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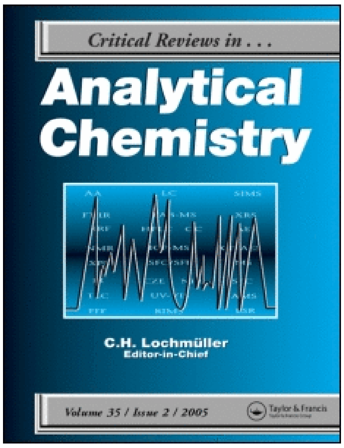

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THE USE OF TRIVALENT MANGANESE COMPOUNDS IN TITRIMETRY

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I. INTRODUCTION

At present, titration methods based on oxidation-reduction reactions form one of the widest and most thoroughly studied fields of analytical chemistry. A great deal of attention continues to be paid to this field in the literature, including development of new oxidants and reductants.

Various compounds of trivalent manganese belong among less common but interesting oxidants. The value of the formal redox potential of the Mn(III)/Mn(II) system and the stability of solutions of these reagents are strongly dependent on the acidity of the medium and on the presence of complexing agents.

In alkaline media, manganese (II) is readily oxidized by atmospheric oxygen. In the presence of substances that form stable complexes with manganese (III) in alkaline media, e.g., cyanide, triethanolamine or various hydroxyacids and polyhydroxycompounds, atmospheric oxygen oxidizes manganese (II) to manganese (III), whereas in the absence of these complexing agents hydrated manganese dioxide is formed. These complexes of manganese (III) that are stable only in alkaline solutions exhibit no oxidizing properties and are thus used only for determination of manganese.

On the other hand, manganese (II) is most stable in neutral or acidic aqueous solutions and consequently all compounds of manganese (III) are strong oxidants in acidic media. The stability of solutions of manganese (III) is adversely affected by disproportionation, but this reaction can be suppressed by adding substances that form stable complexes with manganese (III) or by increasing the concentration of manganese (II) or of hydrogen ions. Among complexing agents, diphosphate, phosphate, and fluoride are most often used, but the complexing properties of sulfuric and acetic acids and of various polyaminocarboxylic acids have also been employed. The stability of solutions of manganese (III) increases with increasing acidity and with increasing concentration of manganese (II), which is utilized especially in the preparation of solutions of hexaquomanganese (III) ions in noncomplexing media of perchloric acid.

Oxidation of many inorganic substances by compounds of manganese (III) is usually a rapid reaction that can be used for direct titration determination. In contrast, in reactions with organic compounds it is often difficult to achieve an unambiguous, stoichiometric, and quantitative reaction course and the reaction conditions, such as acidity, temperature, and the presence of complexing agents, play a greater role. The reaction rate is often insufficiently fast for direct titration and thus an excess of the reagent must be used for a certain time and then the unconsumed fraction back-titrated or a reaction product determined. (The latter approach is often used to improve the selectivity of the determination.)

Efforts to develop improved methods have recently led to the study of the kinetics and mechanisms of redox reactions. On the basis of these studies, not only can the analytical usefulness of a reaction be evaluated, but causes of its nonstoichiometric course or low rate can often be found and a procedure for elimination of these drawbacks can be proposed. From the theoretical point of view, knowledge of the reaction mechanism broadens our general knowledge of the reagent and permits prediction of its reactivity towards other similar substances.

For these reasons, this review discusses not only the preparation, stability, and basic physico-chemical properties of various forms of manganese (III), but also the kinetics and mechanisms of reactions with inorganic and organic substances. In this way, the reader will be helped in understanding the reactivity of these substances as analytical reagents and thus also the potentialities and limitations of their use will become more clear.

II. BASIC PHYSICAL AND PHYSICO-CHEMICAL PROPERTIES OF VARIOUS FORMS OF MANGANESE (III)

In connection with the analytical use of various forms of manganese (III) and with the study of the kinetics and mechanism of oxidation of many organic and inorganic substances, the electrochemical and optical properties of the Mn(III)/Mn(II) system have been studied in detail.

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A. Optical Properties

The absorption spectrum of the diphosphate complex of manganese (III) was studied in detail in order to use it in the spectrophotometric determination of ozone[1] and manganese (II).[2-5] The molar decadic absorption coefficient at the maximum absorbance (510 nm) is 78 $mol^{-1}\ l\ cm^{-1}$. It has been confirmed by the Job method[6] that the complex is $[Mn(H_2P_2O_7)_3]^{3-}$ and its dissociation constant was determined spectrophotometrically[7] to be 9.8×10^{-10}.

The absorption spectra of the fluoride[8,9] and phosphate[10] complexes of manganese (III) have been described in connection with the preparation of these reagents.

It has been found[11,12] that the wavelength of the absorbance maximum of manganese (III) sulfur and the corresponding molar absorption coefficient increase with increasing concentration of sulfuric acid, which has been explained by the formation of the sulfate complex of manganese (III). The disproportionation constant determined spectrophotometrically[11] is approximately equal to 10^{-3} in $4M$-H_2SO_4 and 10^{-4} in $7M$-H_2SO_4. These values are about two orders of magnitude lower than those obtained potentiometrically.[13] This difference has been attributed to an error caused by slow stabilization of the potential of the platinum electrode immersed in a solution containing tetra- and trivalent manganese. The dependence of the absorbance on the manganese (III) sulfate concentration is linear over a range of 15 to 150 μg Mn/ml[5] and has also been used in a spectrophotometric determination of substances that reduce this reagent.[14]

The visible absorption spectra of hexaquo- and hydroxo- pentaquomanganese (III) ions were studied in connection with a study of the hydrolysis of hexaquomanganese (III) ions[9,15] and changes in these spectra on addition of complexing substances are discussed in Reference 16.

It follows from the works cited above that the absorbance of various forms of manganese (III) in the visible region can be used for indirect determination of substances that reduce manganese (III) and for the study of oxidation reactions by photometric monitoring of the manganese (III) concentration.

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B. Electrochemical Properties

The electrochemical behavior of the Mn(III)/Mn(II) system has been studied in many works. It follows from polarographic[17] and potentiometric[18] studies of this system in diphosphate that, at pH 1 to 6, manganese (III) is present as $[Mn(H_2P_2O_7)_3]^{3-}$ and manganese (II) as $[Mn(H_2P_2O_7)_2]^{2-}$; at higher pH values, the corresponding complexes are $[Mn(P_2O_7)_3]^{9-}$ and $[Mn(P_2O_7)_2]^{6-}$. As the diphosphate complexes of tri- and divalent manganese are much stronger acids than diphosphoric acid, it can be assumed that even in strongly acidic solutions, where diphosphoric acid is present as $H_4P_2O_7$, manganese (II) and (III) are present in the same forms as those existing in solutions with pH 1 to 6. The formal redox potential of the Mn(III)/Mn(II) system in the form of the diphosphate complex strongly depends on the pH (equal to 900 mV at pH 1 and 320 mV at pH 6 (vs. SCE, IUPAC convention) in 0.4*M* sodium diphosphate). Its dependence on the diphosphate concentration is less pronounced (at pH 2 it is 825 mV [vs. SCE] in 0.4*M* sodium diphosphate and 885 mV in 0.04*M* sodium diphosphate).[18] The voltammetric behavior of this system in diphosphate was studied using a platinum wire rotating electrode.[19-22]

The phosphate complex of manganese (III) is basically complex bis-(phosphato)-manganic acid, $H_3[Mn(PO_4)_2]$,[23-25] the formal redox potential of the Mn(III)/Mn(II) system being virtually independent of the phosphoric acid concentration (equal to 1.073 V and 1.066 V [vs. SCE] in 3*M* and 12*M* phosphoric acid, respectively). The electrochemical behavior of this complex is described in References 27 and 28.

In a fluoride medium, a number of complexes of manganese (III), from MnF^{2+} to MnF_6^{3-}, is apparently present.[8,29-32] The formal redox potential of the Mn(III)/Mn(II) system then depends both on the pH (860 mV at pH 2.6 and 780 mV at pH 5.4 vs. SCE in 2*M* ammonium fluoride) and on the fluoride concentration (850 mV and 680 mV [vs. SCE] in 0.4*M* and 3.2*M* ammonium fluoride, respectively, at pH 4.2).[29] The polarographic behavior of this complex is described in Reference 33.

Ubbelohde[34] assumed that solutions of manganese (III) sulfate contain the $[Mn(SO_4)_2 \cdot 2H_2O]$ species, whereas other authors assumed the existence of $[Mn(HSO_4)_3(OH)_3]^{3-}$ [35] or $[Mn(SO_4)_3]^{3-}$ [36] ions or of complex acid $H_2[Mn_2(SO_4)_4]$.[37] However, it has recently been confirmed[12] that manganese (III) is present as $[Mn(H_2O)_5HSO_4]^{2+}$ and $[Mn(H_2O)_5(HSO_4)_2]^{+}$ ions. The formal redox potential (vs. SCE) of the Mn(III)/Mn(II) system is 1.261 V and 1.400 V in 9*N* and 24*N* sulfuric acid, respectively,[13] and the standard redox potential at 25°C is 1.247 V (SCE).[38] The potentiometrically measured value of the disproportionation equilibrium constant of manganese (III), $K = [Mn(IV)][Mn(II)]/[Mn(III)]^2$, equals 0.503 in 9*N* sulfuric acid and 0.0013 in 24*N* sulfuric acid.[13] The electrochemical behavior of the Mn(III)/Mn(II) system in sulfuric acid was also studied.[13,38-42]

In a noncomplexing medium of perchloric acid, manganese (III) is present as hexaquomanganese (III) ions,[9,15,43,44] which are converted into hydroxopentaquomanganese (III) at low acidity,

$$\left[Mn(H_2O)_6\right]^{3+} + H_2O \rightleftharpoons \left[Mn(H_2O)_5OH\right]^{2+} + H_3O^+$$

The equilibrium constant of this reaction is 0.88 ± 0.04.[15] Because solutions of this reagent are sufficiently stable only in the presence of a large excess of manganese (II), it is impossible to determine the formal redox potential of the Mn(III)/Mn(II) system in perchloric acid. However, Rosseinsky[45] assumes that it does not exceed 1.324 V (SCE).

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From the study of the electrochemical behavior of all the above forms of manganese (III), optimum conditions have been derived for amperometric[46] and biamperometric[21] titrations with these reagents and it has been found that the reactions of these reagents can be studied by using the polarographic monitoring of the manganese (III) concentrations.[17,28,33,47,48] The Mn(III)/Mn(II) system behaves irreversibly at a platinum electrode; manganese (III) is reduced to manganese (II) at a dropping mercury electrode at a potential corresponding to mercury oxidation.

III. OXIDIZING PROPERTIES OF VARIOUS FORMS OF MANGANESE (III)

Considerable attention has been paid to oxidation of inorganic and organic substances by various compounds of manganese (III), as reflected in a number of reviews.[49-52,60,65] These reactions have been studied preparatively, physicochemically (i.e., to establish their mechanism), and analytically. Because the analytical use of the reactions of manganese (III) is discussed in detail in Section IV, the present chapter is devoted to the kinetics and mechanism of the reactions of various forms of manganese (III) with inorganic and organic substances.

A. Oxidation of Inorganic Substances

The oxidation of many inorganic substances by the diphosphate and phosphate complexes of manganese (III) and by manganese (III) sulfate has been used for the titrimetric determinations of these substances (see Section IV.C.1.), but the kinetics and mechanisms of these reactions have not been studied in detail. This is undoubtedly due to complication of the mechanism by the formation of various strong complexes, leading to more complicated kinetics and more difficult interpretation of the results of kinetic measurements.

On the other hand, considerable attention has been paid to the mechanism of the oxidation of many inorganic ions by hexaquomanganese (III) ions in the noncomplexing perchloric acid medium. These are usually very rapid oxidation reactions, whose kinetics have been studied using the stopped-flow technique.

In oxidation ov V(IV)[56] and Fe(II),[13,53,54] analogous kinetics have been found and thus analogous mechanisms have been proposed:

$$\mathrm{Mn^{3+}_{aq} + Fe^{2+}_{aq} \rightarrow Mn^{2+}_{aq} + Fe^{3+}_{aq}}$$

$$\mathrm{MnOH^{2+}_{aq} + Fe^{2+}_{aq} \rightarrow Mn^{2+}_{aq} + FeOH^{2+}_{aq}}$$

$$\mathrm{Mn^{3+}_{aq} + VO^{2+}_{aq} + H_2O \rightarrow Mn^{2+}_{aq} + VO^{+}_{2\,aq} + 2\,H^{+}_{aq}}$$

$$\mathrm{MnOH^{2+}_{aq} + VO^{2+}_{aq} \rightarrow Mn^{2+}_{aq} + VO^{+}_{2\,aq} + H^{+}_{aq}}$$

In both cases, the oxidation by $\mathrm{Mn^{3+}_{aq}}$ ions is slower than that by $\mathrm{MnOH^{2+}_{aq}}$ ions.

In contrast, it has been found for the oxidation of Hg(I)[45] that the reaction rate decreases with increasing concentrations of Mn(II) and Hg(II). This fact can be explained by the following mechanism assuming disproportionation of manganese (III) and mercury (I), with the latter present as the dimer:

$$2\,\mathrm{Mn(III)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{Mn(IV)} + \mathrm{Mn(II)}$$

$$[\mathrm{Hg(I)}]_2 \overset{\text{fast}}{\rightleftharpoons} \mathrm{Hg(II)} + \mathrm{Hg(O)}$$

$$\mathrm{Mn(IV)} + [\mathrm{Hg(I)}]_2 \overset{\text{slow}}{\rightleftharpoons} \mathrm{Mn(II)} + 2\mathrm{Hg(II)}$$

$$\mathrm{Mn(III)} + \mathrm{Hg(O)} \overset{\text{slow}}{\rightleftharpoons} \mathrm{Mn(II)} + \mathrm{Hg(I)}$$

$$\mathrm{Mn(III)} + \mathrm{Hg(I)} \overset{\text{fast}}{\rightleftharpoons} \mathrm{Mn(II)} + \mathrm{Hg(II)}$$

It is interesting that $[Mn(H_2O)_6]^{3+}$ ions do not perceptibly oxidize Tl(I) in perchloric acid, even at an elevated temperature.[57] The reaction proceeds only in the presence of Cl^- ions, apparently due to the formation of reactive $\cdot Cl_2^-$ ions, according to the scheme

$$\mathrm{Mn}^{3+}_{aq} + \mathrm{Cl}^- \rightleftharpoons \mathrm{MnCl}^{2+}$$

$$\mathrm{MnCl}^{2+} + \mathrm{Cl}^- \rightleftharpoons \mathrm{Mn}^{2+} + \cdot\mathrm{Cl}_2^-$$

$$\mathrm{Tl(I)} + \cdot\mathrm{Cl}_2^- \rightleftharpoons \mathrm{Tl(II)} + 2\mathrm{Cl}^-$$

$$\mathrm{Tl(II)} + \cdot\mathrm{Cl}_2^- \rightleftharpoons \mathrm{Tl(III)} + 2\mathrm{Cl}^-$$

On the basis of a polarographic study,[48] the following mechanism has been proposed for the oxidation of SCN^- ions by manganese (III):

$$2\,\mathrm{Mn}^{3+}_{aq} + \mathrm{SCN}^- \rightleftharpoons \left[\mathrm{Mn\text{-}SCN\text{-}Mn}_{aq}\right]^{5+}$$

$$\left[\mathrm{Mn\text{-}SCN\text{-}Mn}_{aq}\right]^{5+} \xrightarrow{\text{slow}} 2\mathrm{Mn}^{2+}_{aq} + \mathrm{SCN}^+$$

$$\mathrm{SCN}^+ + \mathrm{SCN}^- \xrightarrow{\text{rapid}} (\mathrm{SCN})_2$$

The decomposition of the complex of manganese (III) with the substance to be oxidized is the rate-determining step, in accordance with the experimentally found second order kinetics with respect to manganese (III).

In the oxidation of Br^-, the dissociation of the bromide complex of manganese (III) is the rate-determining step at low bromide concentrations[58]

$$\mathrm{Mn}^{3+}_{aq} + \mathrm{Br}^-_{aq} \overset{\text{rapid}}{\rightleftharpoons} \mathrm{MnBr}^{2+}_{aq}$$

$$\mathrm{MnBr}^{2+}_{aq} \xrightarrow{\text{slow}} \mathrm{Mn}^{2+}_{aq} + \cdot\mathrm{Br}_{aq}$$

$$2\cdot\mathrm{Br}_{aq} \xrightarrow{\text{rapid}} \mathrm{Br}_{2\ aq}$$

However, at higher bromide concentrations the reaction is second order with respect to the concentration of bromide. This fact can be explained by the assumption that Br^- ions are oxidized by the bromide complex of manganese (III), in addition to the above reactions:

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$$\mathrm{MnBr^{2+}_{aq} + Br^-_{aq} \overset{slow}{\rightleftharpoons} Mn^{2+}_{aq} + {\cdot}Br_2^-{}_{aq}}$$

$$\mathrm{Mn^{3+}_{aq} + {\cdot}Br_2^-{}_{aq} \xrightarrow{rapid} Mn^{2+}_{aq} + Br_2{}_{aq}}$$

The decrease in the reaction rate with increasing concentration of Mn^{2+} is explained by the formation of a relatively stable bromide complex of manganese (II) and the dependence of the reaction rate on the acidity by participation of the $[Mn(H_2O)_5OH]^{2+}$ ions in the reaction mechanism.

The reaction of hydrogen azide with manganese (III)[61] at low concentrations is first order with respect to manganese (III) and second order with respect to hydrogen azide and has the stoichiometry

$$\mathrm{2\,Mn(III) + 2\,HN_3 \rightarrow 2\,Mn(II) + 3\,N_2 + 2\,H^+}$$

With a large excess of hydrogen azide[59] the kinetics are more complicated, although the stoichiometry remains unchanged.

Wells and Mays[63] studied the oxidation of hydrogen peroxide by hexaquomanganese (III) ions and proposed a mechanism assuming reversible formation of a complex of manganese (III) with hydrogen peroxide, of the type $[Mn^{3+}HO_2{}^-{}_{aq}]$, which dissociates in the rate-determining step with formation of the $\cdot HO_2$ free radical that is immediately oxidized further to molecular oxygen. On the other hand, Davies and co-workers[64] have proposed a mechanism for this reaction whose first step is reversible oxidation of hydrogen peroxide to give a free radical of the type $\cdot HO_2$ or $\cdot H_2O_2^+$, and which does not involve formation of a complex intermediate.

In contrast, for the oxidation of nitrous acid,[62] corresponding to the stoichiometry

$$\mathrm{2\,Mn(III) + HNO_2 + H_2O \rightarrow 2\,Mn(II) + NO_3^- + 3H^+}$$

the following mechanism has been proposed, in agreement with the experimentally found second order kinetics:

$$\mathrm{Mn^{3+}_{aq} + HNO_{2\,aq} \xrightarrow{slow} Mn^{2+}_{aq} + {\cdot}NO_2{}_{aq} + H^+_{aq}}$$

$$\mathrm{MnOH^{2+}_{aq} + HNO_{2\,aq} \xrightarrow{slow} Mn^{2+}_{aq} + {\cdot}NO_{2\,aq} + H_2O}$$

$$\mathrm{Mn^{3+}_{aq} + H_2O + {\cdot}NO_2{}_{aq} \xrightarrow{rapid} Mn^{2+}_{aq} + NO_3^-{}_{aq} + 2\,H^+_{aq}}$$

B. Oxidation of Organic Substances

Considerable attention has been paid to the kinetics and mechanism of the oxidation of organic compounds by various forms of manganese (III), as illustrated in a number of reviews.[50,51,65,202] A certain selectivity of the effect of these reagents has been found compared, e.g., with permanganate, and very different reactivity of various forms of manganese (III). Below, the kinetics and mechanism of the oxidation of various types of organic substances by the diphosphate and phosphate complexes of manganese (III), manganese (III) sulfate and acetate and hexaquomanganese (III) ions in noncomplexing perchloric acid medium are reviewed.

1. Oxidation of Monobasic Alcohols

It has been found that the diphosphate complex of manganese (III) does not percep-

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tibly oxidize monobasic alcohols. Allyl alcohol is oxidized by this reagent,[55] but very slowly and the kinetic data found do not permit a decision as to whether the oxidation occurs at the double bond or at the CH group. The authors assume that a free radical is formed reversibly in the first step

$$C_3H_5OH + Mn^{3+}_{aq} \rightleftharpoons R\cdot + Mn^{2+}_{aq}$$

which explains the observed retardation by manganese (II) ions. However, the nature of the radical formed, whose presence was detected by induction of radical polymerization, could not be determined, as all possible products of primary oxidation of allyl alcohol are oxidized further by the diphosphate complex of manganese (III). In addition to further rapid oxidation of this free radical, recombination of two free radicals can also occur and thus a varied mixture of products is formed.

The more reactive manganese (III) sulfate oxidizes methyl-, ethyl-, 2-propyl-, butyl, iso-butyl- and amylalcohol,[82] although very slowly. The oxidation of cyclohexanol by this reagent was studied in greater detail[67] and a mechanism involving reversible formation of a complex of manganese (III) with cyclohexanol was proposed. This complex dissociates in the rate-determining step, producing a free radical that is immediately oxidized further to cyclohexanone.

Manganese (III) acetate in acetic acid also reacts with monobasic alcohols, but very slowly.[68]

Hexaquomanganese (III) ions in noncomplexing perchloric acid medium oxidize monobasic alcohols to the corresponding carbonyl compounds. These reactions are also very slow and thus can be monitored only in the presence of a large excess of the oxidized substance.

The following mechanism has been proposed for the oxidation of methanol[69]

$$Mn^{3+}_{aq} \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq}$$

$$CH_3OH + H^+_{aq} \rightleftharpoons CH_3OH_2^+{}_{aq}$$

$$Mn^{3+}_{aq} + CH_3OH \rightleftharpoons Mn^{3+}CH_3OH_{aq}$$

$$Mn^{3+}CH_3OH_{aq} \rightleftharpoons Mn^{3+}CH_3O^-_{aq} + H^+_{aq}$$

$$Mn^{3+}CH_3OH_{aq} \rightleftharpoons Mn^{2+} + \cdot CH_2OH + H^+_{aq}$$

$$Mn^{3+}CH_3O^-_{aq} \rightleftharpoons Mn^{2+}_{aq} + \cdot CH_2OH$$

$$Mn^{3+}_{aq} + \cdot CH_2OH \rightarrow Mn^{2+}_{aq} + HCHO + H^+_{aq}$$

$$MnOH^{2+}_{aq} + \cdot CH_2OH \rightarrow Mn^{2+}_{aq} + HCHO$$

Dissociation of the manganese (III) complex with methanol is the rate-determining step. The formation of this complex was also confirmed spectrophotometrically.[70]

In contrast, no intermediary complex has been detected with 2-propanol,[71] 2-butanol,[72] and cyclohexanol.[72] The oxidation of 2-propanol under anaerobic conditions obeys the mechanism[71]

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$$Mn^{3+}_{aq} + H_2O \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq}$$

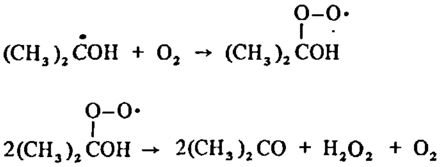
$$(CH_3)_2CHOH + H^+ \rightleftharpoons (CH_3)_2CHOH_2^+{}_{aq}$$

$$Mn^{3+}_{aq} + (CH_3)_2CHOH \xrightarrow{slow} Mn^{2+}_{aq} + (CH_3)_2\dot{C}OH + H^+_{aq}$$

$$MnOH^{2+}_{aq} + (CH_3)_2CHOH \xrightarrow{slow} Mn^{2+}_{aq} + (CH_3)_2\dot{C}OH$$

$$Mn^{3+}_{aq} + (CH_3)_2\dot{C}OH \xrightarrow{rapid} Mn^{2+}_{aq} + (CH_3)_2CO + H^+_{aq}$$

In the presence of oxygen, the $(CH_3)_2\cdot COH$ radical may undergo the reactions



$$(CH_3)_2\dot{C}OH + O_2 \rightarrow (CH_3)_2\overset{O-O\cdot}{\overset{|}{C}}OH$$

$$2(CH_3)_2\overset{O-O\cdot}{\overset{|}{C}}OH \rightarrow 2(CH_3)_2CO + H_2O_2 + O_2$$

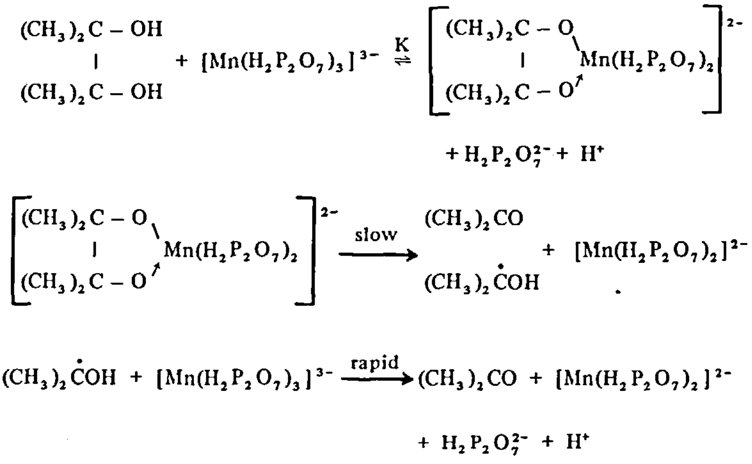
the hydrogen peroxide being oxidized to elemental oxygen by manganese (III).

It follows from the above findings that the oxidation of monofunctional alcohols cannot be analytically utilized because of slow and often unstoichiometric reactions. Monobasic alcohols are often oxidized by compounds of manganese (III) so slowly that, at lower concentrations, they virtually do not interfere in the determination of other substances.[196]

2. *Oxidation of Polybasic Alcohols*

In the oxidation of polyalcohols by various compounds of manganese (III), a complex of manganese (III) with the substance to be oxidized is usually formed and dissociates in the rate-determining step with formation of a free radical that is immediately oxidized further.

The following mechanism has been proposed[73] for the oxidation of pinacol by the diphosphate complex of manganese (III)



$$\begin{array}{c}(CH_3)_2C-OH\\ |\\ (CH_3)_2C-OH\end{array} + [Mn(H_2P_2O_7)_3]^{3-} \overset{K}{\rightleftharpoons} \left[\begin{array}{l}(CH_3)_2C-O\\ \quad | \qquad\quad Mn(H_2P_2O_7)_2\\ (CH_3)_2C-O\end{array}\right]^{2-} + H_2P_2O_7^{2-} + H^+$$

$$\left[\begin{array}{l}(CH_3)_2C-O\\ \quad | \qquad\quad Mn(H_2P_2O_7)_2\\ (CH_3)_2C-O\end{array}\right]^{2-} \xrightarrow{slow} \begin{array}{c}(CH_3)_2CO\\ \\ (CH_3)_2\dot{C}OH\end{array} + [Mn(H_2P_2O_7)_2]^{2-}.$$

$$(CH_3)_2\dot{C}OH + [Mn(H_2P_2O_7)_3]^{3-} \xrightarrow{rapid} (CH_3)_2CO + [Mn(H_2P_2O_7)_2]^{2-} + H_2P_2O_7^{2-} + H^+$$

The experimental finding that the reaction rate increases with increasing concentration of sulfuric acid can be explained by the assumption that increasing acidity suppresses the dissociation of diphosphoric acid and of the diphosphate complex of manganese

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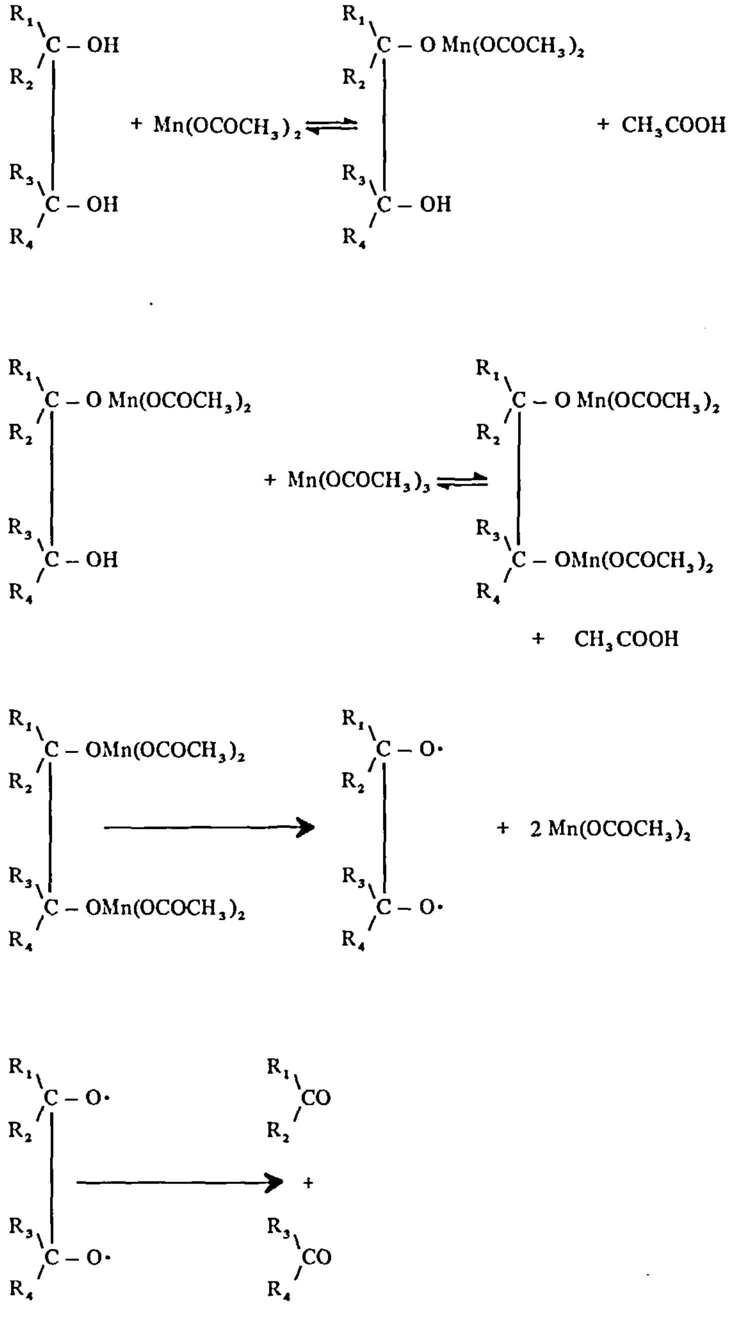
(III). An intermediate complex of manganese (III) with the substance to be oxidized was also detected in the oxidation of *cis*-cyclohexane-1,2-diol by the diphosphate complex of manganese (III).[100] On the other hand, such an intermediate complex is not formed in the oxidation of *cis*- and *trans*-1,2-dimethylcyclopentane-1,2-diol and *cis*- and *trans*-1,2-dimethylcyclohexane-1,2-diol.[100] The formation of free radicals was observed in the oxidation of butane-1,2-diol, butane-2,3-diol, erythritol, mannitol and sorbitol by the diphosphate complex of manganese (III).[205]

The mechanism proposed[101] for oxidation of α-glycols by manganese (III) acetate also assumes the formation of a complex of manganese (III) with the substance to be oxidized



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An analogous mechanism has been proposed for the oxidation of glycerol[206] and other substances of glycolic character[212-214] with this reagent.

For the oxidation of pinacol by hexaquomanganic ions,[123] the mechanism

$$Mn^{3+}_{aq} + H_2O \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq}$$

$$(CH_3)_2COH - (CH_3)_2COH + H^+_{aq} \rightleftharpoons (CH_3)_2COH\text{–}(CH_3)_2COH_2^+{}_{aq}$$

$$Mn^{3+}_{aq} + (CH_3)_2COH - (CH_3)_2COH \rightleftharpoons Mn^{3+}(CH_3)_2COH\text{–}(CH_3)_2COH_{aq}$$

$$MnOH^{2+}_{aq} + (CH_3)_2COH - (CH_3)_2COH \rightleftharpoons Mn^{3+}(CH_3)_2COH - (CH_3)_2CO^-_{aq} + H_2O$$

$$Mn^{3+}(CH_3)_2COH - (CH_3)_2COH \rightleftharpoons Mn^{3+}(CH_3)_2COH - (CH_3)_2CO^-_{aq} + H^+_{aq}$$

$$Mn^{3+}(CH_3)_2COH - (CH_3)_2COH \rightarrow Mn^{2+}_{aq} + (CH_3)_2CO + (CH_3)_2\dot{C}OH + H^+_{aq}$$

$$Mn^{3+}(CH_3)_2COH - (CH_3)_2CO^-_{aq} \rightarrow Mn^{2+}_{aq} + (CH_3)_2CO + (CH_3)_2\dot{C}OH$$

$$Mn^{3+}_{aq} + (CH_3)_2\dot{C}OH \rightarrow Mn^{2+}_{aq} + (CH_3)_2CO + H^+_{aq}$$

was proposed. The dissociation of the intermediate complex is again the rate-determining step.

Attempts at analytical application of the oxidation of polyalcohols by various compounds of manganese (III) have been unsuccessful,[117,198,199] generally for stoichiometric reasons.

3. Oxidation of Saccharides

The diphosphate complex of manganese (III) oxidizes saccharides with a mechanism analogous to that observed with polyalcohols. The stoichiometry of the reaction of this complex with glucose can be expressed by the equation[74]

$$\begin{aligned} C_6H_{12}O_6 + 8\,Mn(III) + 4H_2O \rightarrow 4HCOOH + 2HCHO + 8\,Mn(II) \\ + 8H^+ \end{aligned}$$

This reaction is first order with respect to the concentration of manganese (III) and its rate is proportional to the hydrogen ion concentration and inversely proportional to the sodium diphosphate concentration. Manganous ions exert no effect on the reaction rate. The assumed reaction mechanism can be schematically written as

$$\text{Glucose} + Mn(III) \overset{K}{\rightleftharpoons} \text{complex}$$

$$\text{complex} \xrightarrow{\text{slow, k}} R\cdot + Mn(II)$$

$$R\cdot + Mn(III) \xrightarrow{\text{rapid}} P + Mn(II)$$

where R· is a free radical and P is the product of the primary oxidation of glucose undergoing further oxidation. Mathematical treatment of this mechanism leads to the expression for the reaction rate:

$$-\frac{d[Mn(III)]}{dt} = \frac{k\,K\,[\text{glucose}]\,[Mn(III)]}{1 + [\text{glucose}]}$$

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This equation is in agreement with the experimental reaction kinetics. The experimental kinetics[100] of the oxidation of methyl-α-D-pyranoside and methyl-α-D-manopyranoside also indicates formation of an intermediate complex of manganese (III) with the substance to be oxidized. Oxidation of glucose and saccharose[206] and xylose and arabinose[208] by manganese (III) acetate was also studied.

4. Oxidation of Phenols and Polyphenols

The oxidation of a number of substances with phenolic character by various forms of manganese (III) has chiefly been studied from the analytical point of view (see Section IV). Only for hexaquomanganese (III) ions were the kinetics studied and a mechanism proposed for the oxidation of hydroquinone,[75,76] 1,2-dihydroxybenzene,[77] 4-methyl- and 4-*tert*-butyl-1,2-dihydroxybenzene[78] and 4,4′-diphenyldiol;[79] manganese (III) acetate was used for the study of the kinetics of the oxidation of 2,6-*tert*-butyl-4-methyl-phenol and 2,4,6-tritertbutylphenol.[203]

Kustin and Davies[75] proposed a mechanism for the oxidation of hydroquinone

$$Mn^{3+}_{aq} + H_2O \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq}$$

$$Mn^{3+}_{aq} + H_2Q \rightarrow Mn^{2+}_{aq} + H^+_{aq} + HQ\cdot$$

$$MnOH^{2+}_{aq} + H_2Q \rightarrow Mn^{2+}_{aq} + HQ\cdot$$

$$Mn^{3+}_{aq} + HQ\cdot \rightarrow Mn^{2+}_{aq} + H^+_{aq} + Q$$

$$MnOH^{2+}_{aq} + HQ\cdot \rightarrow Mn^{2+}_{aq} + Q$$

The formation of the HQ· free radical, which is rapidly oxidized further to quinone (Q) is the rate determining step.

In contrast, Wells and Kuritsyn[76] proposed a mechanism for the same reaction involving reversible formation of a hydroquinone complex with manganese (III), whose dissociation is the rate-determining step

$$Mn^{3+}_{aq} + H_2Q \rightleftharpoons MnH_2Q^{3+}_{aq}$$

$$MnOH^{2+}_{aq} + H_2Q \rightleftharpoons MnHQ^{2+}_{aq} + H_2O$$

$$MnH_2Q^{3+}_{aq} \rightleftharpoons MnHQ^{2+}_{aq} + H^+_{aq}$$

$$MnH_2Q^{3+}_{aq} \rightarrow Mn^{2+}_{aq} + HQ\cdot + H^+_{aq}$$

$$MnHQ^{2+}_{aq} \rightarrow Mn^{2+}_{aq} + HQ\cdot$$

$$Mn^{3+}_{aq} + HQ\cdot \rightarrow Mn^{2+}_{aq} + Q + H^+_{aq}$$

$$MnOH^{2+}_{aq} + HQ\cdot \rightarrow Mn^{2+}_{aq} + Q + H_2O$$

This mechanism agrees with the experimental kinetics obtained by the authors.

An analogous mechanism has been proposed[77] for the oxidation of 1,2-dihydroxybenzene. However, it followed from the kinetic measurements that the equilibrium constants for the formation of manganese (III) complexes with this substance are very

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low and so it is difficult to detect these intermediate complexes experimentally. The same also hold for the oxidation of 4-methyl- and 4-*tert*-butyl-1,2-dihydroxybenzene[78] and 4,4'-diphenyldiol.[79] The oxidation of the latter substance is interesting in that the 4,4'-diphenylquinone formed in the first reaction step undergoes further oxidation. The rate of the first reaction step decreases linearly with increasing concentration of perchloric acid, which can be explained by the higher reactivity of the $MnOH^{2+}_{aq}$ ions compared with Mn^{3+}_{aq} ions. The rate of the second reaction step increases with increasing concentration of perchloric acid, which can be explained by protonation of the quinone, followed by hydration and finally by the oxidation of the hydrate formed to a free radical in the rate-determining step.

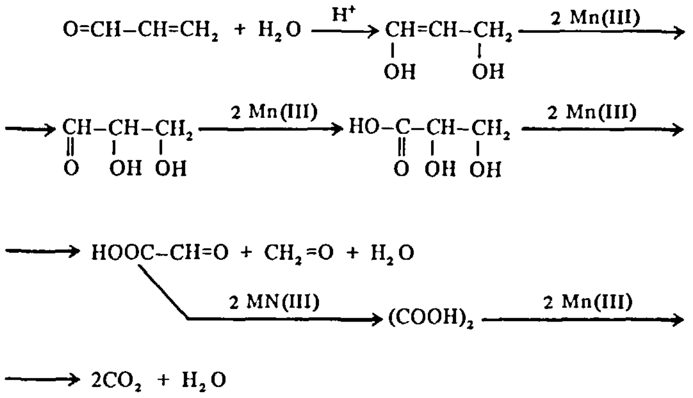
5. *Oxidation of Aldehydes and Ketones*

The diphosphate complex of manganese (III) oxidizes only those aldehydes and ketones that can form enols.[66,80,81] The reaction is then zero order with respect to the concentration of manganese (III) and first order with respect to the H^+ ion concentration. In agreement with this finding, a mechanism has been proposed assuming that slow, acid-catalyzed enolization is the rate-determining step and only the enol formed by this reaction is oxidized by the diphosphate complex of manganese (III). This mechanism can be described by the equation

$$R{-}CH_2{-}CH{=}O \xrightarrow{H^+} R{-}CH{=}CH{-}OH \xrightarrow{2[Mn(H_2P_2O_7)_3]^{3-}}$$
$$R{-}CHOH{-}CH{=}O$$

The α-hydroxyaldehyde formed then undergoes further nonstoichiometric oxidation.

The oxidation of acraldehyde[80] probably proceeds according to the equations



$$O{=}CH{-}CH{=}CH_2 + H_2O \xrightarrow{H^+} \underset{OH}{CH}{=}CH{-}\underset{OH}{CH_2} \xrightarrow{2\,Mn(III)}$$
$$\longrightarrow \underset{O}{\underset{\|}{CH}}{-}\underset{OH}{CH}{-}\underset{OH}{CH_2} \xrightarrow{2\,Mn(III)} HO{-}\underset{O}{\underset{\|}{C}}{-}\underset{OH}{CH}{-}\underset{OH}{CH_2} \xrightarrow{2\,Mn(III)}$$
$$\longrightarrow HOOC{-}CH{=}O + CH_2{=}O + H_2O$$
$$HOOC{-}CH{=}O \xrightarrow{2\,MN(III)} (COOH)_2 \xrightarrow{2\,Mn(III)}$$
$$\longrightarrow 2CO_2 + H_2O$$

The spectrum of the diphosphate complex of manganese (III) changes on addition of acraldehyde, which confirms the existence of an intermediate complex of the reagent with the substance to be oxidized.

On the other hand, oxidations of some aldehydes and ketones by manganic sulfate have been found to be first order reactions with respect to the concentration of manganese (III); their rate, which is independent of the acidity and of the nature of the solvent is greater than the enolization rate under the given conditions. Therefore, a mechanism assuming direct attack of manganese (III) on the keto-form of the substance to be oxidized has been proposed for these reactions; splitting of the C-H bond at the α-position with formation of a free radical is the rate-determining step. The keto-form preferentially forms a complex with manganese (III), because its oxygen

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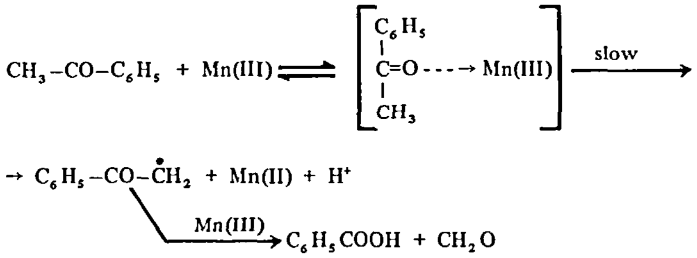
atom is more nucleophilic than that of the enol-form. For the oxidation of acetophenone,[86] the mechanism



has been proposed. The oxidations of methyl ethyl ketone,[35] methyl propyl ketone,[83,84] acetone,[85] formaldehyde,[86] cyclohexanone,[87] *p*-methoxyacetophenone,[89] and acetaldehyde[168] are quite analogous.

The oxidation of some carbonyl compounds by manganese (III) acetate was studied from the point of view of the reaction kinetics and mechanism[90,91] and of monitoring of radical reactions of these compounds initiated by manganese (III) acetate.[92,93,204] The mechanism of these reactions is similar to that of oxidations by manganese (III) sulfate. For example, it has been found[90] that the reaction of aromatic ketones with manganese (III) acetate is first order with respect to the concentrations of the two reactants; its rate is independent of the concentration of manganese (III) ions and decreases with increasing amounts of water in the reaction mixture. The reactivity of ketones of the $R\text{-}C_6H_4\text{-}CO\text{-}CH_3$ type decreases in the order $R = p\text{-}NO_2 > H > m\text{-}NO_2 > p\text{-}Cl > pCH_3 > pOCH_3$. The kinetics of enolization and oxidation are again quite different.

In contrast to the diphosphate and sulfate complexes of manganese (III), manganese (III) acetate oxidizes benzaldehyde and its derivatives.[91] The presence of an electrophilic substituent on the aromatic ring increases the reaction rate and a nucleophilic substituent decreases it, which can be explained by a higher degree of resonance stabilization of radicals with electrophilic substituents. It is assumed that the reaction can be described by the scheme

$$\mathrm{Ar{-}CHO + Mn(III) \xrightarrow{slow} Ar{-}\dot{C}O + Mn(II) + H^+}$$

$$\mathrm{Ar{-}\dot{C}O + Mn(III) + H_2O \xrightarrow{rapid} Ar{-}COOH + Mn(II) + H^+}$$

These reactions are also rather slow, even in the presence of catalysts and with large excesses of the substance to be oxidized and their analytical application is further frequently prevented by a nonstoichiometric reaction course.

6. Oxidation of Simple Carboxylic Acids

Simple carboxylic acids are not perceptibly oxidized by the diphosphate complex of manganese (III). On the other hand, manganese (III) sulfate oxidizes formic acid, with two possible reaction paths.[86,94] At low concentrations of manganese (III) (< 0.01 *M*) in the reaction mixture, the reaction obeys the mechanism[94]

$$\mathrm{HCOOH + Mn(III) \xrightarrow{slow} Mn(II) + H^+ + HCOO\cdot}$$

$$\mathrm{HCOOH \rightleftharpoons HCOO^- + H^+}$$

$$\mathrm{HCOO^- + Mn(III) \xrightarrow{slow} Mn(II) + HCOO\cdot}$$

$$\mathrm{HCOO\cdot + Mn(III) \xrightarrow{rapid} Mn(II) + H^+ + CO_2}$$

so that the overall reaction can be expressed by the equation

$$\mathrm{HCOOH + 2Mn(III) \rightarrow 2Mn(II) + CO_2 + 2H^+}$$

The experimentally found first order kinetics with respect to the reactants and the decrease of the reaction rate with increasing concentration of hydrogen ions are in agreement with these kinetics. At higher concentrations of manganese (III), the relationship

$$-\frac{d[\mathrm{Mn(III)}]}{dt} = k\,[\mathrm{HCOOH}]\,\frac{[\mathrm{Mn(III)}]^2}{[\mathrm{Mn(II)}]}$$

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was found[86] for the rate of oxidation of formic acid and indicates that, at higher concentrations of manganese (III) sulfate, tetravalent manganese also participates in the reaction mechanism, i.e., either Mn(III) attacks the Mn(IV)-formate complex or Mn(IV) attacks the Mn(III)-formate complex. Attention has also been paid to the oxidation of benzoic acid with manganic acetate.[207]

The following mechanism has been proposed[95] for the oxidation of formic acid with manganese (III) in perchloric acid medium

$$\mathrm{Mn^{3+}_{aq} \rightleftharpoons MnOH^{2+}_{aq} + H^+_{aq}}$$

$$\mathrm{HCOOH \rightleftharpoons HCOO^-_{aq} + H^+_{aq}}$$

$$\mathrm{Mn^{3+}_{aq} + HCOOH \rightleftharpoons MnHCOOH^{3+}_{aq}}$$

$$\mathrm{MnOH^{2+}_{aq} + HCOOH \rightleftharpoons MnHCOO^{2+}_{aq} + H_2O}$$

$$\mathrm{Mn^{3+}_{aq} + HCOO^-_{aq} \rightleftharpoons MnHCOO^{2+}_{aq}}$$

$$\mathrm{MnHCOOH^{3+}_{aq} \rightleftharpoons MnHCOO^{2+}_{aq} + H^+_{aq}}$$

$$\mathrm{MnHCOOH^{3+}_{aq} \xrightarrow{slow} Mn^{2+}_{aq} + H^+_{aq} + \cdot COOH}$$

$$\mathrm{MnHCOO^{2+}_{aq} \xrightarrow{slow} Mn^{2+}_{aq} + \cdot COOH}$$

$$\mathrm{Mn^{3+}_{aq} + \cdot COOH \xrightarrow{rapid} Mn^{2+}_{aq} + CO_2 + H^+_{aq}}$$

The dissociation of the intermediate complex of manganese (III) with formic acid is the rate-determining step. However, this reaction is very slow and thus its course can be monitored only at a 1000-fold excess of formic acid over manganese (III).

The oxidation of isobutyric acid with hexaquomanganese (III) ions can be described[96] by the mechanism

$$\mathrm{Mn^{3+}_{aq} + (CH_3)_2CHCOOH \rightarrow (CH_3)_2\overset{+}{C}HCOOH + Mn^{2+}_{aq}}$$

$$\mathrm{(CH_3)_2\overset{+}{C}HCOOH \rightarrow (CH_3)_2CH\cdot + CO_2 + H^+}$$

$$\mathrm{(CH_3)_2CH\cdot + Mn^{3+}_{aq} \rightarrow (CH_3)_2\overset{+}{C}H + Mn^{2+}_{aq}}$$

$$\mathrm{(CH_3)_2\overset{+}{C}H + H_2O \rightarrow (CH_3)_2CHOH + H^+}$$

In the presence of oxygen, further reactions occur:

$$\mathrm{(CH_3)_2CH\cdot + O_2 \rightarrow (CH_3)_2CHO_2\cdot}$$

$$\mathrm{2(CH_3)_2CHO_2\cdot \rightarrow 2(CH_3)_2CHO\cdot + O_2}$$

$$\mathrm{(CH_3)_2CHO\cdot + Mn^{3+}_{aq} \rightarrow (CH_3)_2CO + Mn^{2+} + H^+}$$

The ketone formed then undergoes further oxidation. In view of slow and nonstoichiometric reactions of simple carboxylic acids with various forms of tetravalent manganese, analytical applications are not practical. These substances often do not interfere in the determination of other compounds.[196]

7. *Oxidation of Polycarboxylic Acids*

Oxalic acid is oxidized quantitatively by the diphosphate complex of manganese (III) to carbon dioxide and water.[97,98] The reaction mechanism involves consecutive formation of a number of complexes of manganese (III) with oxalic acid, which dissociate in the rate-determining step to give a free radical.[50]

Unusual second order kinetics with respect to manganese (III) and pronounced retardation of the reaction by manganese (II) ions have been found[99] for the oxidation of malonic acid by this reagent. On the other hand, the oxidation of ethylmalonic and benzylmalonic acids is first order with respect to the concentration of manganese (III) and is not retarded by manganese (II). The oxidation of malonic acid by manganese (III) sulfate[36] follows the same kinetics. The following mechanism, where L is a bidentate ligand (sulfate or diphosphate) and Ma is malonic acid, is consistent with all the above findings:

$$\mathrm{Mn(III)L_3 + Ma \rightleftharpoons Mn(III)L_2Ma + L}$$

$$\mathrm{Mn(III)L_2Ma + Mn(III)L_3 \rightleftharpoons Mn(IV)L_2Ma + Mn(II)L_2 + L}$$

$$\mathrm{Mn(IV)L_2Ma + Mn(III)L_3 \rightarrow Mn(II)L_2 + Mn(III)L_3 + products}$$

$$\mathrm{Mn(IV)L_2Ma \rightarrow Mn(III)L_3 + R\cdot\ (radical\ of\ malonic\ acid)}$$

$$\mathrm{R\cdot + Mn(III)L_3 \xrightarrow{rapid} Mn(II)L_2 + products}$$

This mechanism also explains the observed fact that formic acid is formed in an inert atmosphere (through $CHOH[COOH]_2$ and CHO-COOH as intermediates), whereas malonic acid is completely oxidized to carbon dioxide and water in the presence of oxygen.

Higher dicarboxylic acids are virtually not oxidized by any form of manganese (III)

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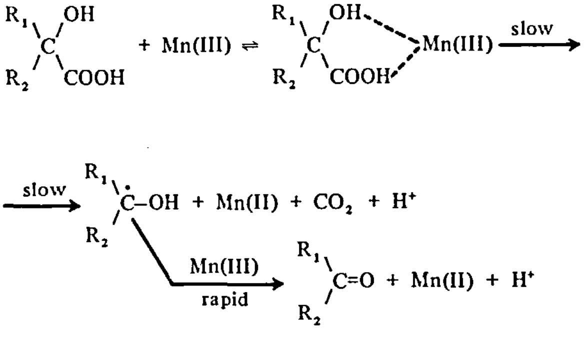
and thus it can be assumed that they will not interfere in the determination of other substances. Analytical use of the oxidation of oxalic and malonic acids is discussed in Section IV.C.2.

8. Oxidation of Unsaturated Carboxylic Acids

The diphosphate complex of manganese (III) does not perceptibly oxidize unsaturated carboxylic acids (maleic, fumaric, cinnamic).[66] Manganese (III) sulfate does oxidize maleic[103] and fumaric[104] acids, but the reaction rate is so slow that the reactions can only be monitored at an elevated temperature (70°C) and in the presence of large excesses of the substances to be oxidized. Hence, it may be assumed that these substances will not interfere in the analytical determination of other substances. Manganese (III) does not oxidize fumaric acid,[104] but oxidizes succinic acid which is formed by hydrolytic decomposition of fumaric acid.

9. Oxidation of α-Hydroxyacids, α-Ketoacids and Polyhydroxyacids

For the oxidation of α-hydroxyacids by the diphosphate complex of manganese (III)[105] and manganese (III) sulfate,[209] a mechanism has been proposed involving reversible formation of a cyclic complex of manganese (III) with the substance to be oxidized. This complex dissociates in the rate-determining step with formation of a free radical that is immediately oxidized further to the corresponding carbonyl compound which, in turn, is subject to further oxidation. This mechanism can be described by the equations



As the formation of a complex of manganese (III) with the substance to be oxidized requires displacement of one of the ligands forming the complex with manganese (III), an increasing concentration of complexing substance leads to a decrease in the reaction rate. The nature of substituents R_1 and R_2 affects the stability of the free radical formed (H << Me << Ph) and thus also the reaction rate and determines the mechanism of the further oxidation of the carbonyl compound formed. For tartaric acid, Waters[105] assumes that the subsequent oxidation of the carbonyl compound formed follows the scheme

$$\mathrm{HOOC{-}CHOH{-}CHO} \xrightarrow{2\,\mathrm{Mn(III)}} \mathrm{HO{-}CH(COOH)_2} \xrightarrow{4\,\mathrm{Mn(III)}}$$
$$\longrightarrow \mathrm{CO_2} + 2\mathrm{HCOOH} + \mathrm{H_2O}$$

however, it has been shown more recently[106] that this further oxidation is actually

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$$\text{HOOC–CHOH–CHO} \xrightarrow{2\ \text{Mn(III)}} \text{CO}_2 + \text{OCH–CHO} \xrightarrow{2\ \text{Mn(III)}}$$

$$\longrightarrow 2\ \text{HCOOH}$$

It is assumed for succinic acid[105] that further oxidation involves the following mechanism:

$$\text{HOOC–CH}_2\text{–CHO} \xrightarrow{2\ \text{Mn(III)}} \text{HOOC–CHOH–CHO} \xrightarrow{6\ \text{Mn(III)}}$$

$$\longrightarrow 2\ \text{CO}_2 + \text{HCOOH} + \text{H}_2\text{O}$$

whereas, with citric acid, the *β*-ketoglutaric acid formed is oxidized according to the equation[109]

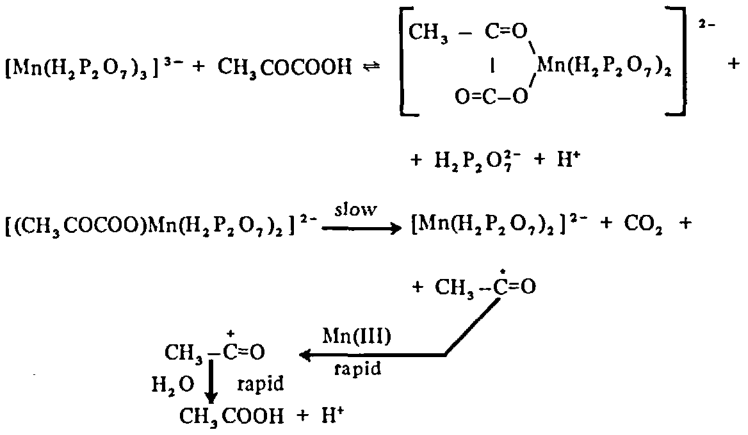
$$\text{OC(CH}_2\text{COOH)}_2 + 12\ \text{Mn}^{3+} + 5\text{H}_2\text{O} \rightarrow 2\text{HCOOH} + 3\text{CO}_2 +$$

$$12\text{Mn}^{2+} + 12\text{H}^+$$

It has been confirmed that benzaldehyde formed by the reaction of mandelic[107] and isopropylmandelic[108] acids is not oxidized further, as it cannot form the enol.

The retardation of the reaction by manganese (II) ions observed can be explained by the assumption that *α*-hydroxyacids can also form complexes with manganese (II) with a consequent decrease in the concentration of free *α*-hydroxyacid, which is the only substance capable of oxidation.

Pyruvic acid[81] is quantitatively oxidized by the diphosphate complex on manganese (III) to carbon dioxide and acetic acid. On the basis of a detailed kinetic analysis, the following mechanism has been proposed for this reaction:



$$[\text{Mn(H}_2\text{P}_2\text{O}_7)_3]^{3-} + \text{CH}_3\text{COCOOH} \rightleftharpoons \left[\begin{array}{l}\text{CH}_3 - \text{C=O} \\ \quad\ \ | \qquad \text{Mn(H}_2\text{P}_2\text{O}_7)_2 \\ \ \ \text{O=C–O}\end{array}\right]^{2-} + \text{H}_2\text{P}_2\text{O}_7^{2-} + \text{H}^+$$

$$[(\text{CH}_3\text{COCOO})\text{Mn(H}_2\text{P}_2\text{O}_7)_2]^{2-} \xrightarrow{\text{slow}} [\text{Mn(H}_2\text{P}_2\text{O}_7)_2]^{2-} + \text{CO}_2 + \text{CH}_3\text{–}\dot{\text{C}}\text{=O}$$

$$\text{CH}_3\text{–}\dot{\text{C}}\text{=O} \xrightarrow[\text{rapid}]{\text{Mn(III)}} \text{CH}_3\text{–}\overset{+}{\text{C}}\text{=O} \xrightarrow[\text{rapid}]{\text{H}_2\text{O}} \text{CH}_3\text{COOH} + \text{H}^+$$

The observed limiting retardation of the reaction by manganese (II) ions was considered anomalous by the authors and was not included in the reaction mechanism.

The oxidation of citric[109] and tartaric[106] acids by manganic sulfate and by hexaquomanganese (III) ions in noncomplexing perchloric acid media and of lactic, mandelic[111] and citric[210] acids by manganese (III) acetate is analogous to the oxidation by the manganese (III) diphosphate complex. It has been shown[106,109] that the free radicals formed during the oxidation of these acids react with oxygen dissolved in the reaction mixture,

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leading to decreased consumption of the oxidant and consequent nonstoichiometry of the reaction; hence empirical oxidation equivalents must be used.[97]

On the other hand, it is evident that a systematic study of the oxidation of various α-hydroxyacids and α-ketoacids in an inert atmosphere can lead to successful determination methods. The study of the kinetics and mechanism of these reactions then enables simplification and shortening of many determinations that have been tedious and often poorly reproducible. Especially, manganese (III) in noncomplexing perchloric acid medium appears to be a promising oxidant for these purposes.

10. Oxidation of Peroxo-compounds

The oxidation of hydrogen peroxide by hexaquomanganese (III) ions was studied by Wells and Mays,[63] who proposed a mechanism involving reversible formation of a complex of manganese (III) with hydrogen peroxide of the type $[\mathrm{Mn}^{3+}\mathrm{HO}^{-}_{2aq}]$ that is decomposed in the rate-determining step with formation of a free radical of the $\cdot\mathrm{HO_2}$ type. This radical is immediately oxidized further to molecular oxygen. In constrast, Davies and co-workers[64] proposed a mechanism whose first step is reversible oxidation of hydrogen peroxide to a free radical of the $\cdot\mathrm{HO_2}$ or $\cdot\mathrm{H_2O_2^+}$ type and which does not assume formation of a manganese (III) complex with hydrogen peroxide as a reaction intermediate.

The oxidation of dicumyl peroxide and tertbutyl peroxide[116] by hexaquomanganese (III) ions has been studied from the analytical point of view, as well as the oxidation of hydrogen peroxide by the other forms of trivalent manganese discussed (see Section IV, C, 2.).

11. Oxidation of Nitrogen-Containing Compounds

The kinetics have been studied and a mechanism proposed for the oxidation of hydrazine by the diphosphate complex of manganese (III),[115] involving both a single-electron and a four-electron reaction. In strongly acidic media the reagent consumption approaches one equivalent, whereas at pH values around seven it is close to four equivalents per mole of hydrazine. This observation has been explained by protonation of nitrogen atoms in acidic media, thus favoring the single-electron reaction.

The oxidation of hydrazine by the phosphate complex of manganese (III)[117] was studied from the analytical point of view and the mechanism of the hydrazine reaction with manganese (III) acetate[118] was investigated in connection with the study of hydrazine oxidation by permanganate. In both cases a dependence of the oxidant consumption on the medium acidity was observed.

The following mechanism has been proposed for the oxidation of hydrazine and its methyl derivatives by hexaquomanganese (III) ions[119]

$$\mathrm{Mn^{3+}_{aq}} \rightleftharpoons \mathrm{Mn^{2+}_{aq}} + \mathrm{H^{+}_{aq}}$$

$$\mathrm{Mn^{3+}_{aq}} + \mathrm{BH_2^{+}} \rightarrow \mathrm{BH}\cdot + \mathrm{Mn^{2+}_{aq}} + \mathrm{H^{+}_{aq}}$$

$$\mathrm{MnOH^{2+}_{aq}} + \mathrm{BH_2^{+}} \rightarrow \mathrm{BH}\cdot + \mathrm{Mn^{2+}_{aq}}$$

where $\mathrm{BH_2^+}$ is the protonated form of the given hydrazine derivative and $\mathrm{BH}\cdot$ is a free radical undergoing a sequence of further reactions; the oxidant consumption again varies in dependence on the reaction conditions.

The mechanism of the oxidation of hydroxylamine by the phosphate complex of manganese (III)[120] strongly depends on the acidity of the medium. In weakly acidic media, the reaction

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$$2\,\mathrm{Mn(III)} + 2\mathrm{NH_2OH} \rightarrow 2\,\mathrm{Mn(II)} + \mathrm{N_2} + 2\mathrm{H_2O} + 2\mathrm{H^+}$$

predominates. With increasing acidity, the reactions

$$4\,\mathrm{Mn(III)} + 2\mathrm{NH_2OH} \rightarrow 4\mathrm{Mn(II)} + \mathrm{N_2O} + \mathrm{H_2O} + 4\mathrm{H^+}$$

$$6\,\mathrm{Mn(III)} + \mathrm{NH_2OH} + 2\mathrm{H_2O} \rightarrow 6\mathrm{Mn(II)} + \mathrm{HNO_3} + 6\mathrm{H^+}$$

play a progressively more important role. The mechanism

$$\mathrm{Mn^{3+}_{aq}} \rightleftharpoons \mathrm{MnOH^{2+}_{aq}} + \mathrm{H^+_{aq}}$$

$$\mathrm{Mn^{3+}_{aq}} + \mathrm{NH_3OH^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{NH_2O\cdot} + 2\mathrm{H^+}$$

$$\mathrm{MnOH^{2+}_{aq}} + \mathrm{NH_3OH^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{NH_2O\cdot} + \mathrm{H^+}$$

$$5\,\mathrm{Mn(III)} + 2\mathrm{H_2O} + \mathrm{NH_2O\cdot} \xrightarrow{\text{rapid}} 5\,\mathrm{Mn(II)} + \mathrm{NO_3^-} + 6\mathrm{H^+}$$

has been proposed[62] for the oxidation of hydroxylamine by hexaquomanganese (III) ions. On the other hand, the oxidation of *o*-methylhydroxylamine[62] obeys the mechanism

$$\mathrm{Mn^{3+}_{aq}} + \mathrm{NH_3OCH_3^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \cdot\mathrm{NHOCH_3} + 2\mathrm{H^+}$$

$$\mathrm{MnOH^{2+}_{aq}} + \mathrm{NH_3OCH_3^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \cdot\mathrm{NHOCH_3} + \mathrm{H_3O^+}$$

$$2\,\cdot\mathrm{NHOCH_3} \xrightarrow{\text{rapid}} \mathrm{N_2H_2(OCH_3)_2}$$

However, the oxidant consumption is dependent on the reaction conditions.

The oxidative dealkylation of various N-dialkylderivatives of aniline by the effect of manganese (III) acetate was studied from the preparative point of view.[196]

12. Oxidation of Sulfur-Containing Substances

Thiourea and its derivatives are quantitatively oxidized by manganese (III) sulfate to the corresponding disulfides, with exchange of one electron.[121] The oxidation of thiourea and its derivatives by hexaquomanganese (III) ions follows the mechanism[122]

$$\mathrm{Mn^{3+}_{aq}} \rightarrow \mathrm{MnOH^{2+}_{aq}} + \mathrm{H^+_{aq}}$$

$$\mathrm{TH^+} \rightarrow \mathrm{T} + \mathrm{H^+_{aq}}$$

$$\mathrm{Mn^{3+}_{aq}} + \mathrm{TH^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{X\cdot} + 2\mathrm{H^+}$$

$$\mathrm{MnOH^{2+}_{aq}} + \mathrm{TH^+} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{X\cdot} + \mathrm{H^+}$$

$$\mathrm{Mn^{3+}_{aq}} + \mathrm{T} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{X\cdot} + \mathrm{H^+}$$

$$\mathrm{MnOH^{2+}_{aq}} + \mathrm{T} \rightarrow \mathrm{Mn^{2+}_{aq}} + \mathrm{X\cdot}$$

$$2\,\mathrm{X\cdot} \xrightarrow{\text{rapid}} \mathrm{X_2}$$

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where T is a thiourea derivative of the $R_2N_2H_2CS$ type, $X\cdot$ is a free radical of the $R_2N_2HCS\cdot$ type and X_2 is a disulfidic compound of the $R_4N_4H_2C_2S_2$ type. The overall reaction stoichiometry can thus be expressed by the equation

$$2\,\mathrm{Mn(III)} + 2\,R_2N_2H_2CS \rightarrow 2\,\mathrm{Mn(II)} + R_4N_4H_2C_2S_2 + 2\,H^+$$

IV. THE USE OF VARIOUS FORMS OF TRIVALENT MANGANESE AS REDOX REAGENTS

The use of compounds of manganese (III) has already been discussed,[49] but new information in this area broadens the approach and frequently can provide conditions for further analytical applications of these compounds.[65] To renew the evaluation of the compounds of manganese (III) as oxidizing agents, it is necessary to consider newly developed methods for rapid and simple preparation of standard solutions using generally available chemicals, knowledge of the stability of solutions of various forms of manganese (III), standardization of individual forms, and knowledge of the oxidizing effect under various reaction conditions. Changes of the reaction conditions and choice of suitable forms of manganese (III) can affect not only the rate of the particular redox reactions but also their stoichiometry. Certain forms of manganese (III) are better suited for work on a semimicro scale (diphosphate and phosphate complexes of manganese (III) or manganese (III) sulfate) and others for work on a micro scale (hexaquomanganese (III) ions in a noncomplexing medium of perchloric acid).

The stability of solutions of various compounds of manganese (III), which changes because of the dependence on the stability of the complex employed, on the concentration of complexing agent, on the concentration of Mn(II) and Mn(III), and on the acidity of the medium, is sufficient under suitable conditions for direct and indirect determinations.

A. The Preparation and Stability of Standard Solutions

As the stability of solutions of manganese (III) is adversely affected by disproportionation,

$$2\,\mathrm{Mn}^{3+} + 3\,H_2O \rightleftharpoons \mathrm{Mn}^{2+} + \mathrm{MnO(OH)}_2 + 4\,H^+$$

manganese (III) is maintained in solution in the form of stable complexes, where the stability in solution increases with increasing concentration of hydrogen ions and manganese (II) ions.

Suitable complexing agents are diphosphates,[1,3,17,19,102,112-114,124-127] phosphates,[10,23,24,128-136] fluorides,[8,29,30,137] sulfuric acid,[11,34,39,102,110,138-145,160] acetic acid,[47,111] and various polyaminocarboxylic acids;[146-155] stabilization with excess divalent manganese or hydrogen ions is used for hexaquomanganese (III) ions in the noncomplexing medium of perchloric acid.[43,45,60,102,156]

Preparation procedures for solutions of various forms of manganese (III) can be divided into three groups: methods based on chemical oxidation of manganese (II) by reagents with sufficiently high redox potentials, methods based on electrochemical oxidation of manganese (II), and methods based on dissolution of various solid compounds of manganese (III).

In the preparation of the diphosphate complex, manganese (III) was oxidized using bromate,[3] permanganate,[102,112,113,114,127] dichromate,[157] ozone,[1] perchloric acid,[114] lead dioxide,[17] or manganese dioxide.[126] In the preparation of the phosphate complex, permanganate,[23,129,136] dichromate,[130,131,133] bromate,[10,128,133] bismuthate,[133] periodate,[133] manganese dioxide,[158] and perchloric acid[159] were employed. In the preparation of

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manganese (III) sulfate, permanganate,[34,102,138] dichromate,[144] peroxodisulfate,[160] and caric salt[110,145] were used. Permanganate was used in the preparation of the fluoride complex,[29,30,137] manganic acetate[111] and manganese (III) in the noncomplexing medium of perchloric acid.[45,102,156,211] Chemical oxidation was also used in the preparation of complexes of manganese (III) with polyaminocarboxylic acids.[145-155]

In the study of the oxidation properties of the discussed reagents it is preferable to use permanganate in their preparation, as the presence of other ions could affect the course of the studied reactions.

Electrochemical oxidation was used in the preparation of the diphosphate,[19] phosphate,[134,135,161] and fluoride complexes and also the sulfate[11,39,139-143,162-164] and acetate[47,165] of manganese (III), and manganese (III) in perchloric acid.[15,43,44] Optimum conditions for the electrochemical generation of the above forms of manganese, especially the acidity, concentration of complexing agent, the concentration of divalent manganese and the current density are discussed in the works.[8,11,19,43,134,135] Generation of manganese (III) in a sulfuric acid medium[11] can optimally be carried out in a medium of 2 to 7*M* sulfuric acid, 0.2*M* manganese (II) sulfate and at a current density on a platinum electrode (anode) of 1 to 4 mA/cm^2. On the micro scale,[143] 0.06*M* manganese (II) sulfate was used. For diphosphate,[19] constant potential coulometry in 0.25*M* sodium diphosphate at pH 2 has been described. In acetic acid,[165] 0.6*M* manganese (II) acetate or nitrate is used at a current density of 0.75 to 7.5 mA/cm^2. It has been recommended that the fluoride complex[8] be prepared using 0.5*M* potassium fluoride, at least 1*M* sulfuric acid and a current density of 10 mA/cm^2. In phosphoric acid,[135] the authors recommended a medium of 1.5 to 7.5*M* H_3PO_4 and 0.1*M* $Mn(ClO_4)_2$ at a current density of 0.4 mA/cm^2 at a platinum electrode.

The third group of methods for preparation of solutions of manganese (III) includes dissolution of manganese (III) phosphate in a hot acidified solution of diphosphate[3,125] to produce the diphosphate complex and dissolution of the oxide[24] or acetate[132] of manganese (III) in concentrated phosphoric acid to yield the phosphate complex of manganese (III).

In addition, the production of compounds of manganese (III) through reduction of permanganate with hydrogen peroxide[166] and through the electrochemical reduction of manganese (IV) or (VII)[60] and the formation of a number of complexes of manganese (III) during addition of complexing agents to a solution of hexaquomanganese (III) ions[60] have been described.

All these principles can be employed in the preparation of standard solutions. A 0.03 to 0.05 *M* standard solution of the diphosphate complex of manganese (III) can be prepared by potentiometric titration of manganese (II) with permanganate in a diphosphate medium of pH 6,[112,127] by oxidation of manganese (II) with permanganate in potassium diphosphate and sulfuric acid[124] or through dissolution of manganese (III) phosphate, prepared by heating manganese (II) chloride with concentrated phosphoric and nitric acids in a hot acidified solution of potassium diphosphate.[125] It is always necessary to adjust the pH of the prepared solution to a value of 6, at which this solution is most stable so that its titer does not change for 3 to 4 weeks. In contrast, in a medium of pH 1 to 2 a precipitate is formed after several hours, whose elemental composition corresponds to $NaMn(HPO_4)_2$.[66]

In a medium of 0.25 to 4 *M* sulfuric acid, in which most indirect determinations with this reagent are carried out, a 0.01*N* solution of this complex can readily be prepared by addition of the necessary amount of permanganate to a solution of manganese (II) and diphosphate in sulfuric acid of a suitable molarity.[102] The titer of a solution prepared in this way, determined reductometrically does not change over 24 hr; however, it has been shown spectrophotometrically that manganese (III) is gradu-

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ally converted from the diphosphate complex to the sulfate complex, so that the reagent should be prepared fresh daily.

A standard solution of the phosphate complex of manganese (III) can be prepared by oxidation of manganese (II) with bromate,[10] permanganate,[136] or manganese dioxide[158] at elevated temperature in concentrated phosphoric acid, in which its titer is constant for about 1 week. In contrast, with a decrease in the concentration of phosphoric acid, the poorly soluble manganese (III) phosphate is precipitated after a short time.

Oxidation of manganese (II) with permanganate in a medium of sulfuric acid can be used for preparing standard solutions of manganic sulfate[34,102,138] and a standard solution of the hexaquomanganese (III) ions in perchloric acid.[102,156] The stability of these standard solutions increases with increasing acidity and concentration of manganese (II), and decreases with increasing concentration of manganese (III) and with increasing temperature.[102] The cited work[102] also specifies acidity and temperature conditions under which various concentrations of this reagent are sufficiently stable for indirect determinations. For example, the titer of a $0.01\,N$ standard solution of manganese (III) sulfate in a medium of $0.1\,M$ manganese (II) sulfate does not change over 10 days in a $6M$ sulfuric acid medium, over 5 days in a $4M$ sulfuric acid medium and over 2 days in a $2M$ sulfuric acid medium by a value of greater than 2.5%. In $4M$ sulfuric acid the titer of a $0.01\,N$ solution decreases after 10 days by 7% in $0.025M$ manganese (II) sulfate and only by 0.2% in $0.2M$ manganese (II) sulfate. A $0.01\,N$ solution of this reagent in $4M$ sulfuric acid and $0.1\,N$ manganese (II) sulfate can be used for indirect determinations at a temperature of 60°C, where its titer decreases by 1.1% after 8 hr, while at 80°C manganese dioxide is precipitated after 1 hr.

A $0.005N$ standard solution of hexaquomanganese (III) ions in $6M$ perchloric acid and $0.4M$ manganese (II) perchlorate can be used for indirect determinations at a temperature of 40°C, where its titer changes by 3% in 6 hr. At 50°C manganese dioxide is precipitated after 15 min. The titer of a $0.01\,N$ solution in $6M$ perchloric acid and $0.4M$ manganese (II) perchlorate decreases by 1% in 12 hr and after 24 hr manganese dioxide is precipiated out. Consequently, this reagent must be prepared the same day as it is used.

So far no information has been published on the stability of a standard solution of manganese (III) acetate, which can be prepared by oxidation of manganese (II) with permanganate in a medium of concentrated acetic acid;[111] however, it follows from this work[111] that its stability is sufficient under suitable conditions for indirect determinations.

Solutions in which manganese (III) is present in other forms have not yet been used for titrations.

B. Determination of the Titer and Indication of the Titration End-Point

The titer of the prepared solutions should be checked daily; however, this determination is very simple and undemanding.

The titer of a standard solution of the diphosphate complex of manganese (III) is found using a ferrous salt[124] or hydroquinone[124,126] potentiometrically or with diphenylamine as an indicator. Similarly, a standard solution of arsenite[167] can be used as a primary standard.

The titer of the phosphate complex of manganese (III) is found using ferrous salts[10,136] or hydroquinone.[10,117]

The titer of a standard solution of manganese (III) sulfate can be found using a ferrous salt,[34] hydroquinone,[169] or arsenite.[170]

The titer of a standard solution of hexaquomanganese (III) ions is then found using ferrous sulfate,[156,171] ferrous chloride,[172] hydroquinone,[171] or potassium iodide[172] as primary standard.

The titer of manganese (III) acetate can be determined by amperometric titration with a standard solution of oxalic acid[47] or iodometrically.[111]

An excess of all these reagents in indirect determinations can be back-titrated using ferrous sulfate[173] or chloride.[174] Iodometry is used for the diphosphate complex,[66] manganese (III) acetate,[111,175] and the phosphate complex.[176] The concentration of manganese (III) in perchloric acid can be determined either spectrophotometrically in the UV region[60] or by adding an excess of iron (II) and determining the iron (III) produced spectrophotometrically in the UV region.[15]

The end point in titrations with the reagents mentioned can be detected electrometrically or visually. Titration with the diphosphate complexes is carried out using diphenylamine or diphenylamine sulfonic acid[124] and also potentiometrically[124] and biamperometrically.[21]

Titrations with manganese (III) sulfate can be indicated visually using ferroin or *N*-phenylanthranilic acid;[170] among the electrometric methods, potentiometry,[140,170,177,178] conductometry,[179] amperometry,[46] and biamperometry[21] are employed. In some titrations with the above reagents, the end point can be determined by observing the coloring of the solution by excess reagent.[34,167]

The end point in titrations with the phosphate complex, manganese (III) acetate and hexaquomanganese (III) ions can most frequently be determined potentiometrically or amperometrically.[47]

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C. Survey of Determination Methods

Inorganic and organic substances can be determined on the basis of their oxidation by compounds of manganese (III) using direct titration with suitable standard solutions or with coulometrically generated reagents and through indirect determinations.

1. Determination of Inorganic Substances

a. Iron

Ferrous salts can be oxidized to ferric ones using the diphosphate complex of manganese (III),[124,125,127,180] the phosphate complex,[10,181-184] manganese (III) sulfate,[14,34,138,169,170,177] hexaquomanganese (III) ions,[43,174] or by generating manganese (III) coulometrically,[134,135,139,140,143,185-188] although some authors[186-188,190] wrongly[11] suggested that this titration involves generation of permanganate.

It is important to note that the ferrous salt can be titrated with manganese (III) — but not with permanganate — in the presence of chlorides.[34] For example, Fe(II) was titrated with the diphosphate complex of manganese (III) using barium diphenylaminesulfonate as an indicator in 5*N* hydrochloric acid.[125] The same reagent was used for the titration of ferrous ions in a medium of concentrated hydrochloric acid.[180] When manganese (III) sulfate is used in a medium of 2*N* sulfuric acid, the end-point can be indicated with ferroin or phenylanthranilic acid as an indicator or potentiometrically using a platinum indicator and saturated calomel reference electodes.[169] Manganese (III) sulfate can be used for titration of ferrous ions in a medium of 1 to 2*N* hydrochloric acid,[170] where iodochloride is used as a catalyst. Here the end point can be indicated visually by using a chloroform layer whose purple color resulting from the presence of free elemental iodine turns pure yellow at the end point as a result of the presence of iodochloride alone. Iron oxides in slags can be determined[181] by oxidizing with an excess of the phosphate complex of manganese (III) and back-titrating with ferrous ammonium sulfate. Compounds of manganese (III) can also be used for the indirect photometric determination of iron on the basis of a decrease in the absorbance after addition of reducing substances.[14] This principle was also employed in the analysis of a mixture of iron, manganese, and zinc oxides[184] and in the analysis of ferrates.[182,183] A nanogram of iron (II) can be determined using a special ultramicro apparatus[143] and coulometric reagent determination with potentiometric end-point determination.

b. Arsenic, Antimony, Tin

The diphosphate and phosphate complexes of manganese (III) have been used for titration of the following ions: arsenic,[10,125,158,167] antimony,[10,167] and tin (II).[10,167] These ions were also titrated with manganese (III) sulfate[177] and coulometrically generated manganese (III),[186,187] which the authors wrongly thought to be permanganate. It has been recommended[167] that the diphosphate complex be used in a medium of 2 to $3N$ hydrochloric acid for the determination of As(III), 1.3 to $1.5N$ hydrochloric acid or $2N$ sulfuric acid for Sb(III) and $3N$ hydrochloric acid for Sn(II). Using manganese (III) sulfate and potentiometric indication a precision of 0.1% was attained,[177] the titration reaction with As(III) being catalyzed by KBr.

c. Other Inorganic Substances

Standard solutions of the diphosphate complex of manganese (III) have also been used for the determination of V(II),[125,127] Mo(III),[127] Ti(III),[127] nitrous acid[125] and hydrogen peroxide.[125,167] V(II) can be determined through its oxidation to V(IV) or V(V), similar to the oxidation of Mo(III) to Mo(V) or Mo(VI). Because direct titration of hydrogen peroxide[125] does not yield satisfactory results, it should be oxidized with excess reagent in $3N$ hydrochloric acid, followed by back-titration with ferrous sulfate.[167]

The phosphate complex of manganese (III) was also used for determining Cr(II), Mo(II), W(II),[10] and also iodide,[10] nitrites[158] and phosphites,[158] hydrazine[117] and for the coulometric titration of V(IV).[161]

Manganic sulfate can be used to determine V(II),[34,189] Mo(IV),[178] $[Fe(CN)_6]^{4-}$,[46,169,177,179] nitrites,[34] iodides,[169] and hydrogen peroxide.[34,169,191] Coulometrically generated manganese (III) sulfate was used to determine $[Fe(CN)_6]^{4-}$,[192] Nb,[162] Sn(II),[186] Sb(II),[186] As(III),[187] iodide,[192] and hydrogen peroxide. Nitrites[164] were determined by oxidation with coulometrically generated excess manganese (III) sulfate; excess reagent was back-titrated with coulometrically generated divalent iron.

Hexaquomanganese (III) ions can be used for direct titration of iodides.[172,174] The titration is best carried out in a medium of $1M$ perchloric acid where the iodides are oxidized to elementary iodine and a $5\times10^{-4}N$ solution of hexaquomanganese (III) ions can be used for potentiometric titration; the potential change at the equivalence point is about 50mV/0.02 mℓ reagent.

In conclusion, it should be noted that the use of complexed forms of manganese (III) in inorganic analysis is limited to titration of systems with relatively low formal redox potentials, where other oxidation reagents can also be used. The more reactive hexaquomanganese (III) ions in perchloric acid have so far been used more for kinetic studies; however, use of this reagent for the microdetermination of some inorganic substances is also promising.[174]

From an analytical point of view, the reactions of various forms of manganese (III) with organic substances, where a certain selectivity compared with permanganate can be observed and where the different reactivity of the mentioned reagents can be used advantageously, is more interesting.

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TABLE I

Survey of the Use of Manganese (III) Compounds for the Determination of Inorganic Substances

Substance determined	Medium	Comments	Ref.
	Use of the Diphosphate Complex of Manganese (III)		
Fe(II)	Acidified with H_2SO_4 or HCl	Mohr salt used for titer determination	124,127
Fe(II)	Also in 5*N* HCl	Indication with barium diphenylamine sulfonate	125
Fe(II)	10% H_3PO_4	Indication with barium diphenylamine sulfonate	125
Fe(II)	Conc HCl	In presence of Sb(III), As(III), Sn(III)	180
V(V)	Reduced with excess Fe(II)	Titrate unconsumed Fe(II)	125
As(III)	2—3*N* HCl	KIO_3 as catalyst	167
As(III)	Acidified with H_3PO_4	Indication with barium diphenylamine sulfonate, OsO_2 catalyst or indirectly iodometrically	125
Sb(III)	1.3—1.5*N* HCl or 2*N* H_2SO_4		167
Sn(II)	3*N* HCl		167
V(II)		Oxidation to V(IV) or V(V)	127
Mo(III)		Oxidation to Mo(V) or Mo(VI)	127
Ti(III)			127
Nitrite	Acidified with H_3PO_4	Titrate reagent with sample	127
Hydrogen peroxide	3*N* HCl	Indirect, back-titration with Fe(II)	167
	The Use of Manganese (III) Sulfate		
Fe(II)		In the presence of Cl^-	34
Fe(II)		Potentiometrically	138

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Fe(II)	$2N$ H_2SO_4	Indicated with ferroin or phenylanthranilic acid or potentiometrically	169,177
Fe(II)		Spectrophotometrically, decrease in absorbance of Mn(III) at 525nm	14
Fe(II)	2—$7M$ H_2SO_4	Coulometrically	140,185-187
Fe(II)	4—$10N$ H_2SO_4	Coulometrically, indication amperometrically	188
Fe(II)		Coulometric ultramicro method	143
Fe(II)	1—$2N$ HCl	ICl catalyst, indication in the chloroform layer	170
Sb(III)	$0.6N$ and more conc HCl		177
Sb(III)		Coulometry	186
As(III)		KBr catalyst	177
As(III)	Acidified with H_2SO_4	Coulometry	187
Sn(II)		Coulometry	186
V(II)		Potentiometrically 45—50°C	34,189
Mo(IV)		Potentiometrically	178
$[Fe(CN)_6]^{4-}$	$2N$ H_2SO_4	Ferroin or phenylanthranilic acid indicator or potentiometrically	46,169,177,179
Nitrites			34
Iodides	Acidified with H_2SO_4		169
Hydrogen	$3.6N$ and more	Potentiometrically	34,169
Peroxide	Conc H_2SO_4	Coulometrically	191,193
Nb	$6N$ H_2SO_4	Coulometrically potentiometric indication, reduction with zinc amalgam	162
$[Fe(CH)_6]^{4-}$	6—$8N$ H_2SO_4	Coulometrically, potentiometric indication	192
Nitrites	4 N H_2SO_4	Coulometric generation of Mn(III) and coulometric back-titration with Fe(II) and potentiometric indication	164

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TABLE 1 (continued)

Survey of the Use of Manganese (III) Compounds for the Determination of Inorganic Substances

Substances determined	Medium	Comments	Ref.
	Use of the Phosphate Complex of Manganese (III)		
Fe(II)	0.04—4.5 *N* HCl; 0.04—8.0 *N* H_2SO_4	Potentiometric	10
Fe(II)		Iron oxides in slags, excess reagent back-titrated with Fe(II)	181
Fe(II)		Analysis of ferrites, spectrophotometric	182,183
Fe(II)		Mixture of Fe, Mn and Zn oxides, spectrophotometric	184
Fe(II)	H_3PO_4; H_3PO_4 + H_2SO_4	Coulometric	135
As(III)	1.5—5.0*N* HCl and H_2SO_4	Potentiometric	10,158
Sb(III)	3*N* HCl		10
Cr(II)	1—2*N* HCl	Potentiometric	10
Sn(II)	3—5*N* HCl	Potentiometric	10
Mo(III)	3*N* HCl	Potentiometric	10
W(III)	HCl	Potentiometric	10
V(II)	3*N* HCl	Potentiometric back-titration with Fe(II)	10
V(IV)	1*M* H_3PO_4	Coulometric	161
Iodide	1.5*N* HCl	Potentiometric	10
Nitrite		Oxidation to nitrate	158
Phosphite		Oxidation to phosphate	158
Hydrazine	1*N* H_2SO_4	Potentiometric	117
	Use of Manganese (III) in Noncomplexing Perchloric Acid Medium		
Fe(II)	0.25—6*M* $HClO_4$	Potentiometric	172,174
Iodide	1*M* $HClO_4$	Oxidation to I_2; potentiometric; down to 5×10^{-4}*N* solutions	172,174

2. Determinations of Organic Substances

a. Phenols and Polyphenols

All forms of manganese(III) can be used to oxidize hydroquinone to quinone with consumption of two equivalents of the reagent per mole of hydroquinone. The determination involves direct titration with the diphosphate complex of manganese (III) in a medium of 2 to 4*N* sulfuric or hydrochloric acid with potentiometric or visual end-point detection using diphenylamine.[194] In this way, 3 to 10 mg of the substance can be determined with an error of 0.2%. Hydroquinone can be titrated with manganese (III) sulfate in a medium of 1 to 2*N* hydrochloric acid with potentiometric or visual end-point detection, the latter using ferroin or *N*-phenylanthranilic acid as indicators.[169] Direct potentiometric titration with hexaquomanganese (III) ions in a medium of 6*N* perchloric acid can be used to determine 0.5 to 5.5 mg hydroquinone in 25 m*l* of solution.[195] This method is very simple, precise, and very reproducible and can also be used for microdeterminations.

Direct potentiometric titration of the phosphate complex of manganese (III) produced by oxidation of the manganese (II) salt with dichromate in 12*M* phosphoric acid[130] or of the analogously prepared diphosphate complex[127] can be used for determining the titer of 0.1*N* to 0.001*N* solutions of hydroquinone.

Compounds of manganese (III) can be used to oxidize *p*-aminophenol with exchange of two electrons to yield *p*-benzoquinoneimine.[117,195] This substance can also be determined by potentiometric titration with the phosphate complex of manganese (III) in a medium of concentrated phosphoric acid[117] and with a standard solution of hexaquomanganese (III) ions in a medium of 6*N* perchloric acid.[195] The latter method can be used to determine 0.7 to 7 mg of *p*-aminophenol with a precision of 0.2%.

Metol is oxidized by compounds of manganese (III) with exchange of two electrons to yield *N*-methyl-*p*-benzoquinoneimine.[117,195] Potentiometric titration with a standard solution of hexaquomanganese (III) ions in a medium of 6*N* perchloric acid can be used for determination of 0.8 to 8.6 mg metol.[195] The potentiometric titration of this substance with the phosphate complex of manganese (III) in a phosphoric acid medium has also been described.[117]

In contrast, the oxidation of resorcinol and floroglucine by hexaquomanganese (III) ions does not proceed stoichiometrically[195] and thus cannot be used analytically.

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b. Carboxylic Acids

Oxalic acid can be determined by direct potentiometric titration with the diphosphate complex of manganese (III) in 2*N* hydrochloric acid or in 3 to 6*N* sulfuric acid at 70°C.[167] This method is, however, not very reliable because of the limited stability of the reagent at elevated temperatures. Oxalic acid and oxalates can be titrated with manganese (III) sulfate in 8*N* sulfuric acid with potentiometric or visual end-point detection, the latter using ferroin or *N*-phenylanthranilic acid[34,169] as indicator. In the potentiometric titration of oxalic acid with hexaquomanganese (III) ions it is necessary to employ a medium of 6*N* perchloric acid at 80°C, where errors caused by reagent decomposition[171] become important. Indirect methods yield better results. In the use of the diphosphate complex, excess reagent was back-titrated ferrometrically after heating for 15 min in a boiling water bath.[97] Newer observations indicate, however, that reaction with excess reagent at laboratory temperature for 20 min is sufficient,[98] and that the back-titration can be carried out using hydroquinone and with diphenylamine as an indicator. When using manganese (III) sulfate,[139] excess reagent is employed in a medium of 3*M* sulfuric acid for a period of 30 min and potentiometric back-titration is carried out with a ferrous salt. Oxalic acid has also been determined indirectly using the phosphate complex of manganese (III) in a medium of concentrated phosphoric acid.[197] Using hexaquomanganese (III) ions, 1.5 to 6 mg of oxalic acid can be determined in such a way that an excess is allowed to react in 6*N* perchloric acid medium for a period of 5 min and then the unreacted reagent is determined ferrometrically.[171] Determination with manganese (III) acetate[175] is carried out by allowing an excess of this reagent to react in a medium of 9*N* acetic acid at 50°C and excess manganese (III) is determined iodometrically. Oxalic acid can also be determined by indirect coulometric titration with manganese (III) sulfate.[163] First, excess manganese (III) is generated in a medium of 0.2 *M* manganese (II) sulfate, 0.1*M* ferric sulfate and 6*N* sulfuric acid; after completion of the reaction, the unreacted portion is then back-titrated with electrogenerated iron (II) with opposite polarity of the generating electrodes.

Malonic acid can be determined indirectly with the diphosphate complex of manganese (III) at elevated temperatures;[97] it is, however, necessary to use an empirical oxidation equivalent. This substance can also be determined indirectly with manganese (III) acetate[175] by reaction with excess reagent at 50°C and determination of the unconsumed portion iodometrically.

c. α-Hydroxyacids and Polyhydroxyacids

An indirect determination of lactic acid involving its oxidation with excess manganese (III) sulfate in a medium of 15*N* sulfuric acid has been described;[200] the acetaldehyde produced must be continuously removed from the reaction mixture to prevent further oxidation. It has, however, been pointed out that the oxidation of lactic acid with the diphosphate complex of manganese (III) is not analytically useful.[198]

Mandelic acid is oxidized by compounds of manganese (III) to give benzaldehyde and carbon dioxide. The indirect determination of this substance is carried out by allowing excess diphosphate complex to react in a medium of 4*N* sulfuric acid for 12 hr and subsequent back-titration with a ferrous salt.[199] In this way, 15 to 50 mg of substance can be determined with a relative error of less than 1%. When using manganese (III) sulfate,[199] excess reagent is allowed to react in a medium of 2*N* sulfuric acid for 2 hr, followed by ferrometric back-titration. In this way, 1.5 to 4.5 mg of substance can be determined with a relative error of less than 1%. Mandelic acid can be determined on a microscale by oxidation with excess hexaquomanganese (III) ions in a medium of 6*N* perchloric acid.[156] The unreacted reagent is determined ferrometrically after 30 min. In this way 0.7 to 2 mg of the substance can be determined with a precision of better than 1%. Mandelic acid can be determined using manganese (III) acetate[175] by reaction with excess reagent in a medium of 9*N* acetic acid at 50°C and the unreacted reagent is determined iodometrically.

Manganese (III) acetate can be used to determine *p*-hydroxybenzoic acid[175] under the same conditions as those described for the determination of mandelic acid with this reagent.

Salicylic acid can be determined by oxidation with the diphosphate complex of manganese (III) at an elevated temperature;[97] however, the reaction does not proceed stoichiometrically, so that an empirical oxidation equivalent must be used.

The indirect determination of tartaric acid on the basis of its oxidation with excess diphosphate complex of manganese (III) at an elevated temperature[97] must also be carried out using an oxidation equivalent; it has, however, been reported that the oxidation of this substance with the phosphate complex of manganese (III) proceeds stoichiometrically.[197] The most recently published results indicate that the indirect determination of tartaric acid with manganese (III) sulfate or hexaquomanganese (III) ions must be carried out in the absence of oxygen to avoid errors caused by reaction of radical intermediates with atmospheric oxygen.[106] Amounts of 6 to 18 mg of tartaric

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acid can be determined by reaction with excess reagent at laboratory temperature in a medium of 4.8*M* sulfuric acid for 5 hr and 0.6 to 1.8 mg of this substance can be determined by reaction with an excess of hexaquomanganese (III) ions at 40°C in a medium of 4.8*M* perchloric acid for 90 min. The excess reagent is back-titrated in both cases ferrometrically.

Citric acid can be determined indirectly using the diphosphate complex of manganese (III) at an elevated temperature and using an empirical oxidation equivalent[97] or employing the phosphate complex of manganese (III).[197] Newer results[109] again indicate that citric acid can be determined using manganese (III) sulfate or hexaquomanganese (III) ions only in an inert atmosphere. An amount of 3 to 11 mg of citric acid can be determined using excess manganese (III) sulfate in a medium of 4.8*M* sulfuric acid for a reaction time of 20 min. 0.3 to 1.1 mg can be determined by reaction with excess hexaquomanganese (III) ions in 4.8*M* perchloric acid for 4 hr. Both reactions are carried out at laboratory temperature and excess reagent is back-titrated with ferrous salt. Citric acid can be determined indirectly using manganese (III) acetate[175] by reaction with excess reagent in a medium of 15*N* acetic acid at 50°C and back-titrated iodometrically.

It has been reported that ascorbic acid can be determined indirectly by potentiometric titration with the phosphate complex of manganese (III) in a medium of concentrated sulfuric acid.[117] Dehydroascorbic acid is produced in the oxidation, but the method does not yield reliable results as a result of subsequent oxidation of this substance. It is preferable to determine this substance directly by titration with a standard solution of manganese (III) sulfate in 4*M* sulfuric acid, where ascorbic acid is dissolved in 3 to 4*N* hydrochloric acid.[170] Iodochloride and chloroform are added to the reaction mixture and the end of the titration is indicated by the transition from the purple color of the chloroform to light yellow as a result of the disappearance of free iodine from solution.

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d. Organic Peroxides

Dicumyl peroxide and tertbutylcumyl peroxide are oxidized by hexaquomanganese (III) ions to oxygen and the corresponding alcohols.[116] Analytical application of this reaction involves a 5 min treatment with excess reagent in a mixed medium of water and acetone and determination of reagent excess ferrometrically.

e. Compounds Containing Nitrogen

Benzidine, *o,o′*-tolidine and *o,o′*-dianisidine are oxidized by compounds of manganese (III) to give the corresponding quinonediimine compounds.[201] These reactions have been used for direct potentiometric titration of the mentioned substances with standard solutions of the diphosphate complex of manganese (III) or manganese (III) sulfate and for indirect determination based either on potentiometric back-titration of excess trivalent manganese with ferrous sulfate or on visual titrations of the intensely colored quinonediimine produced with ascorbic acid after prior removal of excess oxidant. Similarly, the possibility of spectrophotometric determination of these substances based on measurement of the absorbance of the quinonediimine produced has been confirmed.

Direct potentiometric determination of these substances can be carried out in a medium of 4*N* hydrochloric acid; in the indirect determination the acidity of the medium is determined by the amount of acid contained in the oxidizing agent employed.

Determination of hydrazine and of the hydrazide of isonicotinic acid has been described based on direct potentiometric titration with a standard solution of the phosphate complex of manganese (III) in a phosphoric acid medium;[117] however, this

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TABLE 2

Survey of the Use of Manganese (III) Compounds for the Determination of Organic Substances

Substance determined	Oxidation products	Medium	Comments	Ref.
Use of the Diphosphate Complex of Manganese (III)				
Hydroquinone	Quinone	2—4N H_2SO_4 or HCl	Direct titration, potentiometric or visual with diphenylamine	194
Hydroquinone	Quinone	2N H_2SO_4	Titration of the diphosphate complex of Mn(III) is used for the determination of titer of hydroquinone	157
Oxalic acid	CO_2 and H_2O	2N H_2SO_4	Excess reagent back-titrated after 20 min with hydroquinone	98
Oxalic acid	CO_2 and H_2O	$Na_4P_2O_7$, pH = 6	Excess reagent determined after 15 min heating on a water-bath	97
Oxalic acid	CO_2 and H_2O	2N HCl or 3—6N H_2SO_4	Direct titration at 70°C	167
Malonic acid	Empirical oxidation equivalent 4.34 eq/mol	$Na_4P_2O_7$, pH = 6	Excess reagent determined after 15 min heating on a water-bath	97
Tartaric acid	Empirical oxidation equivalent 6.64 eq/mol	$Na_4P_2O_7$, pH = 6	Excess reagent determined after 15 min heating on a water-bath	97
Citric acid	Empirical oxidation equivalent 8.60 eq/mol	$Na_4P_2O_7$, pH = 6	Excess reagent determined after 15 min heating on a water-bath	97
Salicylic acid	Empirical oxidation equivalent 11.60 eq/mol	$Na_4P_2O_7$, pH = 6	Excess reagent determined after 15 min heating on a water-bath	97
Mandelic acid	C_6H_5CHO and CO_2	4N H_2SO_4	Excess reagent is determined ferrometrically after 12 hr	199
o,o'-Dianisidine	Dimethoxy-quinonediimine	0.3N HCl	Excess reagent is determined ferrometrically or the quinonediimine formed ascorbinometrically	201

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TABLE 2 (continued)

Survey of the Use of Manganese (III) Compounds for the Determination of Organic Substances

Substance determined	Oxidation products	Medium	Comments	Ref.
Use of the Phosphate Complex of Manganese (III)				
Hydroquinone	Quinone	$12M H_3PO_4$	Titration of the Mn(III) complex is used for the determination of the titer of hydroquinone	130
p-Amino-phenol	*p*-Benzo-quinoneimine	H_3PO_4	Aqueous solution of the substance is titrated by the reagent in conc H_3PO_4	117
Metol	*N*-methyl-*p*-benzoquinoneimine	H_3PO_4	Aqueous solution of the substance is titrated by the reagent in conc H_3PO_4	117
Oxalic acid	CO_2 and H_2O	H_3PO_4	Indirect determination	197
Tartaric acid	HCOOH, CO_2 and H_2O	H_3PO_4	Indirect determination	197
Citric acid	HCOOH, CO_2 and H_2O	H_3PO_4	Indirect determination	197
Ascorbic acid	Dehydroascorbic acid	H_3PO_4	Aqueous solution of the substance is titrated by the reagent in conc H_3PO_4	117
Isonicotinic acid hydrazide	Isonicotinic acid amide	H_3PO_4	Aqueous solution of the substance is titrated by the reagent in conc H_3PO_4	117
Hydrazine	N_2 and NH_3	H_3PO_4	Aqueous solution of the substance is titrated by the reagent in conc H_3PO_4	117
Hydroquinone	Quinone	$1—2N HCl$	Direct titration	169,170
Hydroquinone	Quinone	$6M H_2SO_4$	Titration with the reagent generated coulometrically	139
Oxalic acid	CO_2 and H_2O	$6N H_2SO_4$	Coulometrically generated Mn(III) back-titrated by generated Fe(II)	163
Oxalic acid	CO_2 and H_2O	H_2SO_4	Aqueous solution of the substance is titrated with the reagent in $8N$ H_2SO_4	34,169

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Oxalic acid	CO_2 and H_2O	3*M* H_2SO_4	Indirect determination	139
Ascorbic acid	Dehydroascorbic acid	3—4*N* HCl	Direct titration in the presence of ICl and chloroform	170
Formic acid	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Malonic acid	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Tartaric acid	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Ethyleneglycol	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Glycerine	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
D-mannitol	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Glucose	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Fructose	CO_2 and H_2O	15*N* H_2SO_4	Treatment with excess reagent at 60°C, with catalysis by Cr^{3+}	200
Lactic acid	CH_3CHO	15*N* H_2SO_4	Treatment with excess reagent; acetaldehyde formed removed continuously to prevent its further oxidation	200
Mandelic acid	C_6H_5CHO and H_2O	2*N* H_2SO_4	Excess reagent determined ferrometrically after 2 hr	139,199
Tartaric acid	HCOOH, CO_2 and H_2O	4—8*N* H_2SO_4	Excess reagent determined ferrometrically after 60 min; inert atmosphere	106
Citric acid	HCOOH, CO_2 and H_2O	4—8*N* H_2SO_4	Excess reagent determined ferrometrically after 30 min	109
Benzidine	Quinonediimine	3*N* HCl	Potentiometric	201
o,o'-Tolidine	Dimethylquinonediimine	3*N* HCl	Potentiometric	201
Thiourea and its derivatives	Disulfide	H_2SO_4 + KI	Visual with starch or poteniometric	121

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TABLE 2 (continued)

Survey of the Use of Manganese (III) Compounds for the Determination of Organic Substances

Substance determined	Oxidation products	Medium	Comments	Ref.
Use of Manganese (III) Acetate				
Oxalic acid	CO_2 and H_2O	9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
Malonic acid		9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
Citric acid		9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
Mandelic acid		9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
p-Hydroxybenzoic acid		9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
Pyruvic acid		9*N* CH_3COOH	Oxidation at 50°C, excess reagent determined iodometrically	175
Use of Manganese (III) in Non-complexing Perchloric Acid Medium				
Hydroquinone	Quinone	$HClO_4$	Aqueous solution of the substance is titrated by the reagent in 6*N* $HClO_4$	195
p-Aminophenol	*p*-Benzoquinone imine	$HClO_4$	Aqueous solution of the substance is titrated by the reagent in 6*N* $HClO_4$	195
Metol	*N*-methyl-*p*-benzoquinone-imine	$HClO_4$	Aqueous solution of the substance is titrated by the reagent in 6*N* $HClO_4$	195
Oxalic acid	CO_2 and H_2O	$HClO_4$	Aqueous solution of the substance is titrated by the reagent in 6*N* $HClO_4$ at 80°C	171
Oxalic acid	CO_2 and H_2O	3*N* $HClO_4$	Excess reagent is determined ferrometrically after 5 min	171

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TABLE 2 (continued)

Survey of the Use of Manganese (III) Compounds for the Determination of Organic Substances

Substance determined	Oxidation products	Medium	Comments	Ref.
		Use of the Diphosphate Complex of Manganese (III)		
Dicumylperoxide	O_2 and ROH	Mixture of H_2O and $(CH_3)_2CO$	Excess reagent is determined ferrometrically after 5 min	116
tert-Butyl peroxide	O_2 and ROH	Mixture of H_2O and $(CH_3)_2CO$	Excess reagent is determined ferrometrically after 5 min	116
Mandelic acid	C_6H_5CHO and CO_2	6*N* $HClO_4$	Excess reagent is determined ferrometrically after 30 min	156
Tartaric acid	HCOOH, CO_2 and H_2O	6*N* $HClO_4$ inert atmosphere	Excess reagent is determined ferrometrically after 60 min	106
Citric acid	HCOOH, CO_2 and H_2O	6*N* $HClO_4$ inert atmosphere	Excess reagent is determined ferrometrically after 4 hr	109

method does not yield very reliable results because of the possibility of side reactions (see Section III.B.11.). The oxidation of hydroxylamine and its derivatives by the phosphate complex of manganese (III) can also not be used for analytical purposes.[120]

f. Compounds Containing Sulfur

Amounts of 50 to 60 mg of thiourea and its alkyl, *o*-tolyl, *o*-methoxyphenyl, and *o*-ethoxyphenyl derivatives can be determined directly by potentiometric titration with a 0.05*N* solution of manganese (III) sulfate or by visual titration after addition of 2% KI and amylose as an indicator.[121] Oxidation of thiourea produces the corresponding disulfide.

CONCLUSIONS

It follows from this review that, because of their reactivity and stability, a number of compounds of manganese (III) are suitable for determination of a range of substances. The advantages depend on the different reactivity of the various forms of manganese (III), the possibility of affecting the reaction rate by changing the concentration of complexing agent and, with some forms (diphosphate or fluoride complexes) also the possibility of working in buffered media.

While the use of manganese (III) in inorganic analysis is practically limited to titrations of systems with relatively low redox potential values, its use in connection with organic substances is more interesting. In contrast to a number of reagents, whose application to organic substances frequently leads to complete oxidation to carbon dioxide and water, the compounds of manganese (III) react more selectively and less drastically. It is frequently possible to increase the selectivity of the determination by determining the amount of oxidation product formed rather than the amount of trivalent manganese consumed.

In indirect determinations it is frequently useful to use more reactive forms of manganese (III) and thus shorten the time necessary for quantitative completion of the reaction, whereas elsewhere it is more useful to employ less reactive forms of manganese (III), to avoid unwanted subsequent reactions connected with further oxidation of the substance being determined. The unreacted excess reagent can then be determined by titration, spectrophotometrically, or polarographically, enabling a marked increase in the sensitivity of the determination.

Recently, much simpler preparation of standard solutions of various forms of manganese (III) by chemical reactions together with the possibility of coulometric generation have been described, forming a basis for further development of the use of these oxidimetric reagents.

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