directly involved in the oxidation but were unable to decide experimentally whether the oxidant was ionic. Leman and Delannoy (88) have studied the oxidation of certain naphthols the rate of which is initially very high but soon decreases.

The oxidation of aromatic alcohols by permanganate has also received some attention. The reactions of benzyl alcohol and of 1- and 2-phenylethanol have been investigated by Cullis and Ladbury (33, 35). In general, these reactions, like those of related aromatic compounds, are initially of the first order with respect to each reactant, although overall second-order kinetics are not maintained as reaction proceeds. With benzyl alcohol, considerable ring rupture occurs during the oxidation (33).

A much fuller study of the reactions of an aromatic alcohol with permanganate has been made by Stewart (126), who has investigated the behavior of benzhydrol. It has been shown that the rate-controlling step is the reaction between the benzhydrylate ion and the permanganate ion. A considerable isotope effect is observed when the α-hydrogen atom is replaced by deuterium. This finding and the fact that, when O^{18}-labelled permanganate is used as the oxidizing agent, no excess O^{18} appears in the product suggest that reaction occurs by transfer of hydride ion from a benzhydrylate ion to a permanganate ion.

c. Sugars

Kuhn and Wagner-Jauregg (82) have studied the rates of oxidation of various sugars, e.g., fructose, arabinose, galactose, maltose, mannose, etc., by permanganate in phosphate-buffered media. With fructose the rate varies with pH, a minimum occurring at pH 4; the mechanism of the oxidation is not discussed however.

d. Aliphatic acids

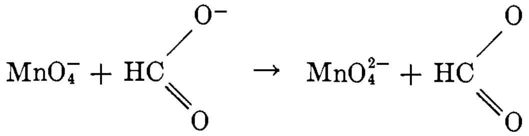
The mechanism of the oxidation of formic acid suggested by Mann and Tompkins (97) has been discussed. An alternative scheme is proposed by Abel (13), who suggests that the first stage in any permanganate oxidation is electron abstraction from the substrate,

$$MnO_4^- + e \rightarrow MnO_4^{2-}$$

which is then followed, in acid media, by the reaction:

$$MnO_4^{2-} + 4H^+ \rightarrow MnO_2^{2+} + 2H_2O$$

The MnO_2^{2+} ion then performs further oxidation. The mechanism for the oxidation of the formate ion, which acts as an electron donor, is given thus:



$$MnO_4^- + HC\begin{matrix}O^- \\ \\ O\end{matrix} \rightarrow MnO_4^{2-} + HC\begin{matrix}O \\ \\ O\end{matrix}$$

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

$$MnO_2^{2+} + HCOO \rightarrow MnO_2^+ + H^+ + CO_2$$

$$MnO_2^+ + HCOO^- \rightarrow MnO_2 + HCOO$$

$$MnO_2^+ + HCOO \rightarrow MnO_2 + H^+ + CO_2$$

For strongly alkaline solution the mechanism is simply

$$MnO_4^- + HCOO^- \rightarrow MnO_4^{2-} + HCOO$$

$$MnO_4^- + HCOO \rightarrow MnO_4^{2-} + H^+ + CO_2$$

i.e., the reduction in these circumstances stops at the manganate ion. The oxidation of formic acid has been studied also by Wiberg and Stewart (145).

The oxidation of citric acid by acid permanganate has been studied by Bhale, Mohammad, Bhagwat, and Bafna (22). They find that the reaction–time curves are sigmoid, and that the rate is decreased by the addition of potassium fluoride and increased by the addition of manganous sulfate. They believe that a mechanism similar to that suggested by Alexander and Tompkins for the oxidation of 2,6-dinitrophenol (16) explains their observations.

A kinetic study of the reaction between acid permanganate and tartaric acid has been made by Sanz-García (116, 117). A two-stage reaction in which complex formation occurs is suggested by this author.

The oxidation of oleic acid by permanganate has been studied by Wiberg and Saegebarth (143) in the course of an investigation into the mechanism of hydroxylation of several olefinic compounds. With the aid of labelled oxygen (O^{18}), it has been shown that the oxygen introduced into oleic acid in its conversion to 9,10-dihydroxystearic acid arises mainly from the oxidizing agent.

e. Aldehydes and ketones

Tompkins (133) has studied the oxidation of benzaldehyde in both acid and basic solution. A mechanism involving complex formation is suggested for the reaction in acid solution. The reactions between permanganate and formaldehyde, acetaldehyde, and benzaldehyde have been studied by Seijoo (120), and the oxidation of formaldehyde in neutral solution has been the subject of an investigation by Holluta and Mutschin (71).

Drummond and Waters (40) make an interesting point concerning the oxidation of aldehydic compounds. With the exception of formic acid and formaldehyde, these substances are oxidized by both permanganate ions and trivalent manganese, while only alkaline permanganate attacks formic acid.

The qualitative observations made by Drummond and Waters (40) concerning the effect of fluoride ions on the reaction between formic acid and permanganate are at variance with the quantitative results of Mann and Tompkins (97), Holluta (68, 70), and Holluta and Weiser (72), who find that fluoride ions accelerate the oxidation and do not retard it, as stated by Drummond and Waters.

These authors (41) have also made kinetic measurements on the oxidation of propionaldehyde and *n*-butyraldehyde by manganic pyrophosphate and find that in the pH range 1–2, the reaction is of zero order with respect to the oxidant and of the first order with respect to the concentration of both the hydrogen ion and the aldehyde. This, they suggest, is due to the preferential attack on the enol form and the dependence of the overall rate on the rate-controlling enolization process, thus:

$$\begin{array}{ccl} \mathrm{RCH_2CHO} + \mathrm{H}^+ & \overset{\text{fast}}{\rightleftharpoons} & \mathrm{RCH_2CH{=}\overset{+}{O}H} \\ & & \quad \upharpoonleft\!\downharpoonright \text{rate-controlling} \\ & & \mathrm{RCH{=}CHOH} + \mathrm{H}^+ \end{array}$$

They also suggest that a similar mechanism operates in the oxidation of aliphatic ketones by manganic pyrophosphate. The control of the rate of oxidation by the enolization step has also been suggested by Cullis and Ladbury (35) in the oxidation of acetophenone by acid permanganate. However, in this case an initial fast reaction is observed, and this is accounted for by assuming a high equilibrium concentration of the enol form initially which is oxidized much more rapidly than it is produced. The rate of the subsequent reaction therefore becomes controlled by the rate of enolization. Evidence for this view is adduced from the observation that the rate of the second stage of the reaction, when the small effect of the direct oxidation of the keto molecule is made zero, is in good agreement with the rate of enolization of acetophenone, under the same conditions, as measured by means of iodine uptake.

IV. Oxidation of Inorganic Substances by Permanganate

A. INTRODUCTION

It is proposed to discuss here only those reactions which have been studied quantitatively. For references (not very up-to-date, however) to qualitative work the reader is referred to Jacobson (76).

Although it is reasonable to expect that oxidation of inorganic substances would be less complicated than oxidation of organic substances, the reactions between permanganate and inorganic substances have received very little attention.

B. HYDROGEN

The reaction of aqueous potassium permanganate with molecular hydrogen was first studied by Just and Kauko (79). Most of their measurements were made in neutral solution, under which conditions it was found that the reaction was of the first order with respect both to the permanganate concentration and to the partial pressure of hydrogen. These authors showed that the reaction was accelerated by addition of alkali but that it was not influenced by the manganese dioxide formed in the reduction process. They suggested the intermediate formation of a species containing Mn(V), which is rapidly decomposed in acid solution, liberating oxygen, but is more stable in alkaline solution. Wilke and Kuhn (146) found that the reduction of permanganate by hydrogen takes place more rapidly in neutral than in acid or alkaline media. Reaction is initially slow but accelerates as reaction proceeds, presumably owing to the formation of manganate or to the production of colloidal manganese dioxide. In accordance with the latter suggestion, reagents which cause precipitation of manganese dioxide retard reaction. The variation of the nature of the reaction products with pH has also been noted by Delwaulle (38). In acid solution, manganese dioxide is precipitated and oxygen is evolved, in neutral solution colloidal manganese dioxide is formed but no oxygen is liberated, while in alkaline solution potassium manganate is formed which slowly decomposes into manganese dioxide.

A recent study of the potassium permanganate–hydrogen reaction has been carried out by Webster and Halpern (141). These workers have studied the kinetics over a wide range of pH, and they find that under all conditions used the reaction is of the first order with respect to both permanganate and hydrogen concentrations. In agreement with Just and Kauko, they suggest a reaction mechanism involving the intermediate formation of some species containing Mn(V) which may perhaps be MnO_4^{3-} or MnO_3^-; the existence of Mn(V) in solution is now well established (108, but *cf.* reference 40), and species derived from this valence state of manganese have been postulated in the reaction of permanganate with various organic compounds including benzaldehyde (133, 144) and the formate ion (97, 145).

Webster and Halpern (141) have also studied the silver-catalyzed reduction of permanganate by molecular hydrogen. The observation that silver ions accelerate the permanganate-hydrogen reaction was first made by Hein and Daniel (58). It was suggested (59) that among the species responsible for the catalysis were solid products such as $Ag_2Mn_2O_5$ and $AgMnO_2$. Kinetic studies (141) show that the rate of the catalyzed reaction is given by

$$-\frac{d[H_2]}{dt} = k[H_2][MnO_4^-][Ag^+]$$

and a mechanism is suggested which involves the intermediate formation of Mn(VI), the formation of which is favored by the presence of a species such as silver ion, which readily accepts an electron or combines with a hydrogen atom.

C. HYDRAZINE

The reaction between hydrazine and permanganate in acid solution generally produces both nitrogen gas and ammonium salts (27). For example, a typical product analysis for the reaction in 10 per cent sulfuric acid at 60–70°C. with permanganate added in excess from a buret while the solution is stirred has been made by Petersen (107), who gives the following stoichiometry:

$$85N_2H_5^+ + 26MnO_4^- + 63H^+ = 50N_2 + 70NH_4^+ + 26Mn^{2+} + 104H_2O$$

Variable stoichiometry is observed for this reaction (18) and this has been the subject of several publications (37, 74, 81 and references therein), the most recent being those of Abel (8) (who discusses the reaction between hydrazine and manganic ions in a subsequent paper (9)) and Higginson, Sutton, and Wright (60, 61). Abel assumes that hydrazine plays a dual role; it can act either as an electron donor:

$$N_2H_4 \rightarrow NH_2^+ + NH_2 + e$$

or as an electron acceptor:

$$N_2H_4 + e \rightarrow NH_2^- + NH_2$$

In the first case, he suggests that nitrogen gas is produced by the following series of steps:

$$Mn^{r+} + N_2H_4 \rightarrow Mn^{(r-1)+} + NH_2^+ + NH_2$$

$$NH_2 + Mn^{r+} \rightarrow Mn^{(r-1)+} + NH_2^+$$

$$NH_2^+ \rightarrow NH + H^+$$

$$NH + Mn^{r+} \rightarrow Mn^{(r-1)+} + NH^+$$

$$NH^+ + H_2O \rightarrow NHOH + H^+$$

$$2NHOH \rightarrow HN{=}NOH + H_2O$$

$$HN{=}NOH \rightarrow N_2 + H_2O$$

The $Mn^{(r-1)+}$ can be MnO_4^{2-}, MnO_2^{2+}, MnO_2^+, MnO_2, Mn^{4+}, Mn^{3+}, or Mn^{2+}. In the case where hydrazine acts as an electron acceptor, ammonium ions are formed and the lower valence states of manganese, which are produced in the previous series of reactions, e.g., MnO_4^{2-} etc., are the electron donors.

$$Mn^{r+} + N_2H_4 \rightarrow Mn^{(r+1)+} + NH_2^- + NH_2$$

$$Mn^{r+} + NH_2 \rightarrow Mn^{(r+1)+} + NH_2^-$$

$$NH_2^- + H^+ \rightarrow NH_3$$

In order to account for the observed stoichiometry it must be assumed that the reaction whereby hydrazine acts as an electron donor occurs to a greater extent than the reaction with hydrazine as an electron acceptor. The mechanism given by Abel (8) should be compared with that of Higginson and Sutton (60), where only an electron-donating tendency of hydrazine is involved; the limiting reactions which Higginson and Sutton propose are as follows:

$$N_2H_4 \xrightarrow{-e} \tfrac{1}{2}N_2 + NH_3$$

$$N_2H_4 \xrightarrow[\text{in stages}]{-4e} N_2 + 4H^+$$

D. HYDROXYLAMINE

The reaction between hydroxylamine and potassium permanganate in acid and alkaline solutions has been studied by Kurtenacker and Neusser (83), who find that in strongly alkaline solution nitrite ions and nitrous oxide are formed, while in weakly alkaline media nitrogen is the oxidation product. In strongly acid solution nitric acid is produced. Riesenfeld and Chang (115) find that the reaction–time curve is wave-shaped. These authors also find a periodic variation of amount of reaction with time in the reactions of permanganate with hydrazine and hypophosphoric acid. The kinetics of the small group of reactions which show wavelike reaction–time curves still awaits elucidation, but it is evident that this feature is often associated with evolution of gas from a solution (106).

E. HYDROGEN PEROXIDE

The stoichiometry of the mutual reduction which occurs between hydrogen peroxide and alkaline permanganate can be represented by the equation

$$2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$$

while in acid media the stoichiometry is given by the equation:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

The latter reaction has been studied by Limanowski (92, 93), who observed that while the purple permanganate color persists in a mixture with fairly concentrated hydrogen peroxide, addition of water causes rapid discoloration. Apparently, hydrogen peroxide in fairly concentrated solutions retards its own reaction with permanganate. The reaction has also been studied by Riesenfeld (114) and Riesenfeld and Chang (115). Bailey and Taylor (19) have shown that the course of the reaction can be represented fairly well by the equation

$$\text{Rate of oxygen evolution} = \frac{k_1[H_2O_2][H_2SO_4][KMnO_4]}{k_2 + k_3[H_2O_2]^2[H_2SO_4]^2}$$

but this does not take into account the effect of manganous ions, which powerfully catalyze the reaction at low concentrations of hydrogen peroxide. These authors were, however, unable to present a detailed mechanism for the reaction.

This reaction has also been the subject of a number of communications by Abel (2, 3, 4, 5, 6, 12) who, in consistency with his earlier view of the mechanism of permanganate oxidations, suggests the intervention of MnO_4^{2-}, MnO_2^{2+}, and MnO_2^+ ions. Fouinat (50, 51) and Fouinat and Magat (52) have studied the reaction in both alkaline and acid media. With alkali present there is good evidence that a heterogeneous reaction occurs on the surface of the manganese dioxide, although not all the reaction follows the heterogeneous path. The reaction–time curves, which are steep initially and then become wavelike, are explained in terms of a sequence of two reactions, one homogeneous and the other catalyzed by the colloidal manganese dioxide. With regard to the reaction in strongly acid media, where colloidal manganese dioxide does not form, they do not draw any valuable conclusions.

F. SULFITE, CYANIDE, NITRITE, AND CHLORIDE IONS

Sulfite ions are rapidly oxidized by permanganate. The variation of pH with time during the reaction has been studied by Sorum, Charlton, Neptune, and Edwards (123). Halpern and Taube (56) have shown by a radiochemical method that no oxygen atoms are transferred from the permanganate to the sulfite. This indicates that, in this reaction at least, the species responsible for oxidation react by an electron-abstraction process.

An opposite result is found in the oxidation of cyanide to cyanate (28), where the use of O^{18} shows that some transfer of oxygen from the permanganate to the substrate does take place.

The oxidation of nitrite to nitrate ions by acid permanganate is quantitative, and the stoichiometry of the reaction is represented by the equation

$$5NO_2^- + 2MnO_4^- + 6H^+ = 5NO_3^- + 2Mn^{2+} + 3H_2O$$

but the kinetics of this reaction have not been studied.

It is well known that the reaction between permanganate and hydrochloric acid produces chlorine gas. This was first investigated by Wagner (137) but has received little attention since. A study pertinent to this reaction was made by Bassett and Sanderson (21), who attributed the evolution of chlorine gas from the reaction between ferrous salts and permanganate in the presence of chloride ions to the reaction:

$$Mn^{3+} + Cl^- \rightarrow Mn^{2+} + Cl$$

The manganic ions are produced in the Guyard decomposition.

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