



Tetrahedron report number 859

Oxidation by permanganate: synthetic and mechanistic aspects

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ARTICLE INFO

Article history:

Received 25 September 2008

Available online 21 October 2008

Dedicated to Professor G. B. Behera on his 70th birthday

Keywords:

Permanganate

Quaternary ammonium permanganate

Metallo-cyclohexane

Hypomanganate ester

Steroid

Nucleotide

DNA footprinting

Silica

Alumina

Heterogeneous medium

Nano manganese compound

Environmental pollution

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Abbreviations: ANT-X, anatoxin-a; BBCP, bis(2,2'-bipyridyl)copper(II) permanganate; BMA, bromomaleic acid; CA, carboxylic acids; CCM, chemical cleavage of mismatch method; CL, chemiluminescence; CMA, chloromaleic acid; CNT, carbon nanotube; CTA, cetyltrimethylammonium; CTAB, cetyltrimethylammonium bromide; CTADC, cetyltrimethylammonium dichromate; CTAP, cetyltrimethylammonium permanganate; CTC, Charge-transfer complexes; CVD, chemical vapour deposition; CYN, cyclin-drospermopsin; DBMA, dibromomaleic acid; DCC, dicyclohexylcarbodiimide; DCM, dichloromethane; DCMA, dichloromaleic acid; DNA, deoxyribonucleic acid; DTA, dodecyltrimethylammonium; ED3A, ethylenediamine-*N,N,N'*-triacetic acid; EDDA, *N,N'*-ethylenediaminediacetic acid; EDTA, ethylenediaminetetraacetic acid; EN, ethylenediamine; FAD, flavin adenine dinucleotide; FMO, frontier molecular orbital; HLB, hydrophilic lipophilic balance; HOMO, highest occupied molecular orbital; IDA, iminodiacetic acid; ISCO, *in situ* chemical oxidation; ISTR, *in situ* thermal remediation; KCAR, K-carrageenan; LUMO, lowest unoccupied molecular orbital; MWCNT, multi-walled carbon nanotube; NADP, nicotinamide adenine dinucleotide phosphate; NMR, nuclear magnetic resonance; PCC, pyridinium chlorochromate; SWCNT, single-walled carbon nanotube; TAA, tetraalkylammonium; TBAP, tetrabutylammonium permanganate; TCA, *trans*-cinnamic acid; TCE, trichloroethylene; TG-MS, Thermogravimetry-mass spectrometry; THF, tetrahydrofuran; THM, trihalomethane; TNT, 2,4,6-trinitrotoluene; TRU, transuranic; TS, transition state; TX-100, triton X-100; XAS, X-ray absorption spectroscopy.

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1. Introduction

A redox process involves electron transfer between an oxidant and a reductant. Permanganate, an important oxidant in many organic and inorganic redox reactions, involves the Mn(VII) entity, which is renowned for its versatility. The permanganate oxidation process is eco-friendly and has gained importance in green chemistry. Chemical oxidation is full of illustrations of the use of many uni-atomic metallic ions as oxidants, e.g., Ag(I), Fe(III), Ce(IV), Cr(VI), Mn(VII), etc., and some large biological oxidants like FAD, NADP, etc. Permanganate, however, in various homogeneous and heterogeneous media, as well as on solid supports and in solvent-free conditions, provides excellent results when used in a large number of oxidation processes.

In the permanganate ion, manganese has an oxidation state of +7. Sodium and potassium permanganates are prepared on a large scale by electrolytic oxidation of basic solutions of MnO_4^{2-} . From the Mn(II) ion, an aqueous solution of MnO_4^- may be prepared with very powerful oxidizing agents such as PbO_2 or NaBiO_3 . In aqueous solution, it gives an intense purple colour and its crystalline salts appear almost black.

The permanganate ion has a tetrahedral geometry with extensive π -bonding. It is stable in neutral or slightly alkaline media, but, in a strongly alkaline medium,^{1,2} it disproportionates or reacts with hydroxide ion to form manganese(V) (hypomanganate) or manganese(VI) (manganate). Consequently, at high pH values, it is sometimes difficult to ascertain whether an oxidation is proceeding via a one- or a two-electron process.

Solutions of MnO_4^- are intrinsically unstable, decomposing slowly, but observably, in an acid medium (Eq. 1):



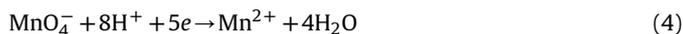
In neutral or slightly alkaline solutions in the dark, decomposition is immeasurably slow. It is, however, catalyzed by light. In basic solution, permanganate functions as a powerful oxidizing agent ($E_0 = +1.23$ V) (Eq. 2):



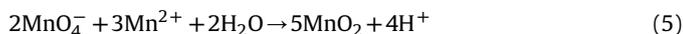
In very strong base and with an excess of MnO_4^- , however, manganate ion is produced ($E_0 = +0.56$ V) (Eq. 3):



In acid solution, permanganate is reduced to Mn^{2+} by an excess of reducing agent ($E_0 = +1.51$ V) (Eq. 4):



Since MnO_4^- oxidizes Mn^{2+} ($E_0 = +0.46$ V), the product in the presence of an excess of permanganate is MnO_2 (Eq. 5):



The highest oxidation state of manganese corresponds to the total number of 3d and 4s electrons. This VII-state occurs in the oxo

compounds MnO_4^- , Mn_2O_7 and MnO_3F . Manganese(VII) is reduced to Mn(II) during oxidation processes via many manganese species having different oxidation states such as Mn(VI), Mn(V), Mn(IV) and Mn(III). The appearance of these intermediate oxidation states depends upon various reaction conditions, types of substrate and their stability. A few compounds of Mn(V) species are frequently postulated as intermediates in the reduction of permanganates. Although Mn(II) is the most stable oxidation state, it is quite readily oxidized in alkaline solution.

Permanganate is a versatile oxidizing agent and is used for studying the oxidation kinetics of many organic substrates. The mechanisms for different organic substrates suggested by various authors are not similar, indicating that a variety of mechanisms are possible, depending upon the nature of the reactive manganese species, the reaction environment and the nature of the substrate.

2. Oxidation of alkenes and their derivatives in aqueous media

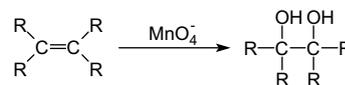
The oxidation of carbon–carbon double bonds by permanganate ion is an important and well-known reaction in organic chemistry, in a mechanistic as well as a synthetic prospective. Under alkaline conditions, olefins are converted into the corresponding diols in good yield,^{3,4} while in neutral or slightly basic solutions α -hydroxy ketones are produced.^{4,5} These reactions are always accompanied by a certain amount of C–C bond cleavage⁶ and, under acidic conditions, the cleavage products predominate.^{7,8}

Aqueous potassium permanganate was used originally for the conversion of alkenes into diols (Wagner dihydroxylation reaction) (Scheme 1).

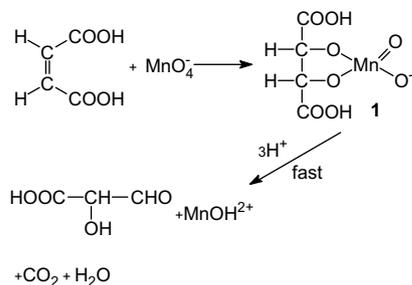
Owing to the rapidity and the complex mechanism of the permanganate oxidations, the mechanisms of oxidation of various olefinic derivatives are still poorly understood.

Permanganate oxidations of alkenes and their derivatives have been suggested to be associated with a cyclic manganese(V) intermediate. In a kinetic study of the permanganate oxidation of maleic and fumaric acids to formyl(hydroxy)acetic acid by a stopped-flow technique at acidic pH, Simandi et al.⁷ have found that the rate-determining step is cis attack of permanganate on the double bond, resulting in the formation of a cyclic intermediate (1) containing manganese(V). A manganese(V) species could not, however, be detected and this is reduced in a fast process (Scheme 2), which leads to a detectable intermediate, Mn(III), and formyl(hydroxy)acetic acid.

In halogen-substituted maleic acids, a four-electron-transfer process occurs initially, followed by reactions between manganese(III) and the organic intermediates.⁹ The permanganate



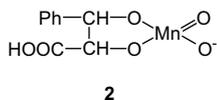
Scheme 1.



Scheme 2.

oxidation of chloromaleic acid (CMA), dichloromaleic acid (DCMA), bromomaleic acid (BMA) and dibromomaleic acid (DBMA), in the presence of a 10-fold excess of pyrophosphate with respect to permanganate, led to the conversion of permanganate into pyrophosphatomanganese(III), which persists for a considerable period of time. Simandi et al. have also observed a short-lived aquomanganese(III) intermediate in permanganate oxidations in acidic media.^{7,10} In the absence of pyrophosphate, Mn(III) disappears by rapid reactions with the organic intermediates or by competitive disproportionation to Mn(II) and Mn(IV). With CMA, DCMA, BMA and DBMA, a transitional absorption maximum at 415 nm was observed, indicating the formation of Mn(III), which undergoes disproportionation rather than reaction with the organic intermediates.

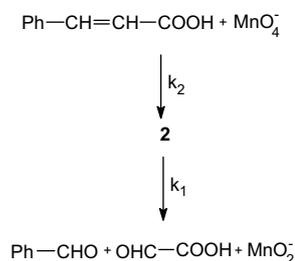
Earlier, Lee and Brownridge¹¹ had detected the Mn(V) intermediate during the oxidation of cinnamic acid by permanganate ion in aqueous perchloric acid solutions as the hypomanganate ester (2). This intermediate, appearing yellow and exhibiting an absorption maximum at 415 nm, decomposes at a slower rate to give benzaldehyde and Mn(III) as the products.



2

When a solution of reaction product is made basic by the addition of sodium hydroxide, a brown precipitate of MnO₂ appears. A probable sequence, which accounts for all of these observations, has been outlined in Scheme 3.

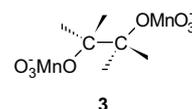
Wiberg and Deustsch¹² have also confirmed the involvement of an intermediate containing Mn(V) by citing direct spectrophotometric evidence. Lee and Brownridge¹³ have discussed the results obtained from a study of the oxidation of *trans*-cinnamic acid (TCA) in aqueous perchloric acid media. The advantage of using TCA is that the absorption spectrum of the intermediate is quite different from that of permanganate ion and may be readily detected either visually or spectrophotometrically.¹¹ After completion of the reactions, the final solutions obtained are colourless, suggesting the oxidation states of +2 or +3 for manganese. It is possible to distinguish one oxidation state from another because Mn(III) disproportionates to Mn(II) and Mn(IV) under alkaline conditions. The Mn(III) intermediate has, however, also been detected by Chaudhury et al.¹⁴ *in situ* in the [MnO₄]⁻-SO₂ electron-



Scheme 3.

transfer process. The Mn(IV) species is easily detected as a brown precipitate of MnO₂ in an alkaline medium.

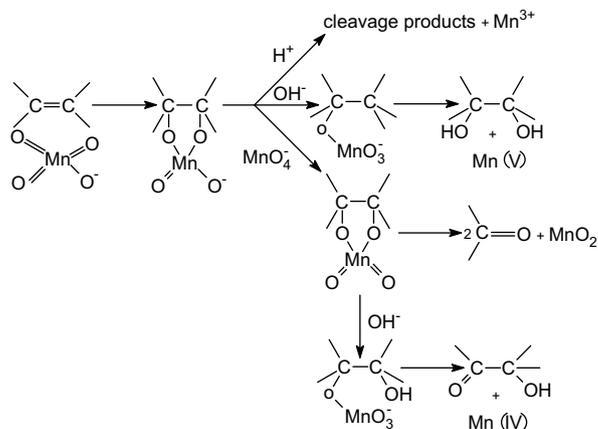
The oxidation of cinnamic acid by permanganate consists of two consecutive steps, the first being a bimolecular formation of an intermediate and the second a unimolecular decomposition of the intermediate.¹¹ The rate of the initial bimolecular reaction is increased ($k_D/k_H=1.3$) by replacement of either the α or the β protons by deuterium. This suggests that the hybridization of both carbon atoms is changing from sp^2 to sp^3 and that the transition state is symmetrical with respect to the extent of rehybridization at both carbons. If the attack had taken place at only one of the carbons before the transition state was achieved, it would have been expected to produce an inverse effect only at that carbon. On the contrary, however, the identical effects observed for the oxidation of both cinnamic acid α -*d* and cinnamic acid β -*d* by permanganate are more consistent with the formation of a cyclic intermediate 2. The only other possibility would be the formation of the diester (3).



3

The possibility of the formation of this intermediate is eliminated because the transition state for this reaction includes only one molecule of permanganate ion.

An investigation on the effect of substituents on the rate of oxidation of the olefinic double bond of cinnamic acid has provided further insight into the reaction mechanism.¹³ The first step of the reaction is found to be relatively insensitive to the nature of the substituents, but the second step is substantially retarded by electron-withdrawing substituents, with the Hammett ρ value being -1.1 . Wiberg and Geer¹⁵ have also noted that substituents have a small effect on the rate of disappearance of permanganate ion when cinnamic acids are oxidized in basic or neutral solutions. The large effect of substituents on the rate of ester decomposition is probably associated with the development of a carbonyl group in the second step of the reaction (Scheme 4).



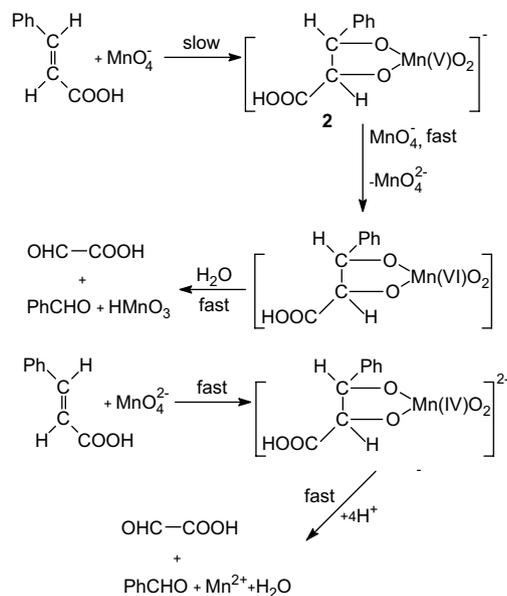
Scheme 4.

These facts support the suggestion first made over a century ago¹⁶ that hypomanganate esters are formed as intermediates in the oxidation of alkenes by potassium permanganate. The transition state for the ester-forming reaction appears to be one in which the olefinic carbons have acquired substantial sp^3 character with the bond rearrangements nearly complete. The transition state for the second step (oxidative decomposition of the ester) probably contains a fairly well developed carbonyl group as evidenced by both isotope and substituent effects. Under these

conditions, the latter step is much slower and it controls the overall rate of the reaction.

Accepting that the hypomanganate esters are the initial intermediates in these reactions under all conditions, a mechanism has been proposed in Scheme 4. The fate of the hypomanganate ester is entirely dependent upon the reaction conditions.

Simandi and Jaky¹⁷ have, however, differed from Lee and Brownridge¹¹ on the point that the oxidation state of manganese in the hypomanganate ester cannot be +5. They have suggested a mechanism, outlined in Scheme 5, consistent with the available information.



Scheme 5.

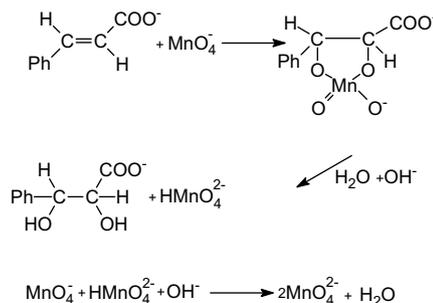
In their opinion, the mechanism includes some of the steps proposed for olefin oxidation in alkaline media.^{12,15,18,19} The formation of manganate esters in acid solutions of TCA was also considered as a possible alternative for the disappearance of hypomanganate.¹¹ Mn(VI) and Mn(V) are regarded as short-lived undetectable intermediates. In the above mechanism (Scheme 5), Mn(VI) is assumed to be a more reactive oxidant than Mn(VII), which is not inconsistent with its increased rate of disproportionation. The second process, however, remains suppressed, due to the relatively large excess of TCA under the reaction conditions. The proposed mechanism accounts for the facts that (i) Mn(III) is not an intermediate in the process and (ii) the single detectable intermediate contains one oxidation equivalent referred to overall manganese: at a maximum concentration of the intermediate, a 1:1 mixture of Mn(IV) and Mn(II) is present. They suggest that the soluble Mn(IV) may be involved in permanganate oxidation more extensively than has been recognized thus far.

Lee and Nagarajan²⁰ have oxidized cinnamate ion by alkaline permanganate and obtained the following conclusions:

- The rate of the reaction is first order with respect to permanganate ion, as well as the substrate.
- Inverse secondary isotope effects are observed when the rates for *trans*-cinnamate ion- α -*d* and *trans*-cinnamate ion- β -*d* are compared with unlabelled *trans*-cinnamate ion.
- Stoichiometric studies indicate that 0.9 mol of permanganate is consumed for each mole of reductant present.

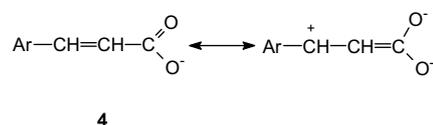
The result thus obtained is consistent with a reaction that is initiated by the formation of a cyclic manganate(V) diester in the

rate-limiting step. The authors have proposed the fate of the manganate(V) diester as depicted in Scheme 6.



Scheme 6.

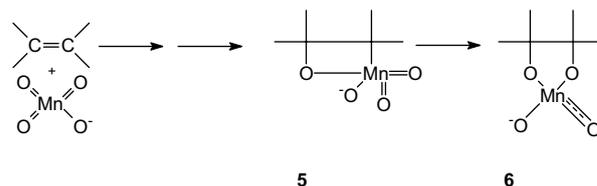
The small positive ρ value obtained by using the Hammett equation suggests the stabilization of the ground state (4) by electron-donating substituents.



4

Lee and Nagarajan²⁰ have concluded from this study that the formation of different products (MnO_4^- and MnO_2) is not associated with any experimental changes in the mechanism of the reaction between the permanganate ion and C–C double bonds. Instead, the change in products appears to be due to the greater reactivity of manganese(V) oxides in the less basic solution.

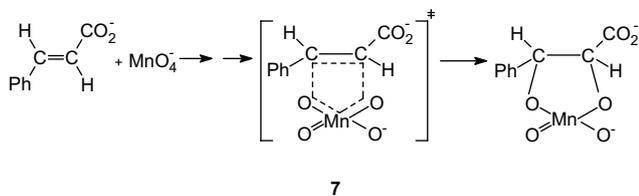
It was generally accepted that the reaction proceeds via a concerted mechanism with a cyclic ester intermediate, until a suggestion was made of a stepwise mechanism involving a metallooxetane intermediate.²¹ Freeman and Kappos²² studied the permanganate oxidation of some cinnamic acid derivatives in phosphate-buffered solutions and suggested the formation of a metallo-cyclooxetane (5) by the reaction of permanganate ion with the C–C double bond, and the subsequent rearrangement of 5 to the five-membered cyclic hypomanganate diester. Formation of the cyclic manganate(V) diester (6) is expected to be enhanced by the simultaneous formation of a triply bonded spectator oxo group, which is formed due to the availability of two d-orbitals of Mn(VII) for bonding to a single oxygen (Scheme 7).²³



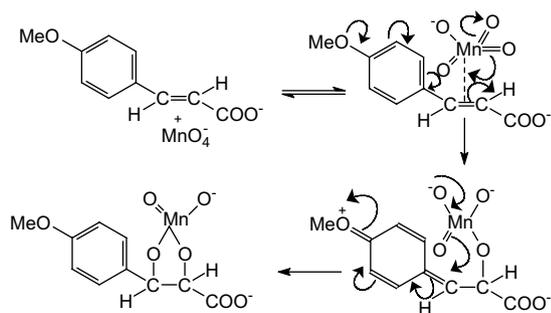
Scheme 7.

It has also been suggested that charge-transfer complexes (CTCs) and/or metallo-cyclooxetanes may be involved prior to the rate-determining step followed by formation of the cyclic manganate(V) diester. The earlier results of a small positive ρ value, large negative entropy of activation and secondary kinetic deuterium isotope effects^{11,20} for the oxidation of cinnamate also corroborate the formation of an activated complex resembling 7 (Scheme 8).

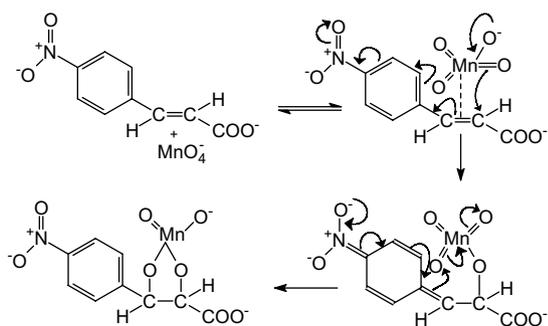
An interesting phenomenon of an increase in the rate of oxidation of substituted *trans*-cinnamate by both electron-releasing and electron-withdrawing groups is observed (Schemes 9 and 10).



Scheme 8.



Scheme 9.



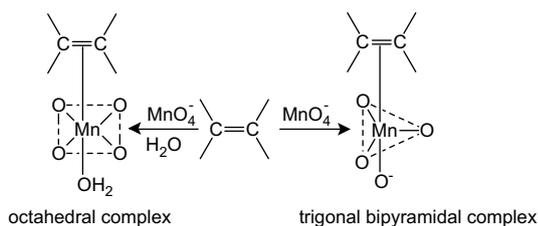
Scheme 10.

The data obtained in this study suggest (i) an ambiphilic nature for the permanganate ion, (ii) an activating complex, which is more stabilized than the reactant state by electron-withdrawing and electron-releasing groups, (iii) a reactant that is stabilized by electron-releasing groups and (iv) a reactant that is destabilized by electron-withdrawing groups.^{13,20}

The involvement of an initial interaction between the double bond and the manganese of the permanganate ion to give an octahedral or a trigonal bipyramidal organometallic complex, which can rearrange to a metallo-cyclohexane or a five-membered cyclic manganese(V) diester (Scheme 11) was suggested.

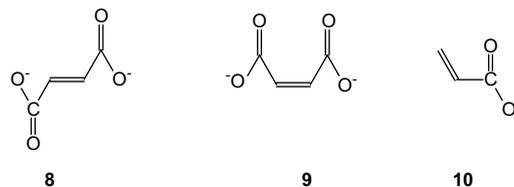
Thus, the formation of a π - and/or σ -complex should precede the formation of the manganese(V) diester.

Freeman and Kappos²⁴ investigated the kinetics of permanganate ion oxidation of a wide variety of unsaturated carboxylate ions, in order to determine whether the permanganate ion is ambiphilic,^{20,22} electrophilic²¹ or nucleophilic²⁵ and to assess the

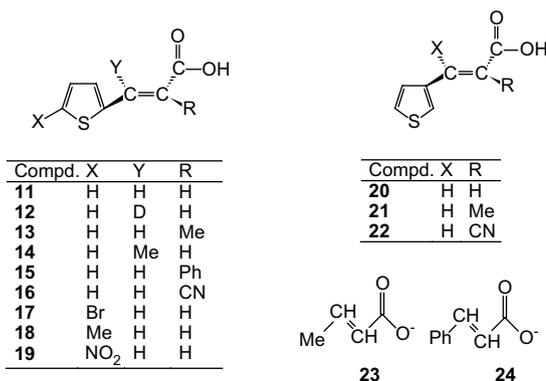


Scheme 11.

influence of substituents on the kinetics and mechanism of the reaction. The relative rate data are not consistent with an electrophilic attack at permanganate ion by the C–C double bond, since increasing nucleophilicity (increasing the number of methyl groups) of the double bond generally accelerates the rate of electrophilic addition. Steric factors also influence the rate of oxidation. The greater the number of substituents, the more the steric hindrance and the slower the reaction. The greater reactivity of (*E*)-2-butenedioate (**8**) relative to (*Z*)-2-butenedioate (**9**) was attributed to steric effects in the activated complex of **9** as the sp^2 -hybridized carbon atoms (bond angle 120°) approach sp -hybridized ones (bond angle 109.5°) and to electronic repulsion between eclipsing *cis*-carboxylate ions. The faster rate of oxidation on a more electron-deficient double bond in **8** than that on a relatively less electron-deficient species **10** suggests permanganate to be nucleophilic.^{15,18,25}



The kinetics and mechanism of the permanganate ion oxidation of (*E*)-3-(2-thienyl)-2-propenoates (**11–19**) and (*E*)-3-(3-thienyl)-2-propenoates (**20–22**) at 418, 526, 584 and 660 nm in phosphate-buffered solutions have also suggested that the rate-determining step is the formation of a metallo-cyclohexane or a cyclic manganese(V) diester, and thus is supported by the low enthalpies of activation, large negative entropies of activation, small substituent effects, steric effects and an inverse secondary deuterium kinetic isotope effect.²⁶ Further, (*E*)-3-(2-thienyl)-2-propenoates (**11–19**) and (*E*)-3-(3-thienyl)-2-propenoates (**20–22**) were found to react with permanganate ion at essentially the same rate and were oxidized faster than (*E*)-2-butenedioate (**23**)^{22,26} and (*E*)-3-phenyl-2-propenoate (**24**),^{22,24,27} respectively.



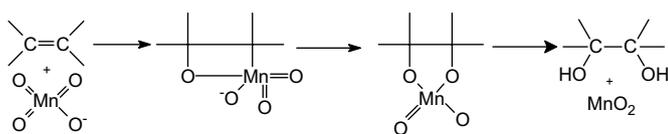
If the attack of permanganate ion on the C–C double bonds in **20** and **22–24** was electrophilic in nature, **20** and **22** would be expected to react very fast, due to the strong resonance donor ability of the thiophene ring system, which overrides its inductive withdrawal effect. Substitution of a methyl group for hydrogen in **11** to give **13** and in **20** to give **21** retards the rate of oxidation due to steric effects (eclipsing of the *cis*-substituents in the activated complex), suggesting the importance of steric factors in the permanganate ion oxidation of C–C double bonds.²²

Replacement of hydrogen by a cyano group at C-2 in **11** to give **16** also retards the rate of oxidation because of steric factors and electron-withdrawal effects. The result of these reactions is consistent with an electrophilic attack by permanganate ion on the C–C double bond. Since the reaction rates are determined by the difference in energy between the ground state and transition state,

there may not be any merits in specifying the first step of a multi-step reaction as being electrophilic or nucleophilic.

Extensive kinetic studies have shown that the reactions of permanganate with alkenes exhibit inverse secondary isotope effects,¹³ as expected, if the reaction involves a transition state in which the hybridization of the olefinic carbon atoms changes from sp^2 to sp^3 . It has been found that the reaction of permanganate with an unsaturated compound proceeds at approximately the same rate under different conditions, and a similar activation parameter is obtained, although quite different products are obtained when the conditions are changed. For example, oxidation under alkaline conditions leads to *cis*-diols and manganese dioxide, while the same reaction under acidic conditions results in cleavage of the double bond to give carbonyl compounds along with Mn^{3+} or Mn^{2+} . Moreover, under neutral conditions a third organic product, the corresponding ketol, is obtained in moderate-to-high yields.²⁸

These observations, taken together, have led to the conclusion that all permanganate/alkene reactions proceed via similar transition states, but the nature of the products is determined by a series of post-transition-state reactions, which are highly dependent on the reaction conditions. Reactions such as that depicted in Scheme 12, therefore, conceal more than they reveal.



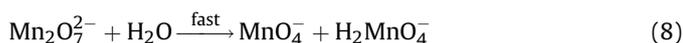
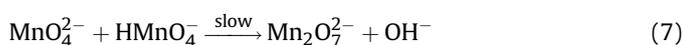
Scheme 12.

The observation that manganese in the cyclic diester is in the +5 oxidation state, while the product is +4 or +6 under basic conditions and +3 or +2 under acidic conditions, leads to a series of questions concerning the course of the reactions in the post-transition state.

In order to throw some light on the nature of the product-forming steps in these reactions, Lee and Chen²⁹ have synthesized manganese species in all possible oxidation states between +7 and +4, and have estimated the rate constant for each possible reaction. The reactions of each manganese species with itself (disproportionation), with the solvent, with other manganese species and with the organic substrates have also been studied. The results thus obtained have been summarized in the following manner:

(i) Reaction of manganate(VI)

Although manganese(VI) is stable under highly basic conditions, disproportionation occurs when the pH is decreased. The product MnO_4^{3-} is unstable and disproportionates with the formation of MnO_2 , as an insoluble product. The order of the reaction is found to be 2 at $pH=9-11$. A reaction scheme consistent with these observations is given in Eqs. 6–8:

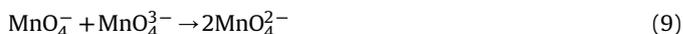


(ii) Reaction of manganate(V)

Disproportionation of manganate(V) results in the formation of a clear green solution with a spectrum similar to that of manganate(VI) and a precipitate of MnO_2 . When the rate of the reaction is monitored by following the increase in absorbance at 438 nm,

a plot of $\ln(dA/dt)$ versus $\ln[Mn(V)]$ becomes linear with a slope of 2.0, indicating the reaction to be second order with respect to the concentration of manganate(V).

The reaction between manganate(V) and permanganate results in the formation of manganese(VI) (Eq. 9):



The disproportionation of manganate(V) is slow at a high base concentration, but is very fast at low basicities, while the converse is reported for its reaction with permanganate.

(iii) Reaction of manganate(IV)

Manganate(IV) is found to react with unsaturated organic compounds under acidic conditions only. In alkaline solutions, manganate(IV) is not reduced by compounds containing C–C double bonds. It appears to be stable and unreactive under basic conditions.

From these results, a general reaction scheme has been proposed (Scheme 13).

3. Oxidation of alkenes and their derivatives by using quaternary ammonium permanganates in organic media

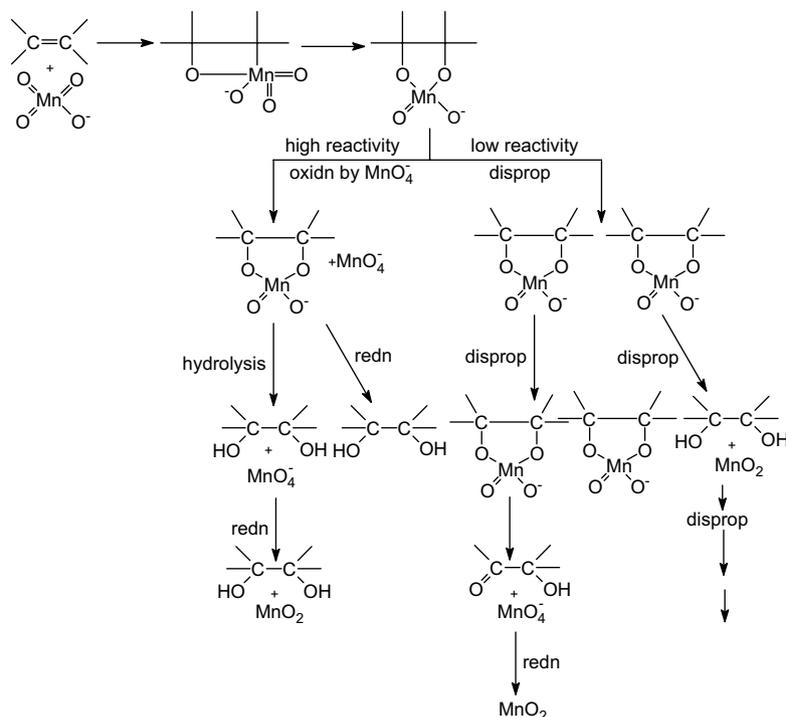
Generally, permanganate oxidations of organic substances are performed in aqueous media with organic co-solvents, in which potassium permanganate shows an appreciable solubility and inertness. The co-solvents mostly used are *tert*-butanol, acetone, pyridine and acetic acid. Acetic anhydride has been used for the oxidation of alkenes to give α -diketones.³⁰ Trifluoroacetic acid is apparently a good solvent for both permanganate and hydrocarbons.

The process of phase-transfer catalysis is a method introduced in the last century to utilize the possibility of extracting anions or cations into an organic layer. The term 'phase-transfer catalysis' has been designated by Starks,³¹ who has presented a plausible mechanism for the reaction as well as requisite proof that the rate-determining step occurs within the organic layer.

Phase-transfer catalysis involves two fundamental processes: the transport of an anion to an organic layer by the use of an 'onium counterion' and the reaction of the anion or ion pair within the organic layer with an alkylating agent. The transport of the anion to the organic layer is usually such a rapid process that the rest of the reaction occurs under equilibrium conditions with respect to the distribution of ions between the layers. An 'onium ion' such as a tetraalkylammonium ion, Q^+ , has therefore become a magic wand, with the help of which it is possible to perform reactions in a two-layer system at a rate, which is often comparable to that obtained in anhydrous dipolar aprotic solvents. This possibility has attracted enormous interest from synthetic as well as kinetic chemists.

Surfactants such as tetraalkylammonium bromides, when combined with potassium permanganate, produce tetraalkylammonium permanganates, which act as excellent phase-transfer oxidants for organic substrates in completely non-polar organic solvents, such as benzene, dichloromethane, chloroform, carbon tetrachloride, toluene, etc., and in completely anhydrous conditions. In some experiments, the soluble permanganate salts are formed in phase-transfer processes and are utilized *in situ* without isolation,^{32–35} while, sometimes, the salts are first isolated and are then dissolved in the desired solvents.^{36–40}

Although most salts exist as discrete ions in aqueous solutions, quaternary ammonium compounds when dissolved in organic solvents are most likely to form ion pairs.⁴¹ Brandstrom has shown that the probability of salts existing as ion pairs is inversely dependent upon the distance between the centers of the two ions and the dielectric constant of the solvents.⁴² By examining the ¹H NMR



Scheme 13.

spectrum of tetraethylammonium permanganate in three solvents, namely D_2O , acetone- d_6 and methylene chloride- d_2 , Lee et al.⁴³ have demonstrated that most quaternary ammonium permanganates exist as ion pairs in all solvents, except in water. In water, a distinct triplet and quartet are apparent, while in acetone and methylene chloride, the resolution is reduced, with the spectrum becoming two broad multiplets in the latter solvent. Assuming that the lack of resolution in the organic solvents is due to close association of the quaternary ammonium ion with permanganate ion, it would appear that tetraethylammonium permanganate exists as separate ions in water, as loose ion pairs in acetone and as tight ion pairs in methylene chloride. In less polar solvents, where theory predicts tighter ion pairs,⁴² the ions must be intimately associated, either in the ground state or in the transition state. Moreover, close contact within the ion pair seems to increase the rate of reaction. For example, the rate constants for the oxidation of methyl cinnamate by methyltri-*n*-octylammonium permanganate are greater than that for tetra-*n*-octylammonium permanganate, because the former allows a greater penetration of the anion into the structure of the cation.^{41,44} It therefore appears that quaternary ammonium permanganates may exist as solvent-separated ion pairs in acetone, but as intimate ion pairs in toluene and methylene chloride.⁴⁵

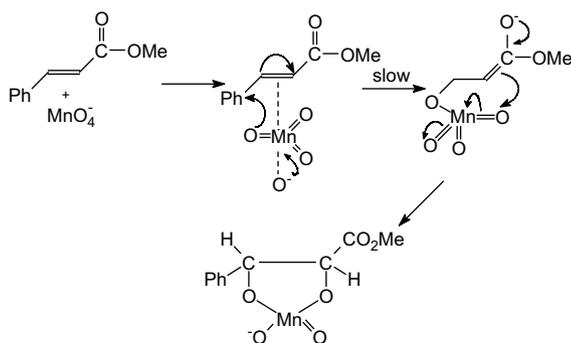
Although alkenes are very susceptible to oxidative attack by permanganate ion, the use of permanganate ion as an oxidant for alkenes or unsaturated fatty alcohols has been of limited use, because of the low solubility of permanganate in most non-polar solvents. With the observation that potassium permanganate could be extracted from water into benzene by the use of phase-transfer catalysts,^{46,47} however, the potential utility of this reagent has increased substantially. Permanganate ion solubilized in benzene or dichloromethane by the use of quaternary ammonium salts,^{46,48–50} dimethylpolyethylene glycol⁵¹ or cryptates⁵² has been successfully used for the oxidation in anhydrous conditions and, in some cases,⁵³ no precipitate of manganese dioxide is formed (e.g., reduction of permanganate). A striking example is 'purple benzene', in which crown ethers can dissolve up to 0.06 M $KMnO_4$ in benzene.⁴⁸ 'Purple benzene' can also be readily prepared by using salts of quaternary ammonium ions as tetrabutylammonium bromide.⁵⁴

Weber and Shepherd⁵⁵ were apparently the first workers to show that certain alkenes, e.g., cyclohexene, *cis*-cyclooctene and *trans*-cyclooctene, can be oxidized stereospecifically to vicinal *cis*-diols by cold, dilute alkaline potassium permanganate in the presence of a catalytic quantity of benzyltriethylammonium chloride as the phase-transfer agent in water/dichloromethane as the solvent. Yields of 1,2-diols do not exceed 50% with the large-ring cycloalkenes, and are substantially lower (15%) with cyclohexene, due to over-oxidation to ketols, ketones and dibasic acids.

Later, Ogino and Mochizuki⁵³ reported certain advantages in the permanganate oxidation of alkenes in a homogeneous, non-aqueous, one-phase system. $KMnO_4$ solubilized in dichloromethane in the presence of an equimolar amount of benzyltriethylammonium chloride readily oxidizes alkenes under anhydrous conditions. Either 1,2-diols or aldehydes are obtained directly in good yields or by decomposition of the reaction intermediates with an aqueous solution, depending upon pH. The advantages of the procedure are that the products are protected against secondary oxidation by MnO_4^- through the formation of stable organomanganese species in non-aqueous solution. As quaternary ammonium salts are cheaper than crown ethers and can be readily washed away by water, this procedure offers a versatile route for the conversion of alkenes into 1,2-diols or aldehydes.

Lee and Brown⁵⁶ have studied the reaction of methyl (*E*)-cinnamate with quaternary ammonium permanganates in methylene chloride solutions. They have proposed that the counterion has a substantial effect on the rate of reaction. This observation is in accordance with theoretical calculations, which indicate that quaternary ammonium permanganates exist as ion pairs in non-aqueous solutions.⁴² For symmetrical tetraalkylammonium ions, there is an inverse relationship between the second-order rate constants and the radius of the cation.⁴⁴ Since the ion-pairing stability is inversely dependent upon the interionic distance between the centers of positive and negative charge, the transition state must form a tighter ion pair than the ground state, i.e., the transition state must derive more stability from close association with the cation than does the ground state. This observation is consistent with the mechanism proposed in Scheme 14 where, in

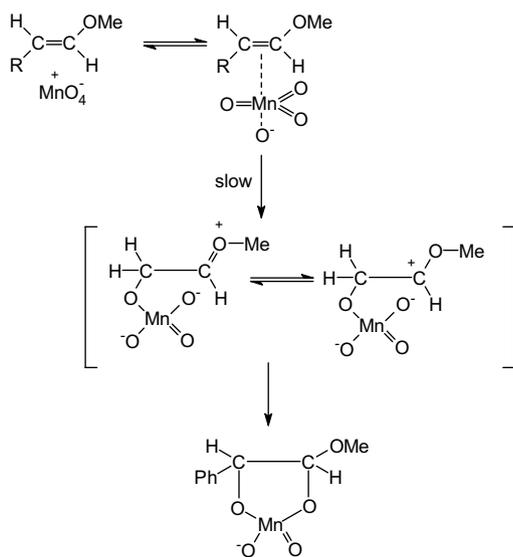
the ground state, the charge is spread over the four permanganate oxygens including the oxygen atoms of the α,β -unsaturated carbonyl groups of the substrate, while the transition state is a more localized enolate ion. Since the interaction with the quaternary ammonium ion would be stronger for the structure in which there is greater localization of the negative charge, it follows that the transition state would benefit more from an interaction with the cation. Hence, smaller cations would promote a faster reaction.



Scheme 14.

The substituent effects obtained with the phase-transfer reagents are in contrast with those reported by Toyoshima et al.⁵⁷ for the oxidation of alkyl vinyl ethers in aqueous dioxane. A proper analysis of the rate data presented by these authors indicates that it conforms to the Taft equation⁵⁸ with a contribution of the steric parameter E_s of 0.33 and a ρ value of -0.6 . The Hammett plot in a series of substituted stilbenes reported earlier⁵⁹ was found to be concave upwards, indicating a change in the reaction mechanism.⁶⁰ For electron-donating substituents, carbocation-like transition states can be stabilized, whereas for electron-withdrawing groups, an anionic transition state can be conceived (Scheme 15).

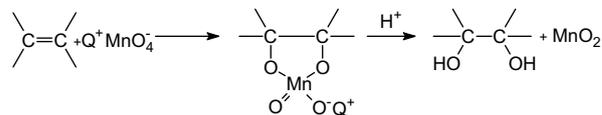
A comparison of Schemes 14 and 15 indicates that both reactions proceed through the same organometallic intermediate, but via different transition states, to the cyclic diester. The principal difference in the transition states is associated with the timing of the reduction of Mn(VII); in Scheme 14, the reduction occurs after the transition state is achieved, while in Scheme 15, the reduction occurs during the formation of the transition state. When styrene derivatives were oxidized by quaternary



Scheme 15.

ammonium or phosphonium permanganates in a polar organic solvent, such as acetone, the substituents have little or no effect on the rate of reaction.⁴³ In less polar solvents, such as methylene chloride or toluene, the rates of the reaction are, however, dependent upon the nature of the quaternary ammonium or phosphonium ions.

Lee and Perez-Benito⁶¹ detected autocatalysis during the reaction of methyltributylammonium permanganate with 1-tetradecene in methylene chloride solutions. The oxidation state of the product was found to be +4. The reaction sequence is presented in Scheme 16.



Scheme 16.

Manganate(V) diesters can be reduced to Mn(IV), possibly by abstraction of a hydrogen atom from the solvent. The product, MnO₂, was found to be colloidal in nature. The intensity of the absorption spectrum of the product increases with time, presumably because flocculation is slowly occurring. The logarithm of the absorption of the product was linearly related to the logarithm of the wavelength, which also supports the formation of colloidal MnO₂.⁶² The autocatalytic nature of the reaction has been confirmed by determining the initial rates in solutions that contain varying concentrations of product obtained from a previous experiment. When fresh methyltributylammonium permanganate is added to solutions in which the permanganate has been completely reduced, the rate of reaction is found to increase with the concentration of Mn(IV) in the solutions. Consequently, it appears that the autocatalysis may be associated with the formation of an Mn(IV) colloid, most likely MnO₂, that provides a surface on which the catalyzed reaction takes place. Many workers have previously detected soluble colloidal MnO₂ as the inorganic product during the oxidation of alkenes.^{63–65}

On the basis of these results, it can be seen that the overall rate law for the disappearance of permanganate ion should take the form:

$$\text{Rate}_{\text{obs}} = \text{Rate}_{\text{solvent}} + \text{Rate}_{\text{alkene}} + \text{Rate}_{\text{cat}}$$

$$\text{where, } \text{Rate}_{\text{obs}} = -d[\text{MnO}_4^-],$$

$$\text{Rate}_{\text{solvent}} = -k_s [\text{MnO}_4^-]$$

$$\text{and, } \text{Rate}_{\text{alkene}} = k_2 [\text{MnO}_4^-] [\text{tetradecene}]$$

According to the empirical isotherm of Freundlich, the amount of permanganate adsorbed on the surface of colloidal MnO₂, y , is related to the amount in solution, c , by Eq. 10:

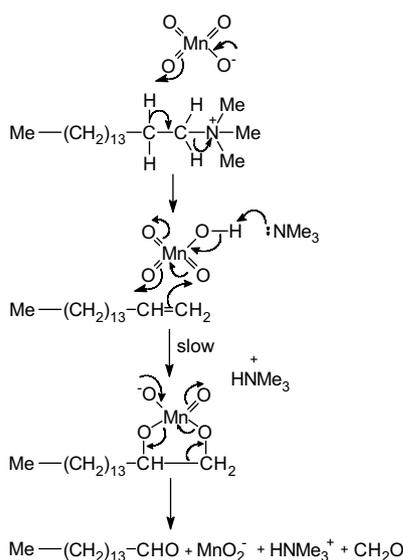
$$y = ac^b \quad (10)$$

where, 'a' and 'b' are constants.⁶⁶ Since 'b' is always less than unity, the observed order with respect to the concentration of permanganate in solution would also be fractional.

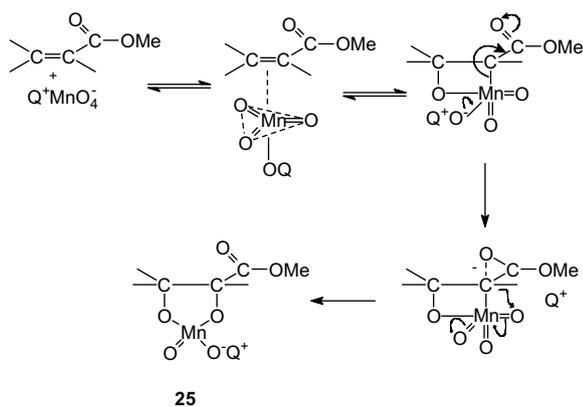
The equation concerning 'Rate_{cat}', which is independent of alkene concentration, probably arises from the thermal decomposition of permanganate, which is known to take place readily in presence of manganese dioxide.¹⁹ The total catalytic contribution to the rate of reaction can therefore be visualized as resulting from

an activation of permanganate by adsorption on the surface of colloidal MnO_2 particles. These 'activated' MnO_4^- ions can then be reduced by reaction with alkene or by thermal expulsion of oxygen.⁶⁷ Activation of permanganate by adsorption on colloidal particles of the product (MnO_2) is therefore responsible for the observed autocatalysis.

A self-oxidation process has been proposed by Dash and Mishra⁶⁸ in the case of cetyltrimethylammonium permanganate (CTAP) used in a chloroform medium. These workers suggested that since CTAP exists as a tight ion pair in a chloroform medium, the permanganate ion easily abstracts a proton from the β -carbon atom of the cetyl chain, thereby producing pentadecanal. The mechanism of the self-oxidation process was proposed with supporting evidence (Scheme 17). It was observed that with an increase in the polarity of the solvent medium, the rate of self-oxidation increases.



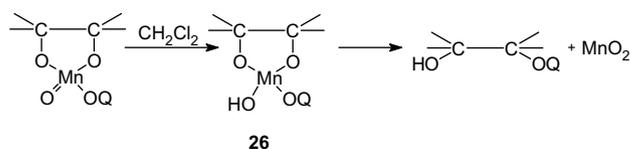
Additional evidence in support of the existence of ion pairs is obtained from a consideration of the effect of substituents on the rate of reaction.⁶⁹ The Hammett ρ value for the oxidation of substituted methyl cinnamates by tetrabutylammonium permanganate is greater in acetone ($\rho=1.43$) than in methylene chloride ($\rho=0.95$). Since the ρ values are positive, the reaction centre has more electron density in the transition state than the ground state. This indication of an electron-rich transition state leads to a reasonable proposition that the rate-



limiting step may involve heterocyclic cleavage of the carbon–manganese bond to give an enolate-like transition state (Scheme 18).

In this scheme, it is assumed that the proximity of the quaternary ammonium ion would increase the stability of the transition state in non-polar solvents, but that this effect would be less in more polar solvents (such as acetone), where the cation could be surrounded by a sheath of solvent molecules.

Although there is good evidence that **25** is an intermediate in these reactions, the yellow-brown product contains manganese in the +4 and not in the +5 oxidation state. Hence, **25** appears to be a very reactive intermediate, rapidly undergoing a one-electron reduction, possibly by abstraction of a hydrogen atom from a molecule of solvent (Scheme 19).

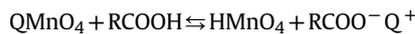


The product of this reaction would be a manganese(IV) cyclic diester **26**, which would decompose to a diol anion and manganese dioxide.

The oxidation of unsaturated carboxylic acids in non-aqueous solvents by methyltributylammonium permanganate⁷⁰ differs, in several ways, both from the corresponding aqueous-phase oxidations²² and from the oxidation of unsaturated esters.¹⁵ The spectrum recorded at the end of the reaction displays an absorbance maximum at 478 nm, which is very near the maximum reported for Mn^{3+} and $\text{Mn}(\text{OH})^{2+}$ in aqueous solutions.⁷¹ Iodometric titration has also suggested 2.99 ± 0.11 as the value of oxidation state for the Mn(III) species. Thus, an Mn(III) species is found to be the final product of the reduction of permanganate by unsaturated acids in methylene chloride solution.⁷⁰ The second-order rate constants for the oxidation of a series of *meta*- and *para*-substituted cinnamic acids exhibit a linear Hammett correlation with a positive slope, indicative of an electron-rich transition state. A similar result has previously been reported for the oxidation of the corresponding methyl esters under comparable conditions.⁵⁶ From these reports, the authors have suggested a reaction sequence where the last step, i.e., cleavage of a carbon–manganese bond, is rate limiting, and this is also supported by the large negative entropies of activation (Scheme 18).

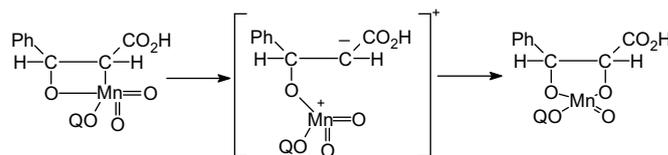
Since the Hammett ρ value is positive, it is apparent that the rate-limiting step must proceed with the development of a negative charge on the α -carbon, as shown in Scheme 20.

The observed catalysis has been attributed to the reaction:

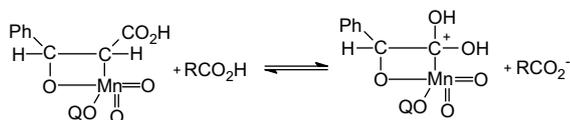


The proton exchange shown above accounts for the catalysis, which results in the production of a powerful oxidant HMnO_4 .⁷²

The involvement of the reaction sequence shown in Scheme 21 accounts for the decrease in the rate observed when tetrabutylammonium acetate is added to the reaction mixture while other



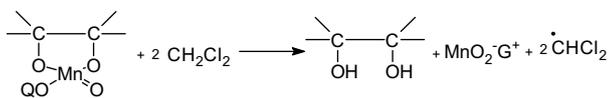
quaternary ammonium salts such as tetrabutylammonium perchlorate do not affect the rate, thus eliminating the possibility of ascribing the suppression in rate caused by the quaternary ammonium acetate to a salt effect.



Scheme 21.

In this study, the authors have indicated the presence of free radicals, which was confirmed by the fact that acrylic and methylacrylic acids are polymerized during the course of these reactions.

It is suggested that these radicals are probably formed during the reduction of the reactive manganese(V) diester to manganese(III), as shown in Scheme 22.

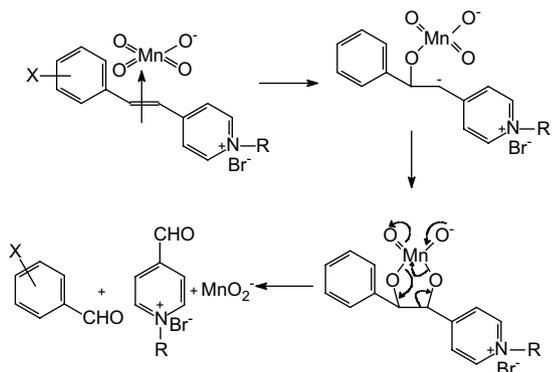


Scheme 22.

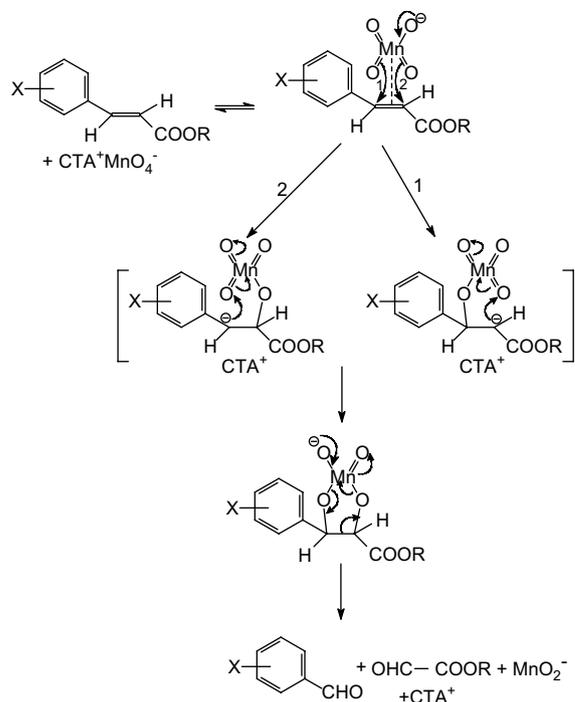
Oxidations of some monochromophoric styrylpyridinium dyes have been carried out in a chloroform medium using CTAP and the results have been compared with the oxidation of the same substrate using KMnO_4 in an acid medium.⁷³ CTAP forms a tight ion pair in a non-polar medium and, because the substrate is also charged, both a hydrophobic interaction and an electrostatic effect bring the reactant and the substrate into proximity, thereby facilitating the reaction. A negative ρ value (-0.21) indicates the presence of an electron-deficient center in the substrate. A mechanism that is consistent with these observations has been proposed (Scheme 23).

The oxidation of some substituted alkyl cinnamates⁷⁴ containing trans-double bonds has been carried out using CTAP in a chloroform medium. Electron-donating groups were found to retard the rate of reaction, whereas the electron-withdrawing groups enhance the rate. The Hammett plot was found to be non-linear with a positive deviation from linearity. Accordingly, the mechanism shown in Scheme 24 has been proposed. Due to the presence of the CTA^+ ion, the transition state with a negative charge was found to be more favourable.

During the oxidation of styrylpyridinium dyes and alkyl cinnamates, which contain trans-double bonds, bond breaking is observed, leading to the formation of carbonyl compounds. In the case

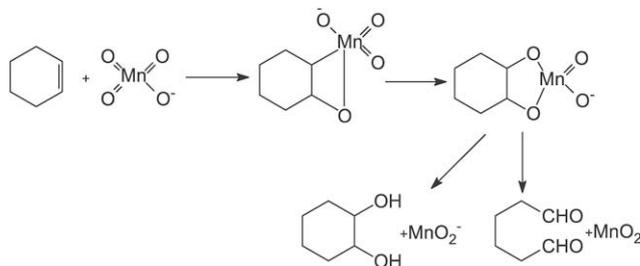


Scheme 23.

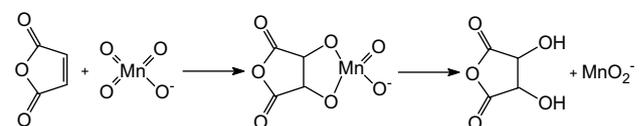


Scheme 24.

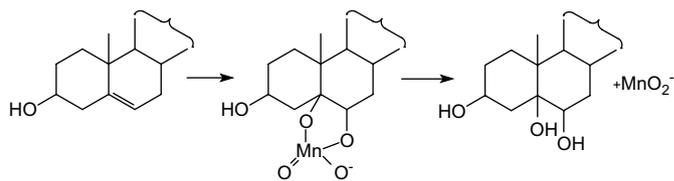
of some compounds containing cis-double bonds, e.g., cyclohexene, maleic anhydride and cholesterol,⁷⁵ however, diols have been observed as the products (Schemes 25–27).



Scheme 25.



Scheme 26.

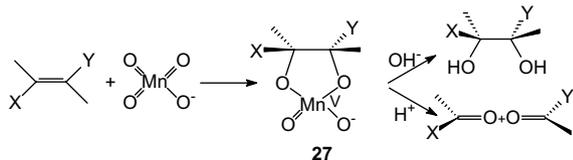


Scheme 27.

4. Intermediates during alkene oxidation in aqueous/organic media

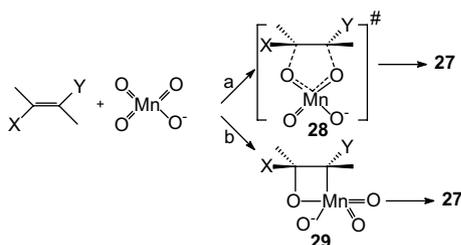
There has been much debate regarding the reaction of alkenes with permanganate in aqueous as well as organic media as far as the reaction intermediate is concerned. Mechanisms have been proposed with a five-membered intermediate resulting from a [3+2] cycloaddition pathway and, at the same time, there have also been propositions that the reaction proceeds through a [2+2] cycloaddition path, resulting in a metallo-cyclooxetane intermediate.

It has been widely accepted that permanganate ion (MnO_4^-) reacts with alkenes in a cycloaddition to form the transient cyclic manganese(V) ester intermediate **27**, which subsequently decomposes into a 1,2-diol or carbonyl compounds, depending upon the reaction conditions (Scheme 28).^{16,18,19,35,76}



Scheme 28.

Two different pathways, both of which lead to the Mn(V) intermediate **27**, have been proposed.⁷⁷ The [3+2] pathway a in Scheme 29 involves a concerted attack of the oxygen atoms on the unsaturated carbons and proceeds via a five-membered cyclic transition state **28**.^{1,78} This mechanism also receives support from the theoretical proposition based on the frontier molecular orbital (FMO) theory⁷⁹ and the Zimmerman treatment.²⁷ The other mechanism, pathway b,⁸⁰ in which a four-membered organometallic intermediate **29** is formed first via a [2+2] cycloaddition and then rearranges to **27**, is based on a general proposal by Sharpless et al.²¹ for the reactions between alkenes and oxo transition-metal species.

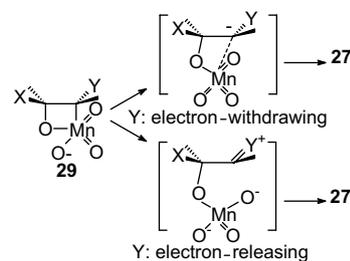


Scheme 29.

Many of the recent theoretical and experimental studies support the [3+2] cycloaddition mechanism.⁸¹ In connection with the ambiphilic reactivity of permanganate ion, Lee and Brown⁸² have put forward an explanation that assumes the occurrence of two different ionic transition states in the [2+2] cycloaddition pathway, depending upon the electronic nature of the substituent on the alkenes (Scheme 30).

Semiquantitative FMO analysis of the substituent effects on permanganate oxidation of aryl-substituted alkenes by assuming the concerted [3+2] cycloaddition model and newly introduced rate equations derived from the general perturbation equation by approximations based on the FMO theory has been used to reproduce Hammett plots theoretically supporting the [3+2] cycloaddition mechanism.^{83,84}

Strassner et al.^{85,86} used the density functional calculations, which strongly favour the [3+2] pathway for permanganate oxidations under basic conditions. No direct interaction of the



Scheme 30.

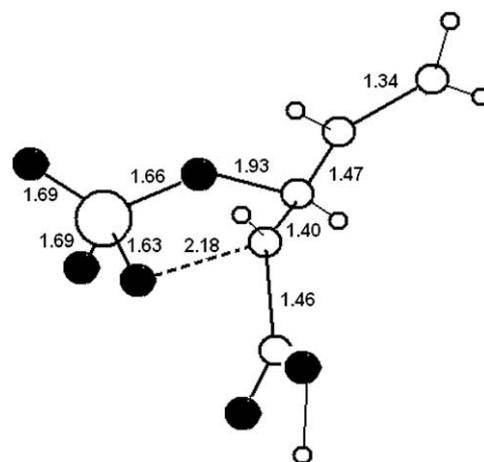
transition metal with the alkene is necessary to explain the different kinetic isotope effects for both of the C atoms of the olefinic double bond. The permanganate transition structure with ethene is nearly the same as that for OsO_4 , and differences in the substituent effects may be attributed to charge differences between the reagents.

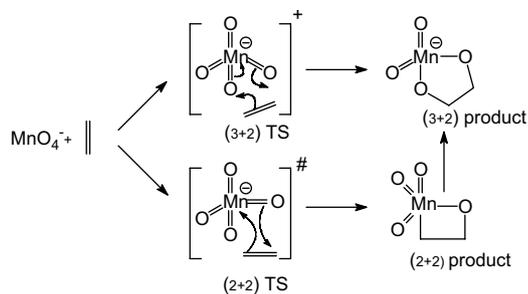
The calculated transition state shown in Figure 1 is very asynchronous. One C–O-forming bond is 0.23 Å longer than the other. The anionic species acts as a nucleophile, with the shorter bond, to the carbonyl group. The reaction is still concerted, with the average bond length equal to the bond length of the synchronous reaction of permanganate with ethylene.

Scheme 31 shows the two proposed pathways.²¹ The stepwise mechanism proceeds via a [2+2] transition state (TS) and a metallooxetane ([2+2] product), which is supposed to rearrange to a cyclic ester ([3+2] product) before the hydrolysis takes place, while the mechanism via the [3+2] transition state is expected to lead directly to the [3+2] product. Hydrolysis of the intermediate is generally accepted to give rise to diols. The density functional theory calculations strongly favour the [3+2] pathway for permanganate oxidations without the necessity of any direct interaction of the transition metal with the alkene to explain the kinetic data.

5. Oxidation of other functionalities in aqueous media

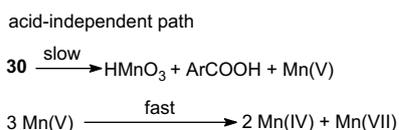
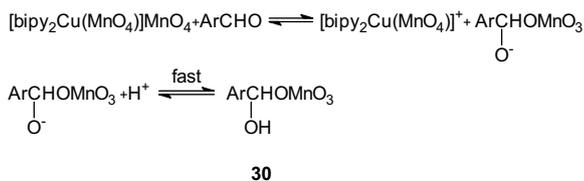
Bis(2,2'-bipyridyl)copper(II) permanganate (BBCP) has been used as a mild and selective oxidant.^{87,88} In aqueous acetic acid, substituted benzaldehydes were oxidized to the corresponding benzoic acids using this oxidant.⁸⁹ The cleavage of the aldehydic C–H bond in the rate-determining step was confirmed by the presence of a substantial kinetic isotope effect. The small magnitude of ρ , which represents the electronic demand at the reaction center, indicates a less pronounced charge separation in the

Figure 1. TS geometry for [3+2] addition to *trans*-2,4-pentadienoic acid.⁸⁵

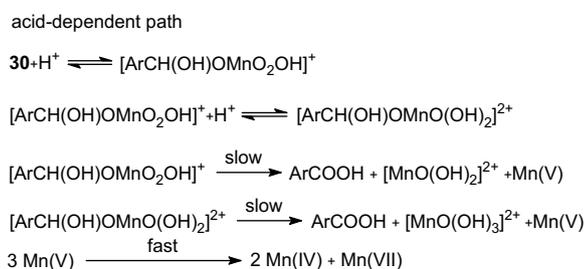


Scheme 31.

activated complex and suggests a mechanism involving a hydride-ion transfer via a permanganate ester. Suitable mechanisms were proposed (Schemes 32 and 33), indicating nucleophilic attack of BBCP on the aldehyde to form an anion, which is rapidly protonated to form a permanganate ester (**30**), which then decomposes in the rate-determining step to yield the ultimate products. The formation of **30** occurs in both acid-independent and acid-dependent pathways. The rate-determining decomposition of an ester intermediate is supported by the steric acceleration due to the presence of an *ortho*-substituent in the substrate. As the sp^3 carbon atom in the ester changes to an sp^2 carbon atom in the activated complex, there is an increase in steric relief with increasing crowding at the reaction center. The formation of an electron-deficient reaction center in the activated complex indicates that the cleavage of the C–H bond proceeds after the formation of the C=O bond.



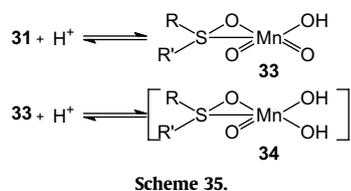
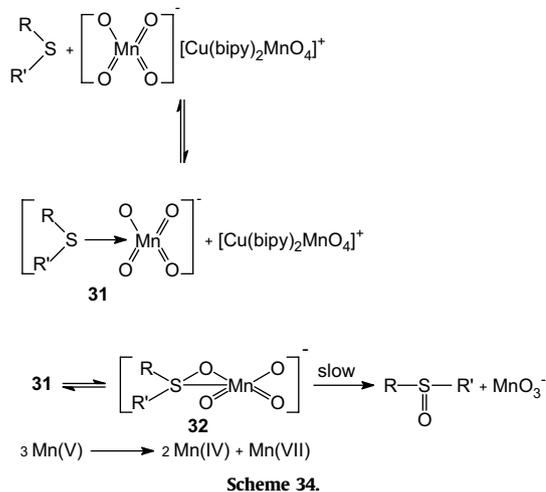
Scheme 32.



Scheme 33.

The oxidation of sulfide compounds by BBCP afforded the corresponding sulfoxides.⁹⁰ The most logical mode of interaction between sulfides and BBCP is a nucleophilic attack at the metal. Donation of an unshared pair of electrons to an empty d-orbital on the metal results in the formation of an intermediate with a coordinate covalent bond (**31**). The initially formed intermediate is likely to undergo a further

rapid reaction in which the incipient oxide and sulfonium ions bond to form a highly structured intermediate (**32**) that rearranges to give a sulfoxide and manganese(V) (Scheme 34). The observed acid catalysis is, perhaps, due to successive protonation of the intermediate **31** producing the protonated species **33** and **34**, prior to further reactions (Scheme 35).



The oxidation of sulfides to sulfoxes by permanganate⁹¹ in anhydrous acetone is only possible if Lewis acids such as ferric chloride or zinc acetate are present.⁹² The essential role of the Lewis acids in these reactions is exemplified by the observation that thioanisole is converted into the corresponding sulfoxide in 100% yield when treated with potassium permanganate and ferric chloride in acetone for 30 min at -25°C , while, in the absence of ferric chloride or other Lewis acids, only a trace of sulfoxide is produced under identical conditions.

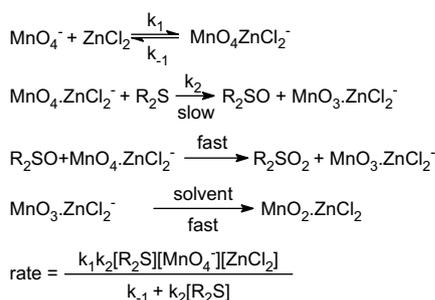
Three possibilities exist for Lewis acids to exert a catalytic effect on the oxidation of sulfides by permanganate:

1. It is known that sulfoxides are more rapidly oxidized than sulfides under certain conditions.^{80,91,93} Hence, a Lewis acid could be complexed with sulfide ($\text{R}_2\text{S} + \text{FeCl}_3 \rightarrow \text{R}_2\text{S}^+ - \text{FeCl}_3^-$) making it more sulfoxide-like ($\text{R}_2\text{S}=\text{O} \leftrightarrow \text{R}_2\text{S}^+ - \text{O}^-$), which provides a plausible explanation for the observed catalysis (Scheme 36).
2. A reaction between permanganate and a Lewis acid is similar to the reaction between permanganate and Brønsted acids, which results in the formation of permanganic acid HMnO_4 ,⁷² a strong oxidant, responsible for the observed acid catalysis, as in many permanganate oxidations (Scheme 37).^{19,94,95}
3. An intermediate formed between the oxidant and the reductant may undergo oxidative decomposition with the assistance of a Lewis acid (Scheme 38).

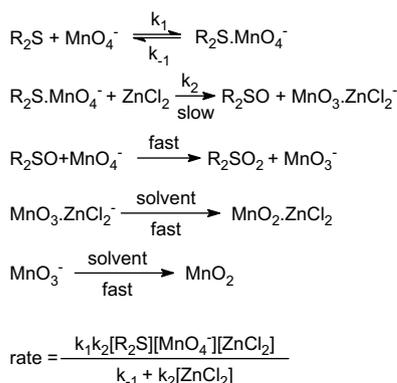
The kinetic study conclusively shows the catalytic effect of Lewis acids on the oxidation of sulfides and sulfoxides by permanganate



Scheme 36.



Scheme 37.

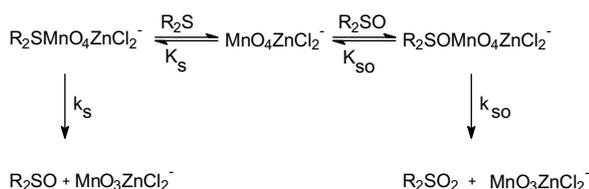


Scheme 38.

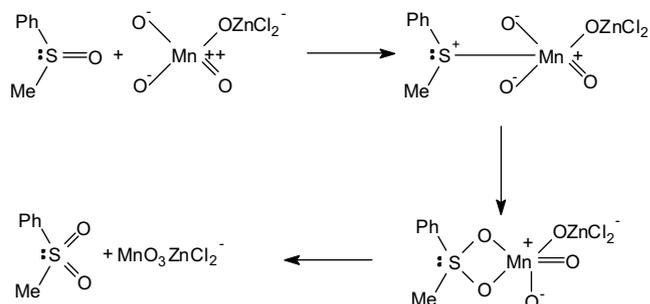
to be due to the complexation of the oxidant with the catalyst prior to reaction with the reductant, as per the second possibility. Substituent and isotope effect studies do not support a single-electron-transfer mechanism for the oxidation of sulfides by permanganate.

Permanganate reacts faster with sulfides than sulfoxides when the individual rates are measured, but, in competitive reactions, sulfoxides are found to react preferentially (Scheme 39).

The mechanism that is consistent with all of the available experimental evidence is summarized in Scheme 40.

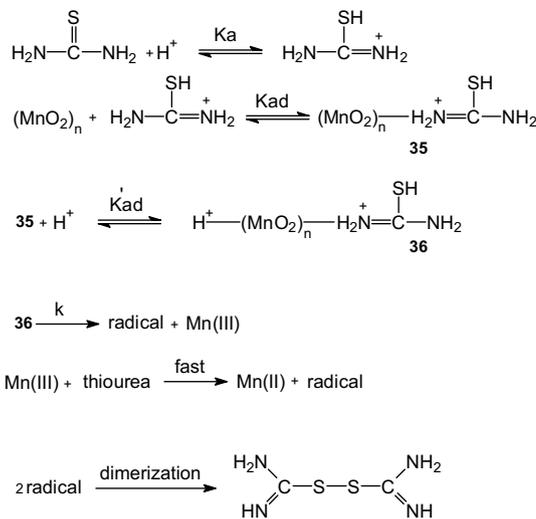


Scheme 39.



Scheme 40.

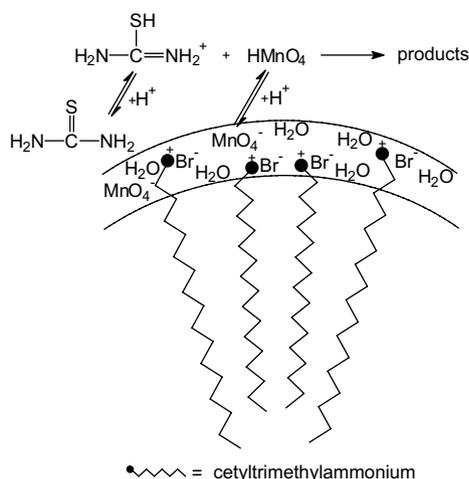
The oxidation of thiourea by permanganate was studied in dilute perchloric acid solution.⁹⁶ The reduction of permanganate by thiourea proceeds through the rapid formation of colloidal MnO₂ as an intermediate. On the basis of the experimental results, the mechanism shown in Scheme 41 has been proposed.



Scheme 41.

As illustrated in this reaction scheme, thiourea and hydrogen ion undergo stepwise adsorption on the surface of colloidal MnO₂ through an electrostatic interaction to afford **35** and **36**, respectively. The fourth step is a one-electron oxidation–reduction rate-determining step, wherein **36** dissociates resulting in the formation of Mn(III), another intermediate, during the course of the reaction. With the use of excess of thiourea over permanganate, further oxidation of the intermediate occurs to yield Mn(II) as the final product. In the presence of externally added Mn(II), the reaction system becomes more complicated, due to the oxidation of Mn(II) by permanganate.

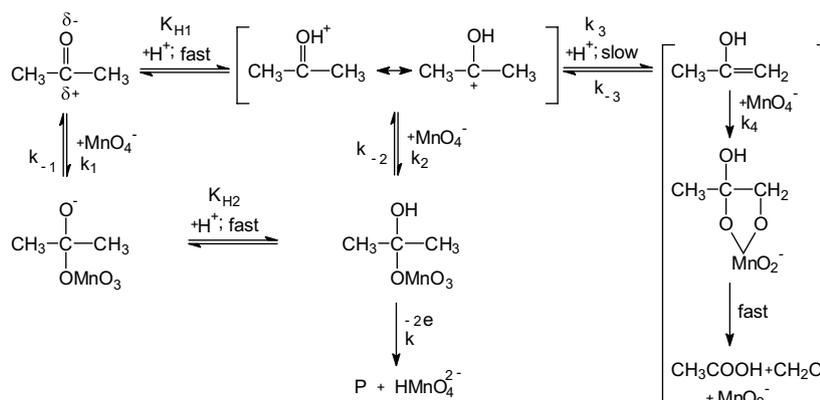
When the oxidation of thiourea is carried out in a micellar medium using the cationic surfactant CTAB, however, the reaction is found to proceed more slowly in the micellar phase than in the bulk phase.⁹⁷ The inhibitory effect of CTAB has been explained in terms of the Menger–Portnoy model, according to which only one reactant, i.e., MnO₄⁻, proceeds towards the cationic micellar phase. The second reactant, i.e., thiourea, exists only in the water phase, since it has a positive charge and therefore undergoes repulsion by the micellar medium. Electrostatic interaction–repulsion is responsible for the inhibitory role of CTAB. The orientation and stabilization of the reactants by cationic CTAB micelles can therefore be visualized as represented in Scheme 42.



Scheme 42.

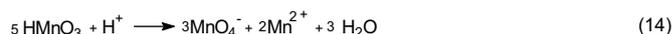
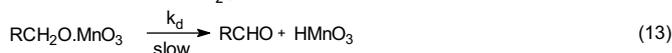
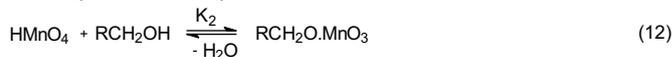
During the oxidation of ketones in acidic media, enolization of the ketones is generally assumed to be the rate-determining step for various oxidants,^{98–105} although, in some cases, radical mechanisms have been proposed.^{106–109} There are also several different proposals for the mechanism in the case of permanganate.^{110–114} Banerji et al.^{112,113} attributed the rate dependence of ketone oxidation on hydrogen ion concentration both to protonation of the permanganate ion and to enolization, while Sen et al.¹¹⁴ assume rapid formation of an intermediate complex, the slow decomposition of which is the rate-determining step. As for permanganate, since Wiberg and Geer¹¹⁵ published their comprehensive study on acetone oxidation in alkali, the decisive role of enolate anion has also been accepted in various reviews.^{80,116} Simon-Trompler et al.¹¹⁷ suggested that the overall oxidation rate and the composition of the intermediates cannot be in accordance with a mechanism based on enolization, since the reaction is first order in permanganate concentration.

The permanganate ion is ambiphilic in nature, since the empty d-orbitals on the central metal are electrophilic whereas the electron pairs on the oxygen atoms are of nucleophilic character.^{118,119} Ketones are reactive to nucleophilic addition, as their carbonyl C-atom is positively polarized, and thus is further enhanced by proton addition on the carbonyl O-atom. Consequently, acid catalysis suggests that the attack of the permanganate ion is not by electrophilic addition on the double bond of the enol, but by nucleophilic addition on the carbon atom of the carbonyl group, resulting in an intermediate permanganate ester, as shown in Scheme 43.



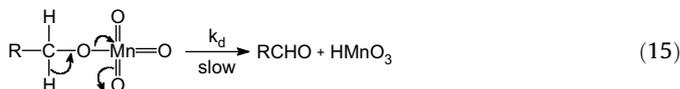
Scheme 43.

The reducing behaviour of methanol and ethanol towards permanganate in a perchloric acid medium has been investigated in the absence and presence of the surfactant Tween-20.¹²⁰ Permanganic acid is the chief oxidizing species, which combines with the alcohol to form an intermediate complex followed by decomposition in the rate-determining step to produce the corresponding aldehyde and Mn(V). The latter disproportionates¹²¹ to Mn(VII) and Mn(II) in the fast step (Eqs. 11–14, Scheme 44).

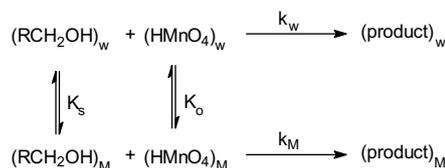


Scheme 44.

The decomposition of the intermediate complex $\text{RCH}_2\text{O} \cdot \text{MnO}_3$ (Eq. 15) may be thought to occur as follows:



In a micellar system, with Tween-20 as the substrate, both the oxidant and the alcohol are found to be partitioned between the aqueous and the micellar pseudophase. Thus, the reaction may proceed according to Scheme 45.



Scheme 45.

With an increase in the surfactant concentration, the overall enthalpy of activation is found to decrease, while the entropy of activation becomes more and more negative. This may be attributed to the fact that with an increase in the surfactant concentration, the 3D-structure of water gradually decreases and free H_2O molecules are formed. In Eq. 15, the transition state needs hydration for efficient electron transfer (Fig. 2).

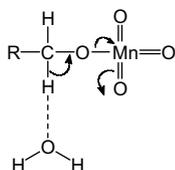
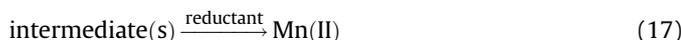
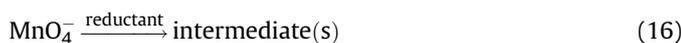


Figure 2. Transition state reaction between Tween-20 and permanganate.

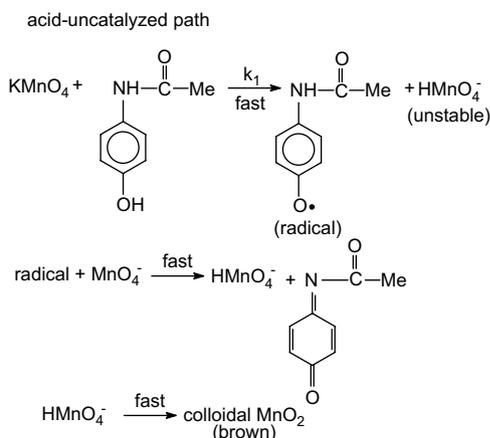
In spite of a decreasing enthalpy of activation, the rate decreases with increasing concentration of the surfactant, indicating that the reaction is entropy rather than enthalpy controlled.

It has become clear that when permanganate and organic substrates are initially present in excess, the reaction involves two steps (Eqs. 16 and 17).^{122–126}

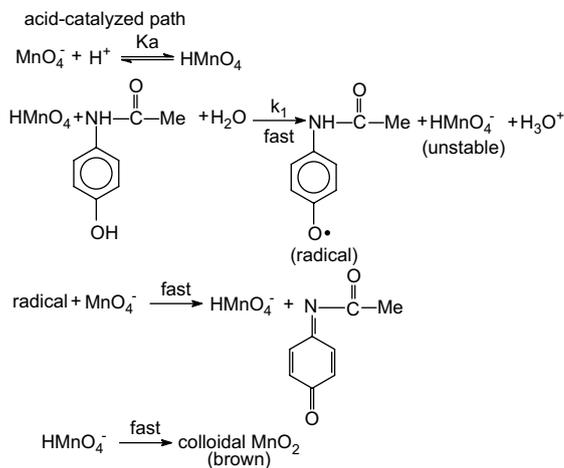


In alkaline or weakly acidic solution, permanganate changes to Mn(IV), while in a strongly acidic medium, permanganate is further reduced, forming Mn(II). It has been reported by different research groups that the intermediate Mn(IV) species could be H_2MnO_4 , H_2MnO_3 or a water-soluble colloidal MnO_2 .^{17,19,77,127} The MnO_2 appears practically only after MnO_4^- has completely disappeared from the system. In the case where permanganate serves as an oxidizing agent in an acid medium, the possible intermediate species are Mn(VI), Mn(V), Mn(III) and Mn(IV). On the other hand, Mn(II), the ultimate reaction product, acts as an autocatalyst. Therefore, the MnO_4^- oxidations provide chemical kinetics with a challenging mechanism, due to the ability of Mn to exist in a multitude of oxidation states.

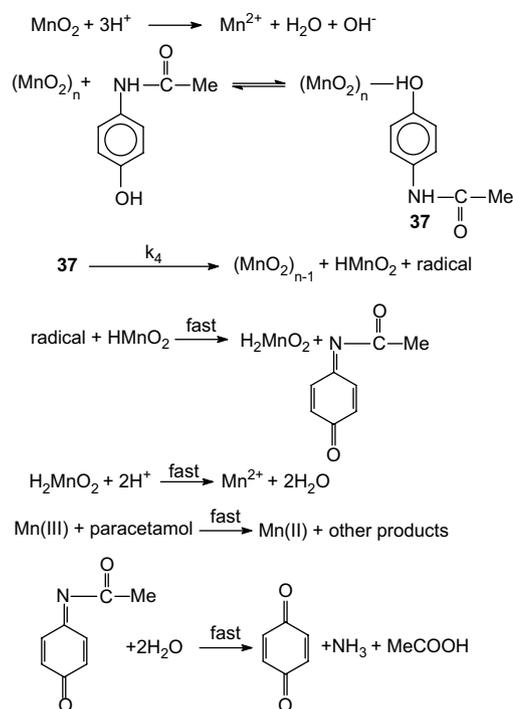
During the oxidation of paracetamol, colloidal MnO_2 was formed in the presence as well as in the absence of acid.¹²⁸ Colloidal MnO_2 was, however, unstable in the presence of acid, due to its reaction with acid producing Mn(II). The formation and reaction of MnO_2 during the oxidation of paracetamol can be explained as shown in Schemes 46, 47 and 48. In the reaction process, paracetamol forms a complex (37) with MnO_2 , which decomposes by a one-step, one-electron oxidation–reduction mechanism to Mn(III) and other products (Scheme 48).



Scheme 46.



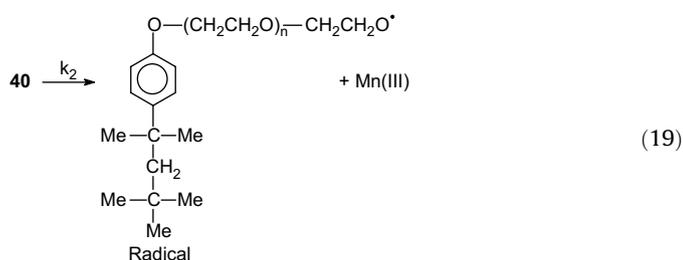
Scheme 47.



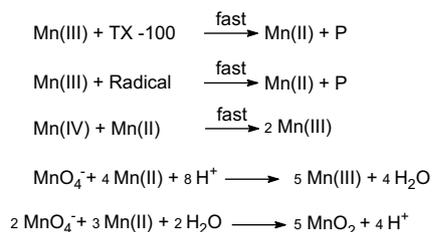
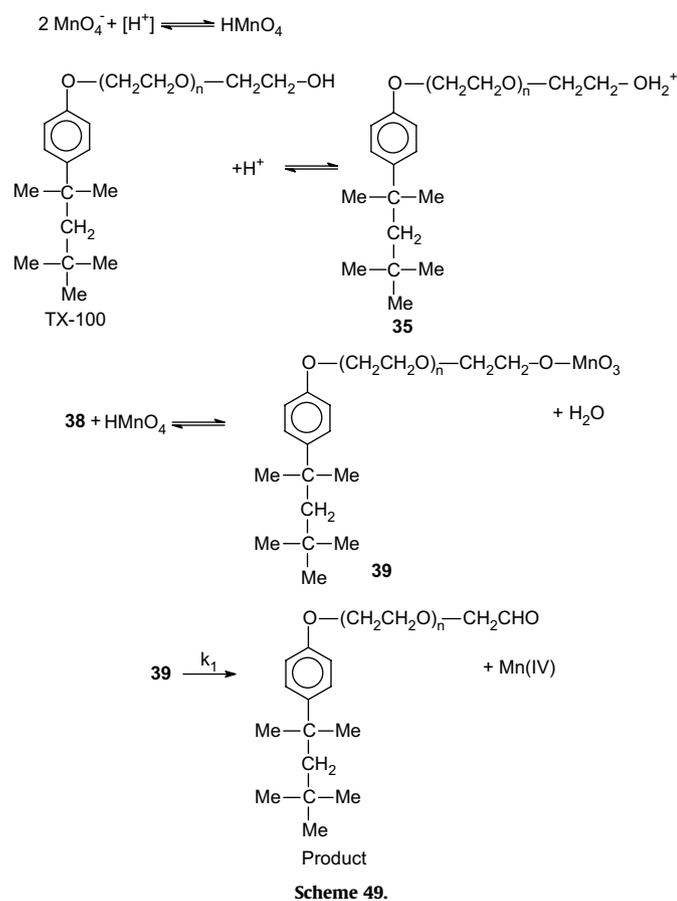
Scheme 48.

Permanganate in the presence of HClO_4 is able to degrade the polyoxyethylene chain of the non-ionic surfactant Triton X-100 [4-(1,1,3,3-tetramethylbutyl)phenyl polyethylene glycol: TX-100].¹²⁹ The oxidation kinetics of TX-100 with permanganate proceed with a slow rate initially, followed by fast rate. The time at which deviation occurs decreases with an increase of each in $[\text{H}^+]$, $[\text{TX-100}]$, $[\text{MnO}_4^-]$ and temperature. The oxidation process is found to be autocatalyzed by soluble colloidal MnO_2 and Mn(III) (formed as the reaction intermediates) and Mn(II) (formed as the reaction product). In a strongly or moderately acidic medium, MnO_4^- ion is protonated to afford HMnO_4 , which is a powerful oxidant. Based on the experimental results, two mechanisms (Schemes 49 and 50) can be proposed.

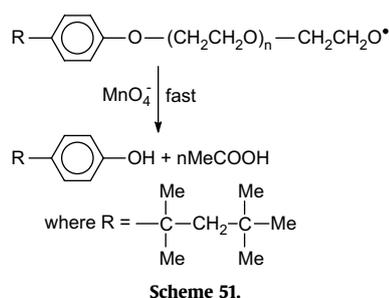




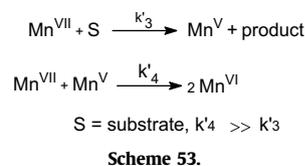
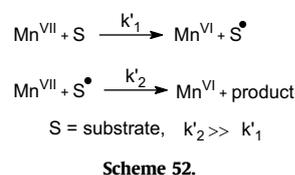
It is worth mentioning that the mechanism shown in Scheme 49 is valid only for higher $[\text{H}^+]$ (first order with respect to $[\text{TX-100}]$), which shows formation of a 1:1 TX-100–Mn(VII) complex (39) from HMnO_4 and protonated TX-100 species (38). In Scheme 50, the first step (Eq. 18) represents the formation of another complex (40) with the colloidal MnO_2 and TX-100. The second step (Eq. 19) is the rate-determining step of the autocatalytic pathway to yield Mn(III) as an intermediate and, therefore, Mn(III) would also participate in the reaction as an autocatalyst.



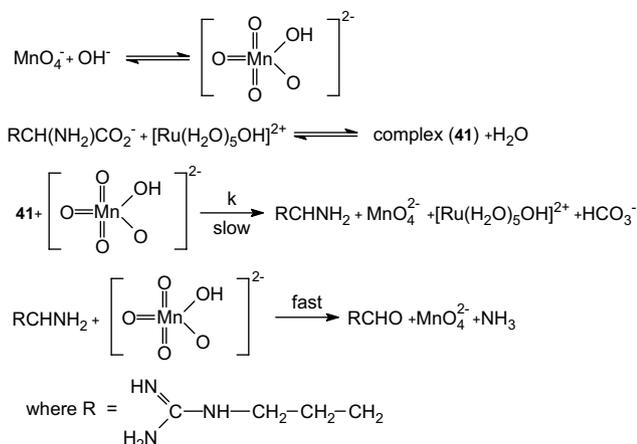
HClO_4 has no effect on the cloud point of the micellar solution, while the addition of permanganate into the same solutions has a drastic effect on the cloud point. This is a clear indication that the decrease in the cloud point is due to the degradation of the polyoxyethylene chain of TX-100, which, in turn, changes the nature of the micelles. Reaction mixtures become turbid at 30 °C as scission reduces the HLB below the critical value. The free radical generated in the oxidation of TX-100 by permanganate undergoes cleavage¹³⁰ at the C–O bond of the polyoxyethylene chain of TX-100, which, in turn, decreases the cloud point of this surfactant. On the basis of the decrease in cloud point and a previous hypothesis,¹³⁰ the additional step (kinetically indistinguishable) shown in Scheme 51 cannot be ruled out, especially in the presence of a strong oxidizing agent, such as permanganate. The cloud point of TX-100 decreases sharply in the presence of MnO_4^- with time.



Halligudi et al.¹³¹ studied the kinetics of the Ru(III)-catalyzed oxidation of L-arginine by alkaline permanganate using a rapid kinetic accessory. In strong alkali, the stable reduction product^{132,133} is generally the manganate ion, MnO_4^{2-} . No mechanistic information is available to distinguish between a direct one-electron reduction to Mn(VI) (Scheme 52) and the formation of a hypomanganate ion in a two-electron reduction, followed by rapid oxidation (Scheme 53).¹³⁴ A microscopic amount of ruthenium(III) is sufficient to catalyze the reaction in the alkaline medium and a variety of mechanisms are possible.¹³⁵



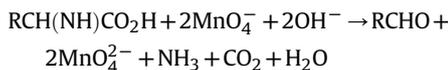
Halligudi et al.¹³¹ proposed a suitable reaction sequence according to the results of their experimental verification, where the alkali combines with permanganate to form an alkali-permanganate species $[\text{MnO}_4 \cdot \text{OH}]^{2-}$ in a pre-equilibrium step.¹³⁶ L-Arginine reacts with Ru(III) species to form a complex (41), which reacts with alkali-permanganate species in a slow step to form a free radical derived from decarboxylated L-arginine, which further reacts with another permanganate species in a fast step to yield the products. Since the reaction orders are the same in both stages, a single mechanism is proposed (Scheme 54).



Scheme 54.

When L-leucine and L-isoleucine were oxidized in the presence of a Ru(III) catalyst, the reaction was found to be similar to that with L-arginine.¹³⁷ The results suggest the formation of a complex between the amino acid and the hydroxylated Ru(III) species (as previously described during L-arginine oxidation), which reacts further with the alkaline permanganate species in a rate-determining step, resulting in the formation of a free radical, which again reacts with the alkaline permanganate species in a subsequent fast step to yield the products. Of the two amino acids, leucine is oxidized at a faster rate than isoleucine.

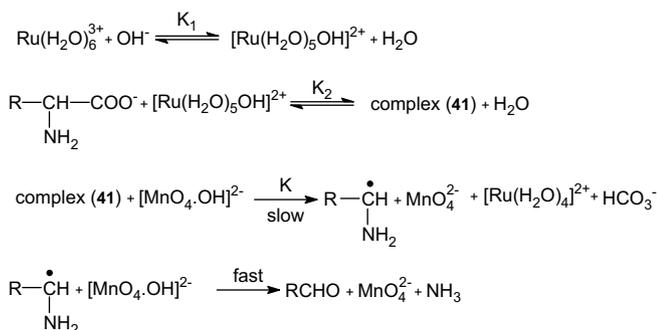
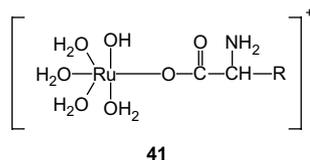
The stoichiometry of the reaction is found to be as follows:



where R = $-\text{CH}_2\text{CHMe}_2$ for L-leucine and R = $-\text{CHMeEt}$ for L-isoleucine.

It is interesting to note that the oxidant species $[\text{MnO}_4^-]$ in this case requires $\text{pH} > 12$, below which the system becomes disturbed and the reaction proceeds further to give a reduced oxidation product such as Mn(IV), which slowly develops a yellow turbidity. Hence, it becomes apparent that, in carrying out this reaction, the role of pH in the reaction medium is crucial. It is also noteworthy that, under the conditions studied, the reaction occurs in two successive one-electron reduction steps (Scheme 55), rather than a two-electron reduction in a single step.

The probable structure of the complex (41) is



Scheme 55.

KMnO_4 is well known as a powerful chemical probe for numerous applications in biological fields, particularly for those used in conformational studies of DNA. The KMnO_4 assay provides essential information for understanding biochemical processes such as sequencing techniques, footprinting assays for transcriptional studies, an interference method for hormone receptor binding assays as well as DNA conformational studies of Z-DNA, Z-Z junctions, hairpins, curvatures, short nucleotide base repeats, binding of intercalators and groove binders, etc. and for detecting aberrant DNA, which is associated with many genetic diseases.¹³⁸

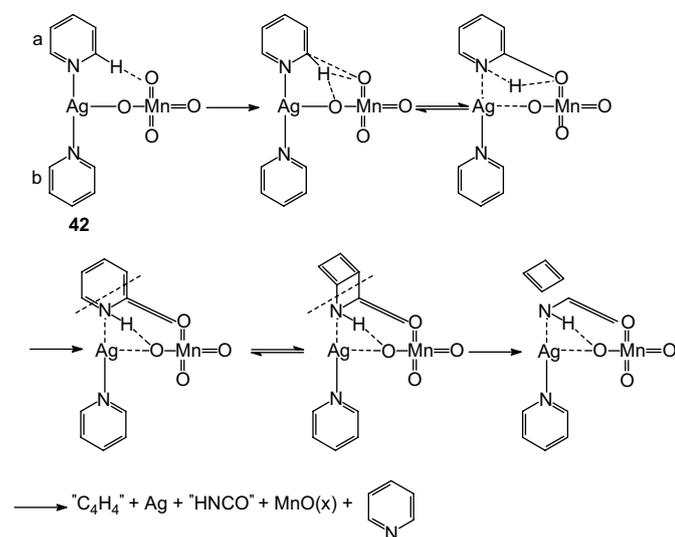
Some free nucleotide bases were oxidized using permanganate in aqueous solutions of tetraethylammonium chloride.¹³⁹ The reaction was found to be highly selective towards thymine and uracil, less so with cytosine, very little reaction was noted on guanine and no reaction on adenine. Hence, KMnO_4 oxidation provides a fundamental background for the identification of oligonucleotides containing single base mismatches by chemical means.¹⁴⁰ It has been successfully applied to detect single base changes and mutations in DNA (chemical cleavage of mismatch method, CCM), as well as other types of base damage (8-oxoguanine and thymine dimers).

Permanganate oxidation reactions of thymine acetic acid were investigated in solution and in the solid phase.¹⁴¹ The spectral data showed the formation of a stable organomanganese intermediate, which was responsible for the rise in the absorbance at 420 nm. This result enables an unambiguous interpretation of the absorbance change at 420 nm, as the intermediate permanganate ions could be isolated on the solid supports.

Hassan et al.¹⁴² detected short-lived hypomanganate(V), $[\text{KCAR}-\text{Mn}(\text{V})\text{O}_4^{3-}]$, and manganate(VI), $[\text{KCAR}-\text{Mn}(\text{VI})\text{O}_4^{2-}]$, intermediates spectrophotometrically through the oxidation of K-carrageenan (KCAR) by potassium permanganate in alkaline solutions of $\text{pH} \geq 12$.

Besides potassium permanganate, silver permanganate complexes have also found applications in oxidation. Three pure compounds have been isolated from a silver permanganate/pyridine/water system, namely $[\text{Agpy}_2]\text{MnO}_4$ (42), $[\text{Agpy}_{2.25}]\text{MnO}_4$ (43) and $[\text{Agpy}_{2.5}]\text{MnO}_4$ or $[\text{Agpy}_2]\text{MnO}_4 \cdot 0.5\text{py}$ (44).¹⁴³ Presuming identical structural motifs for the $\text{Agpy}_2\text{MnO}_4$ blocks in 42, as found in its solvate 44 by single-crystal diffraction, $\alpha\text{-C-H}\cdots\text{O}-\text{Mn}$ H-bonded structures are responsible for a thermally induced low-temperature intermolecular redox reaction. The maximum evolution of pyridine and its degradation products takes place at maximum decomposition temperature. Thus, an intramolecular redox reaction between the coordinated pyridine ligand of the cation and the oxidizing permanganate anion of the complex occurs. Taking the presence of the free pyridine and its degradation products into consideration, the pyridine in complex 42 can be divided into two types. One type (a) is evolved in the first decomposition step as free pyridine and the other type (b) is released in a degraded form in the same decomposition step. The TG-MS profiles of the evolved pyridine and the pyridine oxidation products are the same. This confirms that the pyridine (a type) (Scheme 56) and the pyridine decomposition products (from pyridine b type) are formed in the same thermal decomposition step.

Considering (i) the thermal stability of the $[\text{Agpy}_2]^+$ cation ($T_{\text{dec}} > 147^\circ\text{C}$) with ClO_4^- , BF_4^- , NO_3^- and halide anions, (ii) the lack of oxygen evolution from permanganate ion of the compounds at the decomposition temperature and (iii) the simultaneous formation of pyridine and its oxidative degradation products in the same process, it has been established that the intramolecular redox reaction proceeds in the solid phase involving the permanganate ion and one of the coordinated pyridines (b type) of the $[\text{Agpy}_2]^+$ cation (Scheme 56). The oxidation of the evolved (a type) gas-phase pyridine can be excluded on the basis of (i) and (ii). In the case of compound 43, the same process can take place, with the amount of



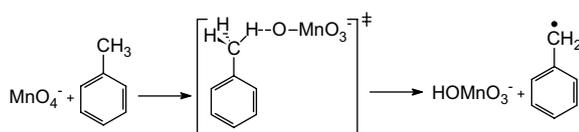
free evolved pyridine being greater [0.25 mol pyridine/mol of complex **43**] than in complex **42**.

Due to the presence of N=C–H...O=Mn structural motifs in compounds **42** and **44**, one of the pyridine rings is attached to the permanganate ion via hydrogen bonding, while the other has no connection with the permanganate ion. This experiment can be utilized for the molecular-level recognition of the pyridine rings in the (Agpy₂)⁺ cation of the pyridine–silver permanganate compounds.

6. Oxidation of other functionalities in organic media

Permanganate has been widely used as a strong, easily handled, readily available and versatile oxidant that reacts with alcohols, alkenes, aldehydes, saturated C–H bonds and other functionalities.^{19,28a,80,119,144} The lack of selectivity of permanganate is due, at least in part, to its ability to react readily by either one- or two-electron pathways, and its conversion into even stronger oxidants such as MnO³⁺.^{144c} The reaction pathway is influenced by solvent, pH, substrate and other variables, thus complicating the mechanistic understanding.

The use of organic solvents allows the substrate and solvent to be in the same phase and avoids some of the complications of aqueous permanganate reactions, such as decomposition at high pH,¹⁴⁵ autocatalysis at low pH,¹⁴⁶ involvement of water in the rate-determining step¹⁴⁷ and limited solubility of the organic substrates of interest.¹⁴⁸ There are reports of C–H bond oxidation by organic-soluble permanganate salts.^{36,37,39} Mayer et al.¹⁴⁹ carried out a mechanistic study during the oxidation of arylalkanes such as toluene, diphenylmethane, triphenylmethane, ethylbenzene, 9,10-dihydroanthracene, xanthene, etc. The first step in these reactions is abstraction of a hydrogen atom by permanganate, as observed in the related CrO₂Cl₂ reactions.¹⁵⁰ The occurrence of these reactions is a direct result of the strength of the O–H bond formed on addition of a hydrogen atom to the oxidant.^{147,150} The mechanism of the reaction is given in Scheme 57.



The rate-limiting step for these reactions is the transfer of H• from the substrate to a manganese oxo group. The enthalpies of activation correlate well with the strength of the C–H bond being cleaved, typical of H• abstraction by main group radicals such as *t*-BuOO•. This correlation includes primary, secondary and tertiary C–H bonds, with no evidence of any steric effects that would accompany the formation of a metal–carbon bond.

The oxidation kinetics of C₄–C₁₀ aliphatic aldehydes by quaternary ammonium permanganates, R₄NMnO₄ (R=Et, Bu, Oct), in dichloromethane are reported with special regard to the colloidal Mn(IV) intermediate.¹⁵¹ Dynamic light scattering measurements have shown that colloidal particles appear at the beginning of the reactions, their dimensions being around 250 nm and having differing polydispersities, which were largest for the reaction mixture with tetraethylammonium permanganate. The stability of the systems was directly proportional to the alkyl chain length of the tetraalkylammonium permanganate used. The absorption spectrum recorded at the end of the reactions (after complete permanganate consumption) showed a uniform increase of absorbance with decreasing wavelength, which is consistent with the Rayleigh law for light scattering.^{62,63}

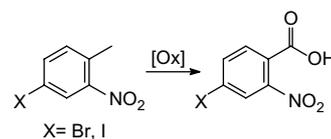
Additional evidence for the colloidal nature of the brown-yellow intermediate of the permanganate reduction was obtained from simultaneous monitoring of the reacting solution at two wavelengths, 418 and 526 nm. Permanganate exhibits its highest absorbance peak at 526 nm, whereas it is almost transparent at 418 nm. As a result it has been shown that the relationship presented in Eq. 20 is valid:^{22,69,127}

$$A(526) = \varepsilon_R^{526} p C_0 - [(\varepsilon_R^{526} - \varepsilon_P^{526}) / \varepsilon_P^{418}] A(418) \quad (20)$$

where *p* is the optical pathlength, C₀ is the initial permanganate concentration and ε_R and ε_P are the extinction coefficients of the reactant (permanganate) and the product (colloidal MnO₂), respectively.

The A(526) versus A(418) plots based on Eq. 20 are very useful in kinetic experiments when colloidal MnO₂ is (i) behaving as a stable species, (ii) being reduced to Mn^{II} and (iii) coagulating.¹⁵² In the case of (i), Eq. 20 leads to a linear relationship between A(526) and A(418), in the case of (ii) it provides a plot showing a concave-downward curvature and in the case of (iii), the A(526) versus A(418) relationship leads to a plot showing a concave-upward curvature.

4-Halo-2-nitrobenzoic acids can be obtained by oxidation of 4-halo-2-nitrotoluene with tetrabutylammonium permanganate (TBAP) in pyridine.¹⁵³ A significant induction period was observed at room temperature, the cause of which was unclear, and the vigorous exothermic reaction presents the risk of a run-away reaction. By control feeding cold TBAP into the reaction mixture at 60 °C, the initiation process is managed and the reaction is safely performed on a multigram scale (Scheme 58).



The kinetics of oxidation of 1-octene and heptanal by 18-crown-6-solubilized KMnO₄ in benzene and dichloromethane (DCM) has been investigated.¹⁵⁴ In benzene, the oxidation of 1-octene is first order with respect to the oxidant and zero order

with respect to the substrate, whereas in DCM, the reaction is first order with respect to both the substrate and the oxidant. The reaction of heptanal followed different kinetics, being first order with respect to both the substrate and the oxidant, regardless of whether benzene or DCM was employed as the solvent.

The rate laws for the oxidation of 1-octene in benzene and DCM represented by Eqs. 21 and 22 have been proposed:

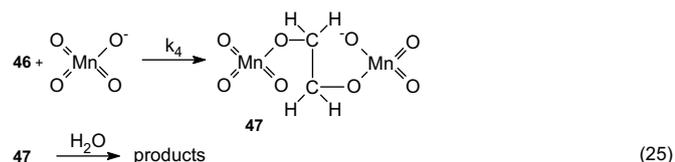
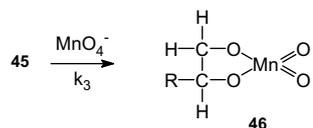
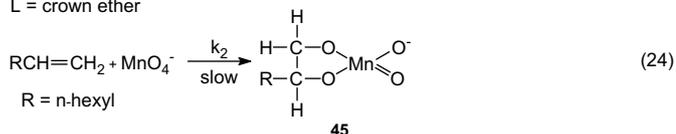
$$\text{Rate} = k_{\text{obs}} [\text{MnO}_4^-] \text{ (in benzene)} \quad (21)$$

$$\text{Rate} = k_{\text{obs}} [\text{MnO}_4^-] [1\text{-octene}] \text{ (in CH}_2\text{Cl}_2) \quad (22)$$

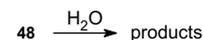
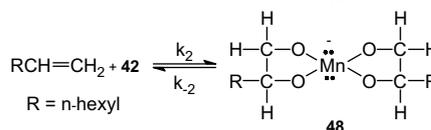
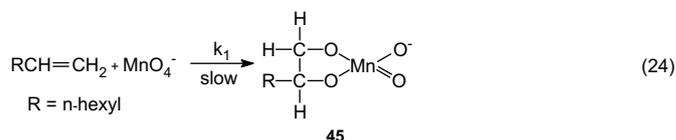
A possible pathway for 18-crown-6-oxidized 1-octene in benzene is presented in Scheme 59. In this mechanism, the dissociation of the complex ion pair (LKMnO₄) to give the complex cation (LK⁺) and the free anion (MnO₄⁻) is assumed to occur in a slow step (Eq. 23). This has been attributed to the non-polar nature of benzene. In the next step (Eq. 24), the permanganate ion couples to the 1-octene to yield the cyclic five-membered manganate(V) diester **45**, and is also the first step in Scheme 60. A similar behaviour has already been proposed for the permanganate ion in an aqueous medium.⁴⁸ The intermediate **45** is then oxidized by another free permanganate ion, via a charge-transfer process, to yield the electrically neutral species **46**. A third free permanganate ion will then couple with **46** to yield the acyclic intermediate **47**, which, in turn, yields the heptanoate upon hydrolysis by water, via Eq. 25. This mechanism accounts for the fact that 3 mol of permanganate ion is needed to oxidize 1 mol of 1-octene. Furthermore, the mechanism explains why, in benzene, the reaction is first order with respect to permanganate and zero order with respect to octene. In methylene chloride, a different pathway is presented in Scheme 60, in which one equivalent of the permanganate ion oxidizes 2 equiv of octene. As mentioned earlier, the first step (Eq. 24) in this scheme involves coupling of the olefin to the permanganate ion to yield intermediate **45** and is assumed to be the rate-controlling step. This is followed by a fast step resulting in the formation of the non-polar intermediate **48**. The mechanism thus presented for the oxidation of 1-octene in DCM accounts for the observed stoichiometry and kinetics.



L = crown ether



Scheme 59.

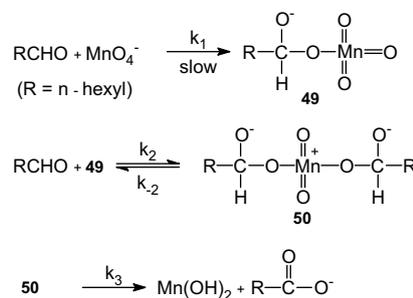


Scheme 60.

The measured rate law for the oxidation of heptanal in both benzene and methylene chloride is represented by Eq. 26.

$$\text{Rate} = k_{\text{obs}} [\text{permanganate}] [\text{heptanal}] \quad (26)$$

The mechanism that best explains the kinetics is presented in Scheme 61. The permanganate ion adds to 1-heptanal in a slow step, yielding the permanganate ester **49**. The intermediate **49** then reacts with another 1-heptanal molecule to yield the diester **50**. Upon hydrolysis, **50** gives the heptanoate anion as the final product.



Scheme 61.

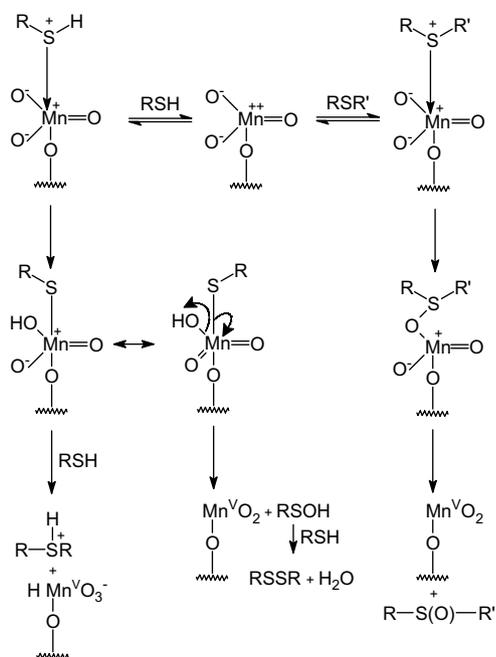
7. Oxidation on solid supports, and in solvent-free and heterogeneous media

Adsorption onto solid supports is known to cause a change in the chemical properties of many reagents.^{144b,155} One of the most striking examples of such a change in chemical reactivity that has been reported to date is with the well-known oxidant, potassium permanganate.¹⁵⁶ When used in solution, permanganate reacts rapidly with alkenes, converting them into diols, ketols or cleavage products.^{19,35} When permanganate is adsorbed onto an inert solid support and used as a heterogeneous oxidant, however, some alkenes are resistant to oxidation and may actually inhibit the rate of oxidation of other reductants.¹⁵⁷

The use of solid supports has become popular, due to their characteristic properties such as enhanced selectivity and reactivity, straightforward workup procedure, milder reaction conditions and associated ease of manipulation.¹⁵⁵ Adsorption of potassium permanganate¹⁵⁶ on the surface of solid supports changes the selectivity and reactivity in various reactions.^{80,158} The uses of potassium permanganate supported on alumina in the oxidation of urazoles to triazolinediones,¹⁵⁹ dehydrogenation of 2-imidazolines to their corresponding imidazoles,¹⁶⁰ oxidation of alcohols to aldehydes and ketones under solvent-free conditions,¹⁶¹ oxidation of sulfides and thiols to sulfoxides and disulfides,¹⁶² oxidative deprotection of trimethylsilyl and tetrahydropyranyl ethers and of ethylene acetals to the corresponding carbonyl

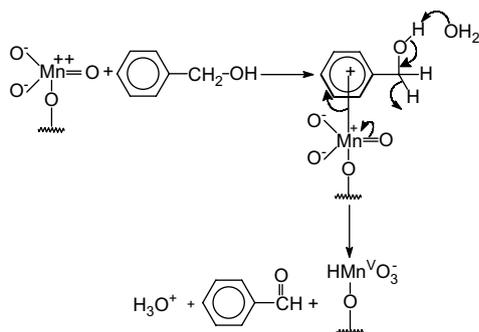
compounds,¹⁶³ conversion of oximes into carbonyl compounds under solid-state conditions¹⁶⁴ and chemical cleavage reactions of DNA on silica support¹⁶⁵ have been reported. There has also been increasing interest in reactions that proceed in the absence of solvents.^{166,167}

Oxidations of alcohols, sulfides, thiols, etc. are inhibited in the presence of alkenes, due to the interaction of the alkene with the active site of the heterogeneous oxidant.¹⁶⁸ The inhibition is, however, less complete with thiols and sulfides than with alcohols, because sulfur, a much better nucleophile than oxygen,¹⁶⁹ can compete for the active sites on the surface of the oxidant. A possible mechanism for the oxidation of these compounds is outlined in Scheme 62. As indicated in the scheme, the products from the oxidation of thiols are disulfides, which could be formed either by nucleophilic attack on the complexed thiol or after it had been oxidized to a sulfinic acid, RSOH.¹⁷⁰ The experimental information currently available does not permit a distinction to be made between these two possibilities.



Scheme 62.

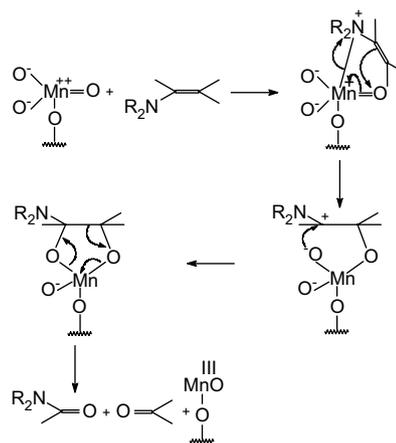
Adsorption of permanganate onto solid supports such as copper(II) sulfate pentahydrate or hydrated alumina promotes the oxidation of alcohols, particularly allyl and benzyl alcohols. Oxidation of benzyl alcohol is facilitated due to positioning of the α -hydrogen closer to permanganate, resulting in an easy hydride transfer. In a similar way, α,β -unsaturated alcohols can be oxidized if their double bonds are complexed with manganese in an



Scheme 63.

analogous manner. Alcohols with one or more methylene groups between the double bond and carbon bearing the hydroxy group cannot, however, be oxidized, due to the absence of such positioning of the α -hydrogen (Scheme 63).

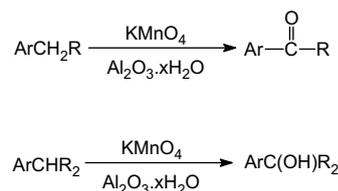
Although alcohol oxidation requires hydrated surfaces, oxidation of enamines occurs in completely anhydrous conditions, because it does not require a proton-accepting species, unlike alcohols (Scheme 64).



Scheme 64.

In the case of enamines, the reaction is assumed to be initiated by bond formation between nitrogen and manganese, followed by oxidative attack on the contiguous double bond.

When aromatic side-chain derivatives are oxidized by permanganate in solution, usually benzoic acid results. In the presence of a solid support, however, the oxidation leads to the formation of aromatic alcohols or ketones, depending upon the nature of the benzylic carbons, i.e., whether they are tertiary or secondary, respectively (Scheme 65).

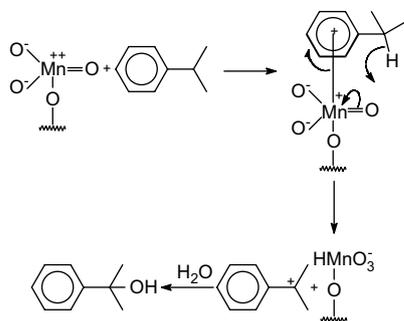


Scheme 65.

The rates of homogeneous hydrocarbon oxidations are usually controlled by the ease of C–H or C–C bond cleavage. Heterogeneous oxidations can also be dependent upon the rate of adsorption of the reactants or the rate of desorption of the products and the need for proper orientation of the adsorbed reactant.¹⁷¹ A probable mechanism for the oxidation of cumene has been suggested, where the initial reaction would be between the electron-rich aromatic ring and the electron-deficient manganese, i.e., electron donation from the aromatic HOMOs to the manganese LUMO. Hydride transfer could then occur, as illustrated in Scheme 66, giving a carbocation, which would react with water to give an alcohol.

Wet silica-supported potassium permanganate was used as an inexpensive and efficient reagent for the conversion of semicarbazones **51a–q** and phenylhydrazones **51r–y** into the corresponding carbonyl compounds **52a–y** under solid-state conditions.¹⁷²

The reaction time is usually short (15–45 min) and isolation of the product is straightforward (Table 1 and Scheme 67).

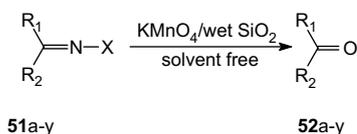


Scheme 66.

Table 1

Conversion of semicarbazones **51a–q** and phenylhydrazones **51r–y** to the carbonyl compounds **52a–y** using $\text{KMnO}_4/\text{wet SiO}_2$ under solvent-free conditions

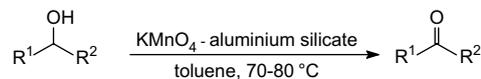
Entry	R ₁	R ₂	Time (min)	Yield (%)
a	Ph	Me	15	90
b	Ph	H	15	85
c	3-ClC ₆ H ₄	H	25	80
d	3-MeOC ₆ H ₄	H	20	91
e	PhCH=CH	H	20	75
f	4-BrC ₆ H ₄	Me	25	70
g	4-PhC ₆ H ₄	Me	30	75
h	4-Pyridyl	Me	20	80
i	1-Naphthyl	H	15	78
j		—	15	90
k		—	15	88
l		H	20	76
m		—	25	91
n		—	30	80
o		—	45	85
p		H	35	81
q	THPO	H	45	82
r	3-MeOC ₆ H ₄	H	40	70
s	3,3-(MeO) ₂ C ₆ H ₃	H	25	77
t	Ph	H	30	72
u	Ph	Me	30	70
v	2-HOC ₆ H ₄	H	40	85
w	2-HO(CH ₂) ₂ C ₆ H ₄	Me	45	78
x	4-HOC ₆ H ₄	H	20	90
y	4-NO ₂ C ₆ H ₄	H	25	90



Scheme 67.

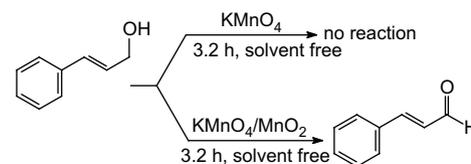
The oxidative cleavage of these derivatives takes place at room temperature in the absence of solvent. In addition, this oxidation system is able to convert complicated semicarbazones in the presence of other oxidizable functional groups into the parent carbonyl compounds.

A new reagent, potassium permanganate adsorbed on aluminium silicate, suitable for the oxidation of primary and secondary alcohols to the corresponding carbonyl compounds has been reported by Lou et al. (Scheme 68).¹⁷³ Aliphatic alcohols such as 1-hexanol or 1-octanol are, however, not efficiently oxidized under these conditions.



Scheme 68.

Addition of MnO_2 accelerates the oxidation of alkyl arenes, sulfides and allylic alcohols by potassium permanganate under solvent-free and heterogeneous conditions (Scheme 69).



Scheme 69.

Addition of MnO_2 increases the yields of ketones obtained from the oxidation of alkyl arenes by up to 50%. The effect of MnO_2 is maximal when the alkyl arenes are oxidized under heterogeneous conditions in methylene chloride. These results, which will be of practical use in synthetic organic chemistry, also present an interesting challenge for physical-organic chemists.¹⁷⁴

Recently, considerable attention has been paid to solvent-free reactions.¹⁷⁵ These are not only of interest from a green chemistry point of view, but, in many cases, they also offer considerable synthetic advantages in terms of yield, selectivity and simplicity of the procedure. These factors are especially important in industry.

A new procedure for the selective oxidation of alcohols to the corresponding aldehydes and ketones with potassium permanganate supported on aluminium silicate at room temperature under solvent-free conditions and with shaking has been reported.¹⁷⁶ This method is an excellent procedure, since it gives high yields in a ca. -60 min time period and can be used for the oxidation of most alcohols, as presented in Table 2.

Table 2

Oxidation of alcohols using potassium permanganate supported on aluminium silicate and with shaking

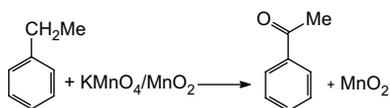
Substrate	Reaction time (min)	Product	Yield (%)
$\text{Me}(\text{CH}_2)_4\text{CH}_2\text{OH}$	60	$\text{Me}(\text{CH}_2)_4\text{CHO}$	81
$\text{MeCl}=\text{CHCH}_2\text{OH}$	40	$\text{MeCl}=\text{CHCHO}$	93
PhCH_2OH	40	PhCHO	97
$\text{PhCH}=\text{CHCH}_2\text{OH}$	30	$\text{PhCH}=\text{CHCHO}$	97
<i>p</i> -MeO-C ₆ H ₄ -CH ₂ OH	30	<i>p</i> -MeO-C ₆ H ₄ -CHO	95
$\text{CH}_2=\text{CHCH}(\text{OH})\text{Me}$	30	$\text{CH}_2=\text{CHC}(\text{O})\text{Me}$	90
$\text{MeCH}_2\text{CH}(\text{OH})\text{Me}$	40	$\text{MeCH}_2\text{C}(\text{O})\text{Me}$	93
Cyclohexanol	40	Cyclohexanone	97
$\text{PhCH}(\text{OH})\text{Ph}$	40	$\text{PhC}(\text{O})\text{Ph}$	98
$\text{PhCH}(\text{OH})\text{COOEt}$	40	PhCOCOOEt	93
$\text{C}_{15}\text{H}_{31}\text{CH}(\text{OH})\text{CH}_2\text{COOEt}$	50	$\text{C}_{15}\text{H}_{31}\text{COCH}_2\text{COOEt}$	89
$\text{PhCH}(\text{OH})\text{CH}_2\text{OH}$	40	PhCOCH_2OH	93
Cyclopropylmethanol	50	Cyclopropylformaldehyde	89
Dicyclopropylmethanol	50	Dicyclopropylketone	90

During the oxidation of arenes and sulfides by potassium permanganate on an Mn(II) sulfate support, the reduction product, manganese dioxide, can be re-oxidized to potassium permanganate after extraction of the organic products (Eq. 27).¹⁷⁷



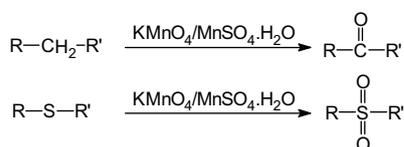
For this purpose, however, the use of potassium permanganate as an oxidant should be carried out under solvent-free or heterogeneous conditions¹⁷⁴ and the potassium permanganate must be activated using a solid support. Unfortunately, many of the common solid supports such as alumina,^{178,179} silica,¹⁸⁰ zeolite,¹⁸¹ montmorillonite K10,¹⁸² cation exchange resins,¹⁸³ molecular sieves¹⁸⁴ or copper sulfate pentahydrate¹⁸⁵ interfere with the re-oxidation process.

It was found that activated manganese dioxide is an excellent solid support that can be recycled,¹⁸⁶ but it is difficult to prepare activated MnO₂. Hence, a method has been developed for carrying out the reaction on a manganese(II) sulfate support in order to bypass activated MnO₂ (Scheme 70).¹⁸⁷



Scheme 70.

The use of an oxidant consisting of KMnO₄ and MnSO₄ · H₂O in a 5:1 ratio (by weight) under solvent-free conditions is reported to be the most satisfactory approach, which can convert arenes into the corresponding carbonyl compounds and sulfides into the corresponding sulfones (Scheme 71).



Scheme 71.

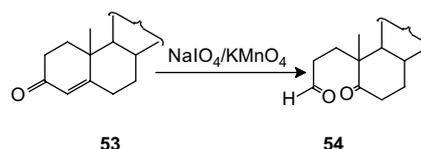
Oxidation of toluene¹⁸⁸ and *p*-xylene¹⁸⁹ using aqueous potassium permanganate was studied under heterogeneous conditions in the presence of hydrodynamic cavitation and compared with the results of the reaction under acoustic cavitation. The reactions were found to be considerably accelerated at ambient temperature in the presence of cavitation. On comparison, it was found that about sixfold more product could be obtained in the case of toluene and sevenfold more product in the case of *p*-xylene with hydrodynamic cavitation than with acoustic cavitation at the same energy dissipation.

8. Oxidation of steroids

Interest in the oxidation of steroids has intensified, spurred on by reports implicating cholesterol oxidation products in adverse effects on human health.^{190,191} Most of the studies on the biological effects of the oxidation products have been carried out on animals. Nevertheless, they have created concerns about the possible presence of such products in human foods and therefore their harmful effects on humans. The adverse effects reported to date include cytotoxicity,^{192–195} angiotoxicity,¹⁹⁶ mutagenicity,^{197–199} carcinogenicity²⁰⁰ and others.^{201–204} Several of these biological activities

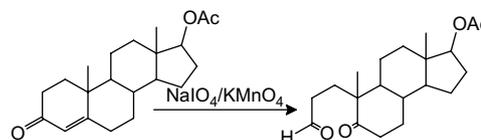
have led researchers to speculate that a link may exist between ingested cholesterol oxidation products and coronary heart disease.²⁰⁵ This notion has been supported by the finding²⁰⁶ that cholesterol oxides extracted from USP cholesterol produce angiotoxicity and arteriosclerosis in rabbits, while purified cholesterol does not.

Δ^4 -3-Keto-steroids (**53**) are cleaved to 5-keto-4-norsteroid-3-carboxylic acids (**54**) in about 70–90% yield by sodium periodate/potassium permanganate in *tert*-butyl alcohol/water (Scheme 72).²⁰⁷



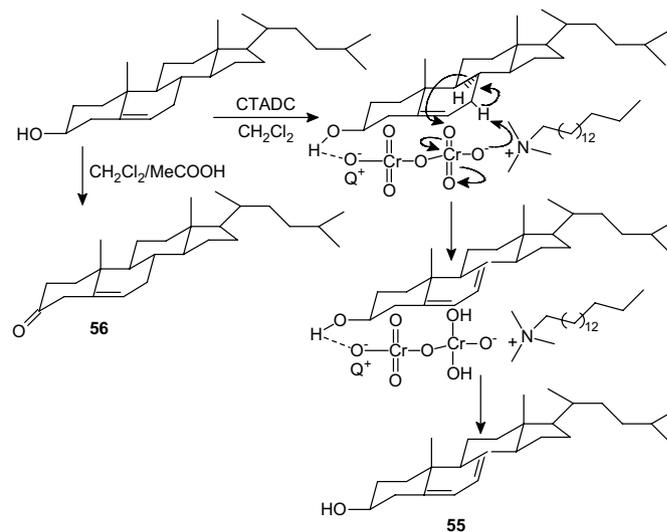
Scheme 72.

A similar permanganate/periodate oxidation of Δ^4 -3-ketones in a series of solasodine and diosgenin derivatives (alkaloidal steroids) has been reported.²⁰⁸ Singh and Paul²⁰⁹ have investigated the oxidation of testosterone acetate²¹⁰ (17 β -acetoxyandrost-4-en-3-one) in 90% aqueous *tert*-butyl alcohol by periodate/permanganate. In this process, the ester function is hydrolyzed, and the product is found to be 17 β -hydroxy-5-oxo-4-nor-3,5-secoandrost-3-oic acid (Scheme 73).



Scheme 73.

Recently, Patel and Mishra²¹¹ have reported the oxidation of cholesterol by CTADC (Scheme 74). When cholesterol was refluxed with CTADC in dichloromethane (DCM) for 6 h, 7-dehydrocholesterol (**55**) was obtained, which was characterized from its ¹³C NMR, ¹H NMR and FABMS spectral characteristics. For the dehydrogenation, a remote-functionalization mechanism akin to that reported by Breslow et al.²¹² was proposed. An association of the 3-OH group with the chromate ion of CTADC may initiate the reaction process and



Scheme 74.

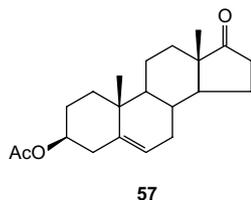
subsequent reaction takes place at an equidistant site of the active center of the reagent at the cholesterol nucleus. The secondary overlap of the p-orbitals of cholesterol at the C5–C6 position with that of Cr=O may assist the system to achieve a proper orientation for the reaction. The dehydrogenation occurs through a seven-membered cyclic transition state involving a change of oxidation state of Cr(VI) to Cr(IV). At reflux conditions, from a solution of CTADC and cholesterol in 20% acetic acid in DCM, 5-cholesten 3-one was isolated (**56**).

Samokhvalova et al.²¹³ have studied the catalytic activity of metal porphyrins by comparing cholesterol and Mn-porphyrin with 1-hexene and Mn-porphyrin. They have indicated that a ternary olefin/catalyst/O₂ complex is an intermediate. In the case of cholesterol, it was proposed that the rate-determining step for the formation of the intermediate is the activation of O₂ by the catalyst, whereas in the case of 1-cyclohexene, the rate-determining step is complexation with Mn.

Adducts from ergosterol 3 β -benzoate, 4-phenyl-1,2,4-triazolin-3,5-dione and 1,4-dihydrophthalazine-1,4-diol have been oxidized by permanganate.²¹⁴ The medium used was toluene and the oxidant was potassium permanganate in the presence of dicyclohexyl-18-crown-6.

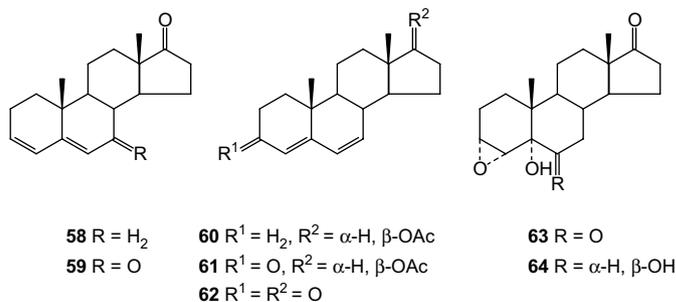
Sodium perborate, with potassium permanganate as a catalyst, has been shown to be a novel reagent for the epoxidation of steroidal 5-enes, with the attack occurring predominantly on the β -face. Many years ago, it was shown²¹⁵ that potassium permanganate in acetic acid would epoxidize 3 β -acetoxyandrost-5-en-17-one (**57**), although, at that time, the stereochemistry of the epoxides was not known. Hanson et al.²¹⁶ report the major product to be the 5 β ,6 β -epoxide (2:1; β -epoxide/ α -epoxide). The epoxides may be clearly distinguished by the position of the 6-H resonance in the ¹H NMR spectrum (δ H 2.87, α -epoxide; δ H 3.07, β -epoxide).²¹⁷

Potassium permanganate/sodium perborate/glacial acetic acid is a novel, cheap epoxidizing system that, in this instance, has afforded epoxides, albeit in moderate yields, that differ in their stereochemistry from those formed by conventional peracids.²¹⁸ Sodium perborate in glacial acetic acid has proved to be an epoxidizing agent for alkenes. With **57**, it slowly gave a mixture of the 5 α ,6 α - and 5 β ,6 β -epoxide, containing predominantly the 5 α ,6 α -epoxide. In the presence of catalytic amounts of potassium permanganate, however, the reaction was much faster and the stereoselectivity was reversed, with the β -epoxide now predominating.

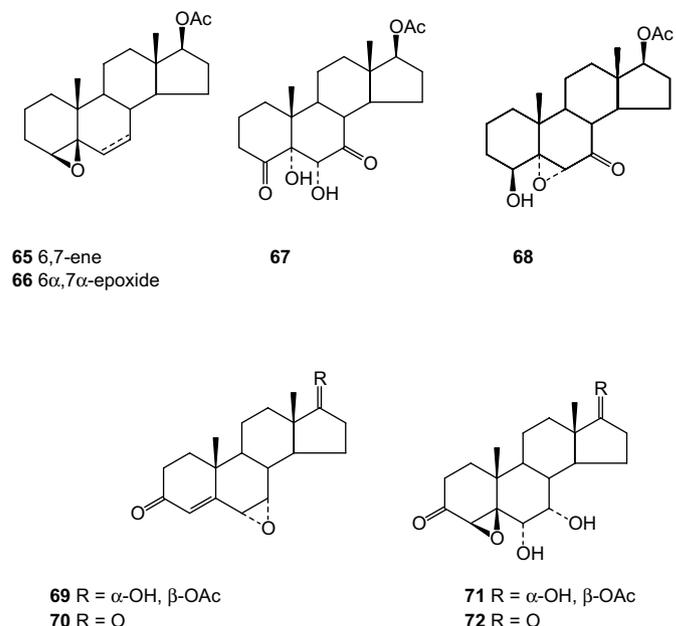


The products of oxidation of steroidal alkenes by the biphasic system, KMnO₄/CuSO₄, differ from those produced by homogeneous oxidation using potassium permanganate.^{80,157,219–222} Other metal sulfates such as ferric sulfate have also been used in the biphasic system.²²³ Some relatively inaccessible β -oriented epoxides, rather than vicinal diols, have been obtained from steroidal alkenes using these systems. The stereochemical results have been rationalized in terms of an initial pseudo-axial attack by the electron-deficient manganese on the alkene, followed by the formation and subsequent decomposition of a manganate to produce the epoxide, the latter step being facilitated by the metal sulfate.^{221,222} This view was challenged,²²⁴ however, with the suggestion that the stereochemistry is determined by the initial formation of a π -complex with the copper on the less hindered

face of the alkene, directing the subsequent attack of the permanganate to the more hindered face.



The oxidation of two heteroannular dienes, androsta-3,5-dien-17-one **58**²²⁵ and 17 β -acetoxyandrosta-4,6-diene **60**,²²⁶ has been examined, together with their related C-7 and C-3 ketones **59**,²²⁷ **61** and **62**²²⁸ by this system. On oxidation, compound **58** yields **63** and **64**, **60** yields **65–68**, **61** yields **69** and **71**, **62** yields **70** and **72** and **59** yields **73** and **74**. The results are given in Table 3.



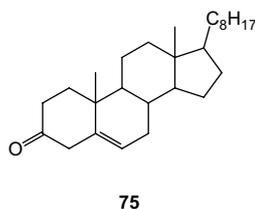
If the stereochemistries of the products were to be determined by the initial formation of a copper π -complex on the less hindered face of the alkene, directing attack of the permanganate to the more hindered face, it would be difficult to explain the formation of the 3 α ,4 α - and 6 α ,7 α -epoxide and the products derived from them.²²⁹

The oxidation of cholesterol has been studied using platinum catalysts.^{230,231} Oxygen-catalyzed autooxidation^{232,233} has also been studied in different media. The oxidation of cholesterol²³⁴ by singlet oxygen has been studied in ethanol, benzene and carbon tetrachloride. The oxidation is found to be most pronounced in carbon tetrachloride, in which singlet oxygen has a lifetime of

Table 3
Products of potassium permanganate oxidation of dienes

Substrate	Product	Yield (%)
Androsta-3,5-diene-17-one 58	63	42
	64	19
17 β -Acetoxyandrosta-4,6-diene 60	65	3
	66	5
	67	12
	68	39
17 β -Acetoxyandrosta-4,6-dien-3-one 61	69	25
	71	12
Androsta-4,6-diene-3,17-dione 62	70	33
	72	19
Androsta-3,5-diene-7,17-dione 59	73	30
	74	20

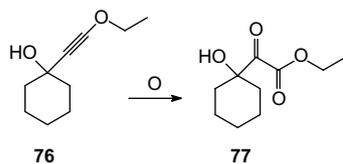
700 μ s, the major products of the oxidation being C-7 ketone derivatives of cholesterol. Parish et al.²³⁵ and Wang et al.²³⁶ used PCC (pyridinium chlorochromate) for the oxidation of cholesterol in chloroform, with the formation of a ketone product (**75**).



9. Oxidation of alkynes

Potassium permanganate is an excellent oxidant and has been used in many complex synthetic programmes where it is necessary to maintain some desired stereochemistry of the products²³⁷ and a rapid reaction and high yield are required.

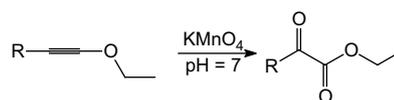
Potassium permanganate in a buffered (pH 7.0–7.5) aqueous acetone mixture is well known to oxidize alkynes to α,β -diketones²³⁸ and was found to rapidly oxidize alkynyl ethers to the corresponding substituted α -keto esters.²³⁹ As an example, the oxidation of the alkynyl ether **76**, obtained by condensation of lithioethoxyacetylene with cyclohexanone using standard conditions,²⁴⁰ was complete at room temperature within 2 min, affording the α -keto- β -hydroxy ester **77** in 98% isolated yield (Scheme 75). This result was compared to those obtained by the reaction of the same substrate using other oxidative methods (Table 4).²⁴¹



The KMnO_4 oxidation was applied to a variety of alkynyl ethers (Table 5). The majority of the substrates utilized were synthesized by the reaction of the corresponding ketone (entries 1–6), alkyl halide (entry 8) or aldehyde (entries 9–10) with lithioethoxyacetylene in THF at low temperatures. The substrate used for entry

Table 4
Comparison of oxidative ability of potassium permanganate with other oxidants

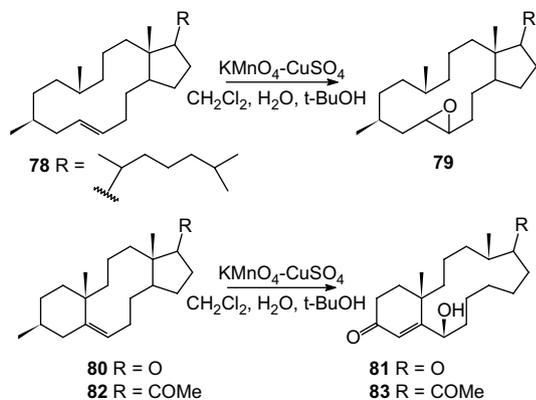
Oxidant	Time (min)	Yield (%)
KMnO_4	2	98
$\text{PhIO/RuCl}_2(\text{PPh}_3)_3$	30	48
OsO_4	1080	42

Table 5
Oxidation of alkynyl ethers by KMnO_4 in buffered aqueous acetone

Entry	Substrate	Yield (%)
1		97
2		98
3		95
4		97
5		91
6		80
7		97
8		93
9		78
10		76

7 was prepared via a Pd/Cu-mediated coupling of iodobenzene with ethyl ethynyl ether.²⁴² The time required to effect complete oxidation was similar for each substrate and the product yields were consistently high.

There has been considerable interest in recent years in the synthesis of α,β -epoxides on the steroid nucleus.^{243–246} Epoxidation with peroxyacids is known to produce predominantly the α,β -epoxide, because of steric hindrance from the angular methyl groups at C-10 and C-13. A mixture of $\text{KMnO}_4/\text{CuSO}_4$ in methylene chloride has been found to conveniently and effectively provide steroidal α,β -epoxides in high yields.^{219,220} This reagent system serves as a phase-transfer catalyst and is believed to function in the ω -phase, which is formed by water and *tert*-butyl alcohol over the surface of the inorganic salt, in the epoxidation with $\text{KMnO}_4/\text{CuSO}_4$ in methylene chloride and in the presence of water and *tert*-butyl alcohol.²²⁰

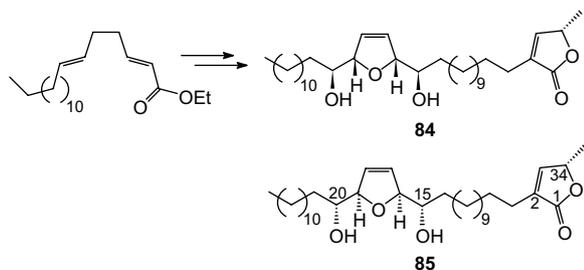


Scheme 76.

In order to further explore this oxidizing reagent system, its reaction with different homoallylic sterol substrates **78**, **80** and **82** to yield **79**, **81** and **83**, respectively, was studied (Scheme 76).²⁴⁷ These results have further confirmed the importance of the substrate structure as a factor in product formation.

The oxidation with permanganate ion provides an alternative and streamlined synthesis of this type of structure in one step from commercially available starting materials.

cis-Solamin (**84**) and its diastereoisomer **85** have been synthesized in 13 steps using the diastereoselective permanganate-promoted oxidative cyclization of 1,5-dienes to create the tetrahydrofuran diol core (Scheme 77).²⁴⁸ Notably, no protecting groups are required during the stages of fragment assembly.²⁴⁸



Scheme 77.

The key step in the syntheses involved oxidative cyclization of a 1,5-diene using permanganate under phase-transfer conditions.²⁴⁹ Hydroxyl protecting groups were not required during the final assembly of the fragments. These efforts can be extended to the oxidative cyclization methodology to the synthesis of adjacent and non-adjacent bis-THF acetogenins.

10. Applications of permanganate oxidations

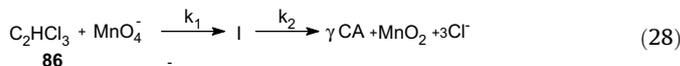
10.1. Environmental applications

Our present society is highly cursed with environmental pollution, which threatens the very existence of life. Organic and nuclear pollutants challenge the present living conditions to a great extent. Potassium permanganate has long been a suitable oxidant to neutralize some of these pollutants and many studies are progressing in this direction.

A study was undertaken to understand fully the kinetics and mechanism of the oxidation of trichloroethylene (TCE, **86**), an important pollutant present in ground water, using potassium permanganate. The study was undertaken to (i) identify the reaction products, (ii) elucidate the reaction pathways and their pH dependence, (iii)

develop a kinetic model and (iv) determine the rate constants for all of the major reactions in the $\text{KMnO}_4/\text{TCE}/\text{H}_2\text{O}$ system.²⁵⁰

The TCE degradation was postulated to involve the sequential reactions shown in Eqs. 28 and 29:



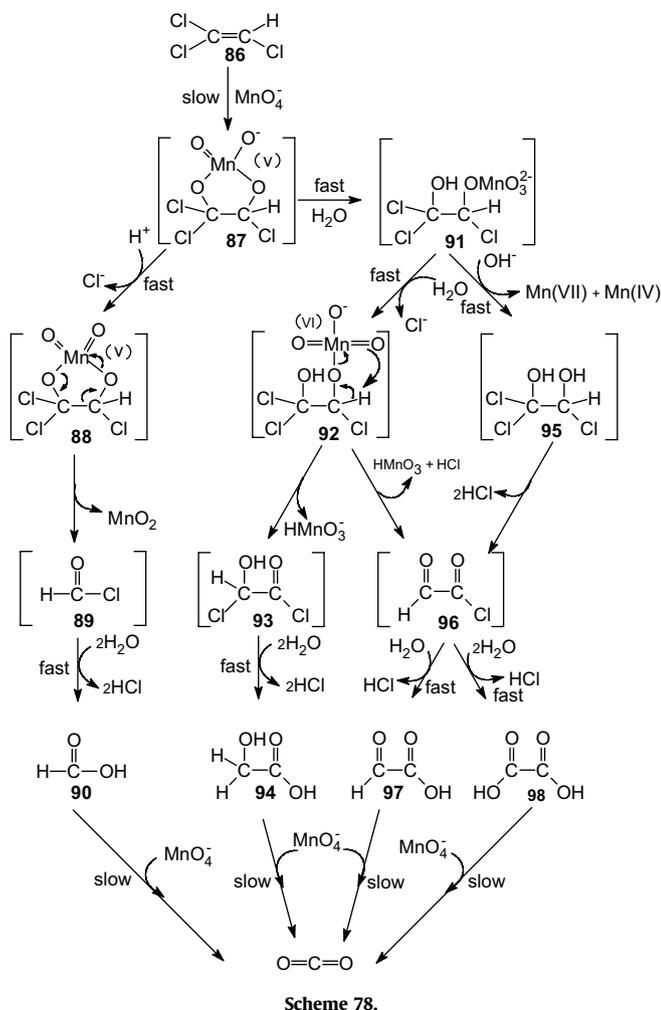
where *I* is a cyclic complex, CA are various carboxylic acids, γ and η are stoichiometric coefficients, and k_1 , k_2 and k_3 are rate constants. In the first reaction, TCE disappearance was found to be independent of pH. Complete chlorine liberation was thought to occur in the second step of Eq. 29.

TCE oxidation is initiated by the attack of permanganate ion, as an electrophile, on the carbon–carbon double bond.²⁵¹ An intermediate, cyclic hypomanganate ester **87**, is formed via an activated organometallic complex.^{21,22,82} The rapid decomposition of this cyclic ester **87** can follow several different pathways in an aqueous system such as oxidative-hydrolysis and normal hydrolysis. Oxidative hydrolysis transforms the cyclic hypomanganate ester **87** rapidly through disproportionation²⁵² to the cyclic manganate(VI) ester **88**, followed by subsequent fragmentation of **88** to form formic acid **90** via **89**. Two other possible pathways involve the hydrolysis of the cyclic ester **87** to the acyclic hypomanganate(V) ester **91**. The acyclic manganate(VI) ester **92**, oxidatively hydrolyzed from **91**, may undergo a rapid electron transfer and then either hydrolysis to form glycolic acid **94** via **93** or release of one hydrogen chloride molecule and hydrolysis to form glyoxylic acid **97** or oxalic acid **98** via **96**. In weak alkaline solutions, the acyclic ester **91** may simply hydrolyze to trichloroglycol **95**, which rapidly releases two hydrogen chloride molecules to form **96**. Compound **96** is subsequently hydrolyzed to either glyoxylic acid **97** or oxalic acid **98**. The intermediates **89**, **93** and **96** are all acyl halides that are so reactive, hydrolysis of which is easily carried out to form carboxylic acids.²⁵³ The carboxylic acids **90**, **94**, **97** and **98** are further oxidized to carbon dioxide at a relatively slow rate (Scheme 78).

The rate of TCE disappearance is independent of pH, whereas the fate of the cyclic hypomanganate ester and the product distribution are strongly dependent upon pH. Two major decomposition pathways for the cyclic hypomanganate ester have been proposed. At pH 4, the transformation of the cyclic ester to formic acid is overwhelmingly dominant and at pH 6–8, decomposition favours the formation of oxalic and glyoxylic acids. A different reaction pathway has been suggested for this higher pH range in which most of the cyclic esters transform to the acyclic esters **91** and **92**, followed by hydrolysis to form **98** and **97** via **96**.

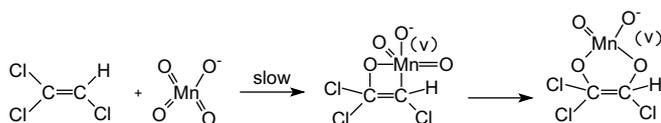
The fact that the loss of TCE is independent of pH, but that the nature and the distribution of products are highly dependent upon pH, strongly supports the existence of a short-lived intermediate in the initial stage of the oxidation. The initial reaction proceeds with a 2+2 insertion of an alkene π -bond directly into a metal–oxo bond of manganese, forming a transient organometallic complex,²¹ followed by rearrangement to the cyclic ester.^{22,82} This theory was confirmed by showing that a relatively lower activation energy was required for the 2+2 reaction pathway, as compared to the 3+2 route.^{23a} With the theory, TCE is more likely attacked by the electropositive metal (manganese) via a transition state given in Scheme 79.

This reaction mechanism more reasonably explains why permanganate ion with electron-rich oxygen termini could attack the carbon–carbon double bond electrophilically. The attack is controlled by orbital overlap via a delocalized charge-transfer interaction, rather than a net charge.^{57,82} Combination of permanganate with a suitable surfactant can speed up the removal of this



contaminant.²⁵⁴ TCE and tetrachloroethene oxidations have further been achieved using phosphate-buffered solutions under constant pH,²⁵⁵ cosolvent-enhanced *in situ* chemical oxidation (ISCO),²⁵⁶ non-aqueous phase,²⁵⁷ column experiments,^{258,259} slurry experiments for subsurface sediments²⁶⁰ and ISCO coupled with *in situ* thermal remediation (ISTR)²⁶¹ methodologies, which give excellent ground-water as well as sediment treatments.

The kinetics of oxidation of some contaminants like 1,4-dioxane, methyl *tert*-butyl ether, methyl ethyl ketone, 2,4,6-trinitrotoluene (TNT), the pesticides, aldicarb and dichlorvos, and many substituted phenols, were measured through ISCO with permanganate.²⁶² The kinetics were found to be first order with respect to both the contaminant and the MnO_4^- concentrations, from which the second order rate constants (k') were readily obtained. The rate constants for contaminant oxidation are comparable to those of tetrachloroethene and TCE and the contaminants are therefore good candidates for remediation with MnO_4^- in the field. Several mechanisms by which MnO_4^- oxidizes contaminants have been identified, including addition to double bonds, abstraction of hydrogen or hydride and electron transfer.

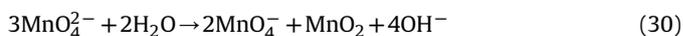


Cyanobacteria produce toxins that may contaminate drinking water sources. Among others, the presence of the alkaloid toxins, cylindrospermopsin (CYN) and anatoxin-a (ANTX), constitutes a considerable threat to human health, due to the acute and chronic toxicity of these compounds. It was found that the reactivity of CYN with chlorine reaches a maximum at pH 7. The oxidations of CYN with chloramine and permanganate are, however, rather slow processes. The reactivity of ANTX with chlorine and chloramines is still slower.²⁶³ Permanganate effectively oxidizes ANTX, while chlorine oxidizes CYN, and ozone is capable of oxidizing all the toxins with the highest rate. The formation of trihalomethanes (THMs) in the treated water may be a restriction on the application of sufficiently high chlorine doses.²⁶⁴

The degradation of nuclear wastes like EDTA and a model compound ethylenediamine (EN) in alkaline media was explored by permanganate treatment of the wastes. High pH and high ionic strength improve the separation of the target species, because of the breakdown of EDTA (and other organic ligands present in the wastes) caused by permanganate oxidation and concomitant formation of manganese solids.²⁶⁵

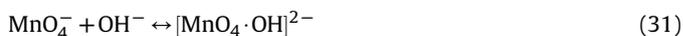
In acidic or circumneutral solutions, the oxidation of EDTA is accompanied by the release of ethylenediamine-*N,N,N'*-triacetic acid (ED3A) and CO_2 as the major products of EDTA degradation and Mn^{2+} as the final product of MnO_4^- reduction.²⁶⁶ Microbiologically mediated degradation of EDTA in circumneutral pHs also proceeds via the formation of ED3A, *N,N'*-ethylenediaminediacetic acid (EDDA), iminodiacetic acid (IDA) and low-molecular-weight compounds.^{267,268} The reduction of permanganate could be quantified by the disappearance of the distinct permanganate absorbance band located in the range of wavelengths 490–590 nm and the formation of bands with maxima at 347, 439 and 606 nm characteristic of manganate MnO_4^{2-} for pH 12 and 14, respectively. The apparent rate of reduction of permanganate to manganate increased with pH. No evidence for hypomanganate MnO_4^{3-} with maxima located at 313 and 667 nm was seen in these experiments.

The reduction of MnO_4^- results in the formation of manganate that is evident from the absorbance spectra. The manganate then disproportionates to form permanganate and manganese dioxide,¹⁴⁸ as shown in Eq. 30.

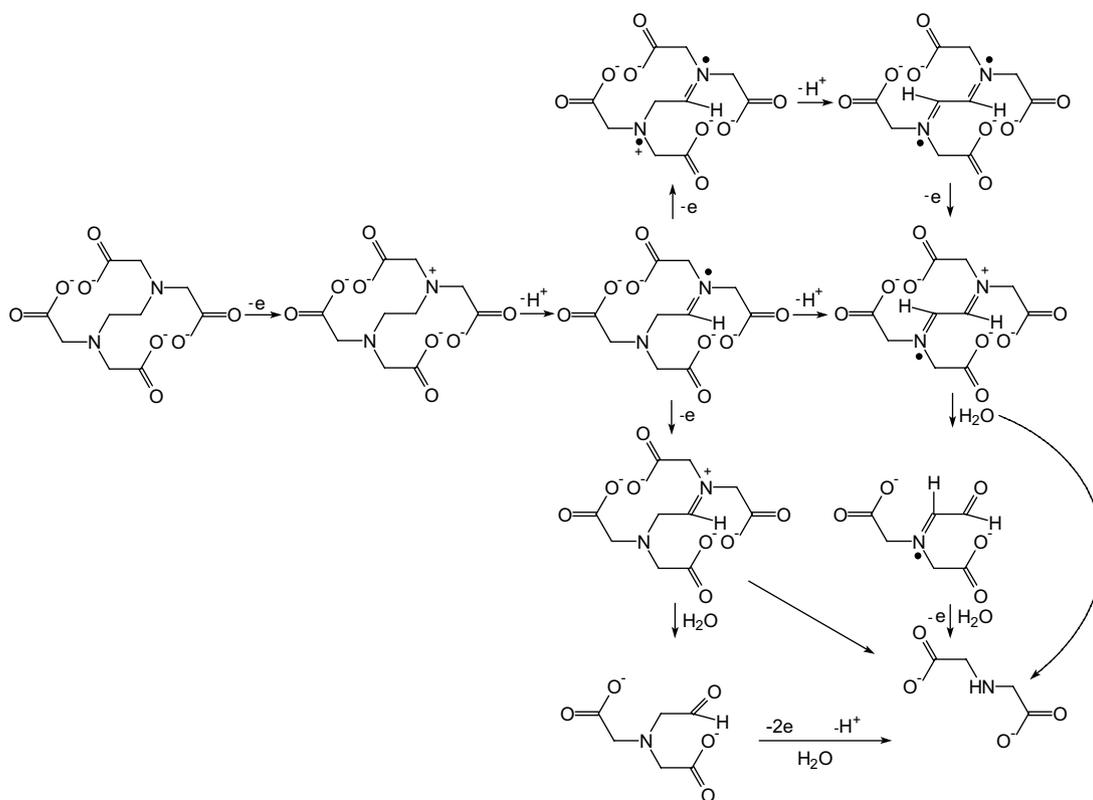


MnO_4^- is expected to be the acceptor of electrons, but not necessarily the actual oxidizing agent, in the reaction sequences shown in Scheme 80.

The generation of hydroxyl radicals preceded by the formation of a transient monohydroxo complex of permanganate and followed by the release of manganate (Eqs. 31 and 32) was hypothesized to occur in oxidations by alkaline permanganate,^{269,270} in agreement with the fact that, at high pH values, almost all of the oxygen transferred to the organic substrate being oxidized originated from water molecules, rather than from the permanganate per se.¹⁴⁸



Permanganate has been successfully used for the *in situ* degradation of many organic contaminants.^{271,272} The solids formed by the reduction of permanganate at high pH play a crucial role in the removal of TRU (transuranic) elements and metals present in wastes. Experiments were designed where EDTA was used as a representative chelating agent that was oxidized by MnO_4^- , Cu^{2+} , Zn^{2+} and Ni^{2+} were chosen as target metals to quantify the incorporation of cations present in the wastes into the solid



Scheme 80.

substrate.²⁷³ The structural data obtained using X-ray absorption spectroscopy (XAS) show that Cu^{2+} binding sites were located within MnO_6 octahedra-comprised sheets that constitute birnessite, while Zn^{2+} was positioned between them. Precipitation of birnessite was accompanied by the removal of Zn^{2+} and Cu^{2+} released as a result of the breakdown of their complexes with EDTA, although Ni^{2+} was not removed from the supernatant.

10.2. Industrial applications

Nanotechnology, nowadays, is at the cutting edge of research. The preparation of nano-manganese compounds, the cutting of carbon nanotubes (CNTs), etc. involve potassium permanganate and quaternary ammonium permanganates as suitable agents. Manganese oxides are important materials in many applications such as catalysis, electrodes, high-density magnetic storage media, ion exchangers, sensors, molecular adsorption, and electronics.^{274–277} In particular, Mn_3O_4 (hausmannite) is known to be an efficient catalyst in the decomposition of waste gas NO_x , reduction of nitrobenzene and oxidation of methane.²⁷⁸ It has been widely used for the preparation of Li–Mn–O electrodes for rechargeable lithium batteries and for soft magnetic materials such as manganese zinc ferrite, which are applicable as magnetic cores in transformers for power supplies.²⁷⁹

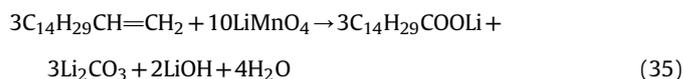
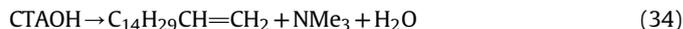
Permanganate is a useful manganese source to synthesize various manganese oxides or Mn-based oxides by means of various reactions.²⁸⁰

- (1) redox reactions of manganese between Mn^{7+} (AMnO_4 , $\text{A}=\text{K}$, Na , Li , Mg , H) and Mn^{2+} in different pH solutions;
- (2) reduction reactions of Mn^{7+} (AMnO_4 , $\text{A}=\text{Li}$, K , Na , NH_4 , TAA (tetraalkylammonium; alkyl=methyl, ethyl, propyl and butyl), and DTA (dodecyltrimethylammonium)) with reducing reagents, such as H_2 , H_2O_2 , HCl , KBH_4 , LiI , methanol, ethanol,

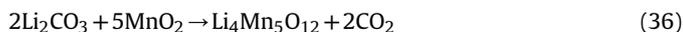
- 2-butanol, glucose, cyclodextrin, oxalic acid, fumaric acid, maleic acid, etc., or by electrochemistry and
- (3) hydrothermal reactions of AMnO_4 ($\text{A}=\text{K}$, Na , CTA) in acidic medium or in LiOH solution, and solid-state reactions of AMnO_4 ($\text{A}=\text{Li}$, K).

The structures, properties and morphologies of the resultant manganese oxides are very sensitive to the synthetic routes and synthetic conditions, such as concentrations of the reactants, pH value of the medium, reaction temperature and time.

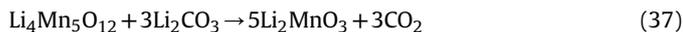
The hydrothermal reactions of cetyltrimethylammonium permanganate (CTAP or CTAMnO_4) in various concentrations of LiOH , NaOH and KOH aqueous solutions have been carried out to produce M–Mn–O nanoparticles ($\text{M}=\text{Li}$, Na , K).²⁸⁰ Nanostructured spheres and nanoparticles of spinel Li–Mn–O could be synthesized using CTAP as a manganese source in LiOH solution under hydrothermal conditions, and the spinel Li–Mn–O was produced at 70°C . Hydrothermal reactions of CTAP are dependent upon the concentration of the LiOH solution. The final product was Li_2MnO_3 in 1.5 M LiOH solution, whereas LiMn_2O_4 was the sole product in 0.3 M LiOH solution. According to the well-known Hofmann elimination, when a quaternary ammonium hydroxide is heated, it decomposes to an alkene, a tertiary amine and water. CTAOH is formed in the present system, and subsequent reactions occur as shown in Eqs. 33–35:



Precipitated amorphous Li_2CO_3 supplies a more concentrated base environment and a higher Li^+ concentration, which is effective in the growth of $\text{Li}_4\text{Mn}_5\text{O}_{12}$ (Eq. 36), and can resist a further reducing reaction of manganese dioxide, because Mn^{4+} was stable in a concentrated base environment.



The reaction shown in Eq. 37 occurs between Li_2CO_3 and $\text{Li}_4\text{Mn}_5\text{O}_{12}$:



Niederberger et al.²⁸¹ prepared nano-manganese oxides through the reaction of benzyl alcohol with two precursors, potassium permanganate and manganese(II) acetylacetonate, $\text{Mn}(\text{acac})_2$. Depending upon the precursor used, the composition of the final product can be varied in such a way that in the case of KMnO_4 , mainly Mn_3O_4 is formed, whereas $\text{Mn}(\text{acac})_2$ leads predominantly to MnO . The magnetic characterization of the MnO nanoparticles clearly revealed their super-paramagnetic (monodomain) behaviour, and the enhanced magnetic anisotropy and defects may alter the antiferromagnetic ordering in MnO nanoparticles, resulting in a finite magnetic moment below 120 K. The decrease in the effective magnetic moment for Mn^{2+} in the MnO nanoparticles compared to the expected value can be interpreted in terms of the superstructure of the ordered Mn vacancies in the MnO .

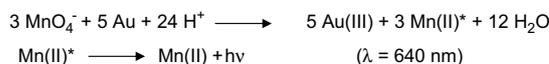
A single-step direct pyrolysis of cetyltrimethylammonium permanganate in specially made Let-lock union cells provides a simple and facile synthetic process for MnO octahedral nanocrystals and MnO coated with carbon (MnO-C) core-shell composite nanoparticles.²⁸² The product consists mainly of octahedral MnO nanocrystals and MnO-C . The core-shell particles are observed only when the core size is smaller than 150 nm. The shape of the nanocrystals can be controlled by varying parameters such as reaction temperature and duration. As the temperature increases from 600 to 800 °C, the octahedral MnO crystals without any carbon shell are obtained. The electrocatalytic activities of the products for the oxygen reduction reaction in an aqueous basic medium are found to be higher than that of bulk MnO .

MnO_2 nanoparticles have been synthesized and embedded into the wall of first ordered mesoporous carbon (CMK-3) materials by a redox reaction between permanganate ions and carbons, thus producing a novel structured MnO_2 /mesoporous carbon (MnC) composite.²⁸³ When the pores of CMK-3 are treated with different concentrations of aqueous potassium permanganate solution, different MnO_2 contents could be introduced while retaining the ordered mesostructure and larger surface area. Increasing the MnO_2 content did not result in a decrease in pore size, indicating that the MnO_2 nanoparticles are embedded in the pore wall. Large specific capacitances of over 200 F/g for the MnC composite and 600 F/g for the MnO_2 were observed and these materials have high electrochemical stability and high reversibility.

The self-limiting reaction of aqueous permanganate with carbon nanofoams produces conformal, nanoscopic deposits of birnessite ribbons and amorphous MnO_2 throughout the ultraporous carbon structure.²⁸⁴ The MnO_2 coating contributes additional capacitance to the carbon nanofoam, while maintaining the favourable high-rate electrochemical performance inherent in the ultraporous carbon structure of the nanofoam. Such a three-dimensional design exploits the benefits of a nanoscopic MnO_2 -carbon interface to produce an exceptionally high area-normalized capacitance (1.5 F/cm²), as well as a high volumetric capacitance (90 F/cm³).

Potassium permanganate reacts with gold nanoparticles in a strongly acidic medium to generate particle size-dependent chemiluminescence (CL).²⁸⁵ For gold nanoparticles with a size of 2.6 or 6.0 nm, the reaction was fast and could produce the excited

state $\text{Mn}(\text{II})^*$ with light emission around 640 nm (Scheme 81). The CL mechanism suggests the reduction of potassium permanganate by gold nanoparticles in the strongly acidic medium to the excited state $\text{Mn}(\text{II})^*$, yielding light emission. The CL reaction was considered to be of potential use for bioanalytical applications.



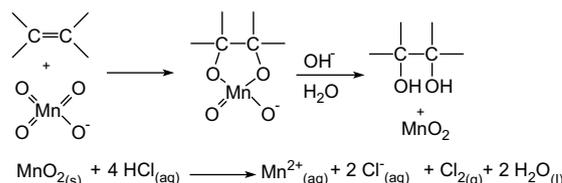
Scheme 81.

Purification of single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs) has been a challenge to scientists. The production of MWCNTs leads to amorphous carbon and onion impurities, where the onions refer to multishelled fullerenes. In the research reported to date, all MWCNT purification processes consume the amorphous carbon, onions and nanotubes simultaneously, but to a different extent, due to different degrees of reactivity. If the process is particularly harsh (i.e., treatment with $\text{HNO}_3/\text{H}_2\text{SO}_4$ (3:1)),²⁸⁶ the nanotubes will also be cut (i.e., shortened in length), as the nanotube ends are more reactive than the side walls.²⁸⁷ The onions, however, are very difficult to remove without destroying the nanotube integrity, as the chemical treatments that are required to altering the nanotube surface chemistry.²⁸⁸

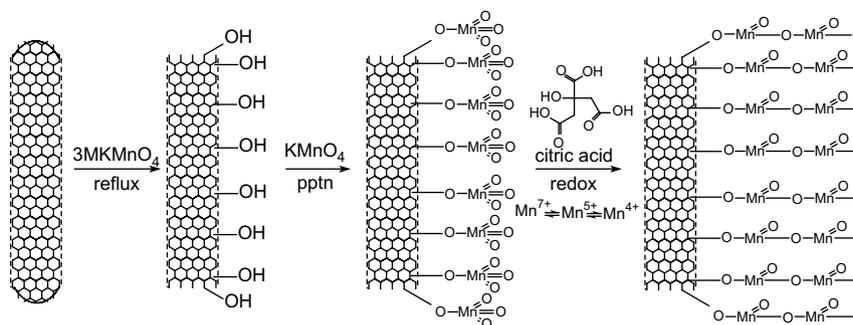
In order to cause functionalization by a chemical oxidation method, while maintaining the nanotube integrity, the relative reactivity of certain sites on the nanotubes is used. These sites are the end caps and the defect sites. In a chemical oxidation process, these sites are converted into carboxylic acid (R-COOH) groups, which leave further functionalization opportunities.²⁸⁹ The impurities (i.e., amorphous carbon and onions) are chemically oxidized to form CO_2 gas or removed by either filtration or centrifugation by virtue of their high degree of polarity resulting from the abundant surface hydroxyl, carbonyl and carboxylic acid groups formed.²⁹⁰

Treatments for the purification and cutting of carbon nanotubes with potassium permanganate in either acidic or alkaline conditions (a milder oxidant than the harsh processes of ozonolysis,²⁹¹ nitric acid treatment²⁹² and combined nitric and sulfuric acid treatment²⁸⁶) allow a controllable degree of oxidation, as it is dependent upon the reaction time and is capable of generating new defect sites, where the quinone groups formed are intermediates towards oxidation to carboxylic acids in a further step.²⁹³ The nanotubes, however, become coated with $\text{MnO}_2(\text{s})$ and require HCl washing to remove the deposit.²⁹⁴ This MnO_2 deposit, however, allows a higher degree of suspension stability and thus could be beneficial for future applications.²⁹⁵

Some work on the potassium permanganate purification and functionalization of nanotubes has been reported for carbon nanotubes produced by chemical vapour deposition (CVD).^{294–298} The use of such potassium permanganate purification on much more impure, arc-discharge nanotubes, however, requires the purest form of KMnO_4 , which does not result in an MnO_2 deposit. For this purpose, the potassium permanganate used was recrystallized from a saturated aqueous solution under nitrogen,²⁹⁹ resulting in a more stable solution than the as-received KMnO_4 . During filtration, rinsing with 0.4 g/l NaOH solution, Na_2SO_3 and



Scheme 82.



Scheme 83.

1 M H₂SO₄ was employed to remove most manganese oxides. This rinsing stage was repeated until no brown colour was visible in the resulting residue and was then followed by a final rinse with concentrated hydrochloric acid to remove any remaining MnO₂.

The reaction mechanisms for the oxidation step (reflux stage) are shown in Scheme 82, where the permanganate ion becomes attached to the nanotubes and then requires sodium hydroxide for subsequent removal, while simultaneously being oxidized. Following this pathway, the hydroxyl groups formed can be further oxidized to carbonyl groups and hydrochloric acid is used to remove the MnO₂.^{300,301}

When thermal annealing was used in combination with the potassium permanganate treatment, successful cutting and further purification of the nanotubes can be effected, forming more carboxylic acid groups. The simultaneous deposition of manganese oxide onto the nanotubes can be subsequently reduced to an insignificant concentration. The carboxylic acid groups formed can then be successfully functionalized by alkylamines through a diimide-activated amidation process, using DCC as the coupling agent.

Xie and Gao³⁰² prepared morphologically uniform MnO₂/MWCNT composites using an alkaline potassium permanganate solution, which served as an oxidant and a precursor simultaneously, and characterized their electrochemical behaviour.

An ε-MnO₂ uniform layer with a thickness of about 6.2 nm was intimately coated onto the surface of MWCNTs through a reflux process (Scheme 83). Both the pure MWCNTs and the MnO₂/MWCNT electrodes exhibit capacitive behaviour, but very different magnitudes of current response. It was calculated that the specific capacitance of the composite reaches up to 250.5 F/g, about eightfold higher than that of the pure MWCNTs. The composite electrode possesses favourable capacitance features in the lower-frequency region. The promising MnO₂/MWCNT composite is expected to promote the electrochemical applications of CNTs.

11. Conclusions

Permanganate oxidation has gained momentum since more than a century ago. Innumerable substrates have been oxidized using this reagent, both in aqueous and in organic media. Recently, a large number of studies have been carried out in heterogeneous and solvent-free conditions, as well as on solid supports. The oxidizing capability of permanganate has also been exploited in more modern areas such as biochemical footprint assays, nanotechnology, environmental pollution control and bioluminescence. Much work has been done to elucidate the mechanisms of permanganate oxidation of organic substrates in various media, but a feeling of obscurity and ambiguity still persists, which needs further clarification through theoretical comparative studies. Despite such a large volume of work, there is still scope to explore the mechanistic viewpoints, synthetic uses and industrial and biochemical

utilities. The oxidation reactions using permanganate adsorbed on solid supports and the proper mechanism of such reactions need further exploration.

Acknowledgements

The authors are grateful to the Department of Science and Technology, and the University Grants Commission, New Delhi for financial support through the FIST and DRS programmes.

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