

Bleach and oxidation catalysis by manganese–1,4,7-triazacyclononane complexes and hydrogen peroxide

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Abstract

The dinuclear manganese compound, $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{tacn})_2](\text{PF}_6)_2$ (**1**) with Me_3tacn = 1,4,7-trimethyl-1,4,7-triazacyclononane, catalyzes a variety of bleaching processes and organic substrate oxidations using hydrogen peroxide as oxidant. Bleaching reactions in aqueous solution include stain bleaching for laundry cleaning, stain and starch removal for machine dishwasher cleaning, and wood pulp bleaching. Model substrate conversions indicate that in aqueous and non-aqueous media (**1**) catalyzes both oxygen and electron-transfer reactions. A wide variety of substrates are efficiently converted in non-aqueous media, like alkenes into epoxides and *cis*-diols, alkanes into their corresponding alcohols and ketones, alcohols into aldehydes and sulfides into sulfoxides and sulfones. Yield and selectivity of reactions frequently depend on the conditions chosen. Dismutation of H_2O_2 can be controlled by using the appropriate solvent (e.g. acetone) or applying an additive, like oxalate or ascorbic acid. Addition of trichloroacetic acid 2,6-dichlorobenzoic acid to (**1**)/ H_2O_2 has been shown to give a selective *cis*-dihydroxylation versus epoxidation (7:1 ratio). © 2006 Elsevier B.V. All rights reserved.

Keywords: Manganese; Triazacyclononane; Bleaching; Oxidation; Hydrogen peroxide

1. Introduction

Hydrogen peroxide is widely employed as an environmentally benign bleaching agent used to bleach wood pulp, paper, raw cotton and stains on textile and hard surfaces [1]. A variety of chromophores present on the substrates need to be whitened or removed using bleaching chemicals. For example for laundry cleaning a wide variety of stains needs to be bleached, such as tea, wine, fruit, and curry stains. As the chromophores vary in chemical nature, different types of reactivity are required [2].

The main bleaching systems used for laundry cleaning, raw cotton bleaching and pulp–paper bleaching are chlorine-based bleaches, hydrogen peroxide, ozone and peracids. Although hydrogen peroxide is from an environmental point of view together with O_2 the most favorable bleaching agent, long reaction times or high temperatures are required to attain sufficient bleaching of chromophores, like 3 h at 90 °C for wood pulp. As most consumers do not wash generally at this temperature, alternative bleaches for laundry applications were developed. They

are mostly based on peracids, such as peracetic acid or nonanoyl peracid [2]. Peracids give bleaching at considerably lower temperatures, but are still not active enough below 40 °C. Most consumers world wide wash under ambient conditions, even as low as 5 °C. It is thus desirable to use bleaching systems that operate well at lower temperatures, shorter reaction times and/or using lower chemical charges than current, without causing unacceptable damage to dyes or textile fibers. Catalysts that activate H_2O_2 will lead to pulp delignification/bleaching processes that use the bleaching chemicals more efficiently, operate at lower reaction temperature and reduce the reaction time [3].

Especially in the detergent area much attention has been paid to the development of new bleaching catalysts that activate hydrogen peroxide or even dioxygen. An overview of this development can be found in another manuscript [2]. Further, a review has been recently published that highlights the catalysts studied towards pulp and paper bleaching [3].

Manganese complexes containing 1,4,7-triazacyclononane catalyze a wide variety of substrate conversions both in aqueous and non-aqueous media. This includes both industrial applications (bleaching of stains and lignin and organic substrate conversions) and oxidation of model substrates. In this contribution, an overview of the published bleaching and oxidation reactions catalyzed by these complexes in scientific papers and patent applications will be given.

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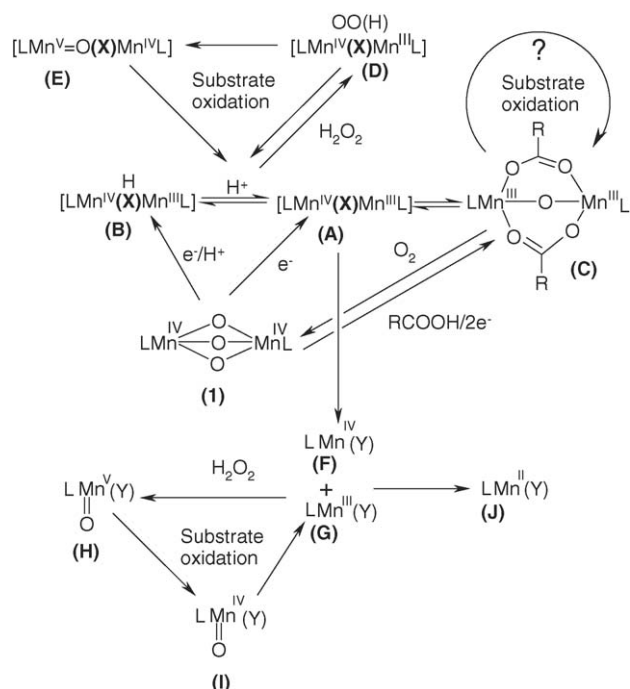
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2. Stain and pulp bleaching

Stability in alkaline aqueous media is one of the main challenges to be overcome when developing new bleaching catalysts suitable for detergent applications. Whilst initially the use of manganese salts to activate H_2O_2 was shown to give increased stain removal, the alkalinity in the solution caused the precipitation of brown manganese oxides on the garments [4]. However, it did show that H_2O_2 could be activated in aqueous detergent solutions and attempts were made to stabilize the manganese species. This led to the discovery that manganese complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane (Me_3tacn) in combination with H_2O_2 bleach tea stains efficiently at low temperature [5,6]. Also bleaching of other stains such as wine, fruit and curry stains was improved. The efficiency of tea stain bleaching depends very much on the conditions, such as pH, buffer, and temperature. Bleaching is optimal between pH 9 and 11, although even at pH 7 still considerable activity was noted [6]. $[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{tacn})_2](\text{PF}_6)_2$ (Fig. 1; **1**) was employed in laundry detergents in 1994, but the detergent product containing this catalyst was withdrawn from the market after it was alleged that the product yields increased fabric- and dye-damage [7]. The catalyst is still applied in machine-dish washing products and catalyzes the removal of tea, coffee, wine and starch residues.

Apart from compound **1**, other dinuclear and mononuclear complexes containing the same ligand show similar bleaching activities [6]. Also mixing the ligand with a Mn(II) salt furnished efficient bleaching. Even using the ligand without a manganese salt increases bleaching on tea stains in the presence of H_2O_2 [10]. Presumably manganese ions present in the stain complex with the ligand in situ, thereby forming the bleach-active species. A disadvantage is that the bleaching performance by using only the ligand depends highly on the nature of the stain, tap water used, and presence of complexing agents. A related compound is the mixed-valent $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-CH}_3\text{COO})(\text{Me}_4\text{dtne})](\text{PF}_6)_2$ (**2**) with $\text{Me}_4\text{dtne} = 1,2\text{-bis-(1,4,7-dimethyl-1,4,7-triazacyclonon-1-yl)-ethane}$ (Fig. 1). In this com-



Scheme 1. Mononuclear (F–J) and dinuclear (A–E) species postulated to be involved in the oxidation catalysis by **(1)**/ H_2O_2 . (X) denotes one or more bridging ligands between the Mn ions and (Y) denotes ancillary ligands bound to the Mn(Me_3tacn) moiety. L denotes Me_3tacn (for species A–J) or the dinucleating Me_4dtne ligand (for species (A), (B), (D) and (E)).

plex the two triazacyclononane rings are tethered together by an ethylene bridge. This compound catalyzes tea stain bleaching as well, but the pH profile is different. It works best at pH 9.5 and higher, but at $\text{pH} < 9$ the activity is very low [6].

$[\text{Mn}^{\text{IV}}_2(\mu\text{-O})_3(\text{Me}_3\text{tacn})_2](\text{PF}_6)_2$ was originally synthesized by Wieghardt and co-workers from $[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{tacn})_2]^{2+}$ (species C in Scheme 1) and air [8,9]. It was intended to be a model for manganese-containing enzymes such as containing catalase enzymes and the water oxidation

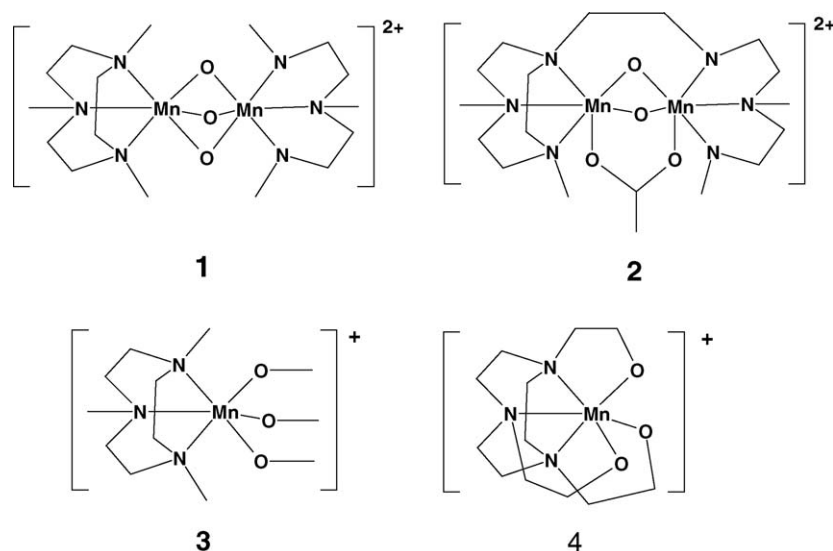


Fig. 1. Schematic representation of the manganese–triazacyclononane catalysts.

catalyst in plants and algae. Also the bridged $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-CH}_3\text{COO})(\text{Me}_4\text{dtne})](\text{PF}_6)_2$ originates from Wieghardt and co-workers [11,12]. Unilever patented the use of this class of compounds for bleaching and oxidation catalysis [13–15]. In a later patent the application in machine dishwash products was covered [16]. Related to this filing are patents describing the use of this class of catalysts for starch modification and degradation for industrial processes [17–19]. Various other patents were published to claim the manufacture of the ligand and/or metal complexes [20–23]. Furthermore, the synthesis of (1) could be improved by reacting $\text{Mn}(\text{II})\text{Cl}_2/\text{KPF}_6$ with Me_3tacn , and then subsequently adding $\text{H}_2\text{O}_2/\text{NaOH}$ [22].

Some years later Patt et al. found that $[\text{Mn}^{\text{IV}}\text{Mn}^{\text{III}}(\mu\text{-O})_2(\mu\text{-CH}_3\text{COO})(\text{Me}_4\text{dtne})]^{2+}$ in combination with H_2O_2 bleaches wood pulp to a similar extent at 50°C as compared to 90°C in conventional H_2O_2 bleaching [24–26]. In the same patent it was shown that (1) catalyzes pulp bleaching as well [24]. The chromophores of tea stains and lignin in wood pulp are chemically related (Fig. 2) suggesting that similar chemical pathways are required to bleach these substrates. Whilst (1) gives cellulose damage, indicated by loss of viscosity when dissolving the pulp in a cupric ammonium solution, (2) does not exhibit any significant viscosity loss. Further information on the different pulp bleaching processes using (2) can be found in the above-mentioned and other related papers [24–28].

(1) was subsequently studied for bleaching and delignification of wood pulp and similar or even higher activity than (2) was reported [29–31]. The extent of bleaching of different types of pulp highly depends on the level of catalyst, NaOH and H_2O_2 levels [32,33]. Undesired decomposition of H_2O_2 is a key factor when applying this type of catalysts. The pulp bleaching decreases when the rate of H_2O_2 decomposition becomes too high, for example when high levels of catalyst were combined with high levels of NaOH . It is therefore imperative to evaluate bleaching catalysts under a variety of

conditions, including ones that are outside the current window of application.

3. Mechanistic and model substrate oxidation studies in aqueous media

Tea or fruit stains and lignin are complicated mixtures of polyphenolic substrates (Fig. 2) and as such difficult to employ when elucidating the bleaching mechanisms. Therefore various attempts have been made to study the reactivity of this catalyst with simpler model substrates based on phenolic compounds and olefins. Further, spectroscopic and electrochemical measurements were performed to elucidate the nature of the species formed in the bleach solution. (1) itself is fairly stable in alkaline solutions without or with hydrogen peroxide, but forms various species upon reduction. Based on EPR (electron paramagnetic resonance) measurements, it was proposed that the first step involves a one-electron-transfer process from the phenolate ion to the EPR-silent (1), yielding EPR-active $[\text{LMn}^{\text{III}}(\text{X})\text{Mn}^{\text{IV}}\text{L}]$ exhibiting a characteristic 16-line signal and subsequently mononuclear Mn^{IV} species showing an EPR signal at $g=4$ [6,34,35] (see Scheme 1, species (A) and (F)). Reacting (1) with the vitamin E model Trolox (Fig. 3), phenoxy radical were detected by UV-vis and EPR spectroscopy, suggesting involvement of electron-transfer or H^{\bullet} transfer [34]. Hage et al. published a systematic pH-dependent electrochemical study on (1) [36]. Below pH 5 an electron-proton coupled reduction process is operative indicating that in the alkaline aqueous solutions, typically employed in detergents, the first reduction step only involves electron-transfer yielding a mixed-valence $[\text{LMn}^{\text{III}}(\text{X})\text{Mn}^{\text{IV}}\text{L}]$ species (species (A) Scheme 1). Also Gilbert et al. proposed a mixed-valent $[\text{LMn}^{\text{III}}(\text{X})\text{Mn}^{\text{IV}}\text{L}]$ as first intermediate [37]. There is no conclusive information available what the bridging atom(s) X are, but it has been proposed based on resonance Raman spectroscopy that initially the core of the three

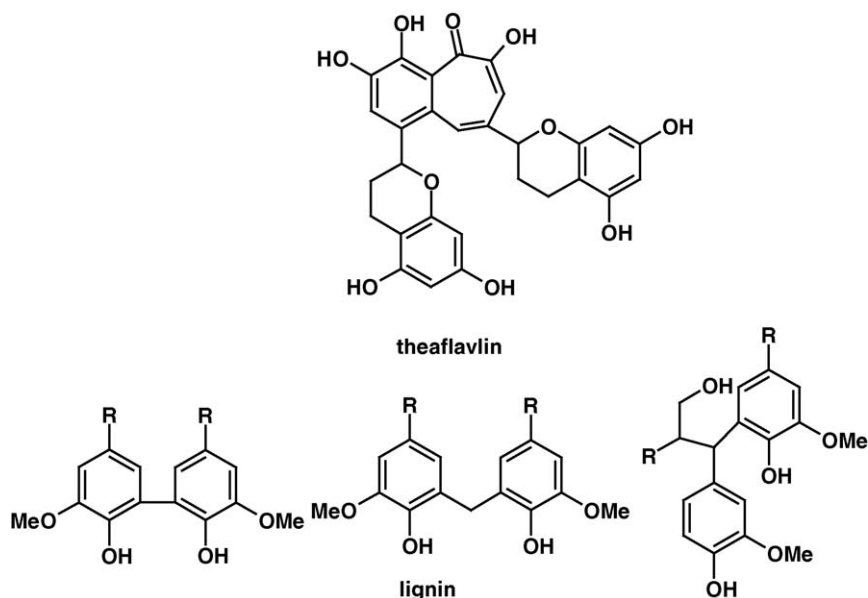


Fig. 2. Representative structures of theaflavin present in tea (top) and lignin after the pulping process, with R being side groups including lignin polymers (bottom).

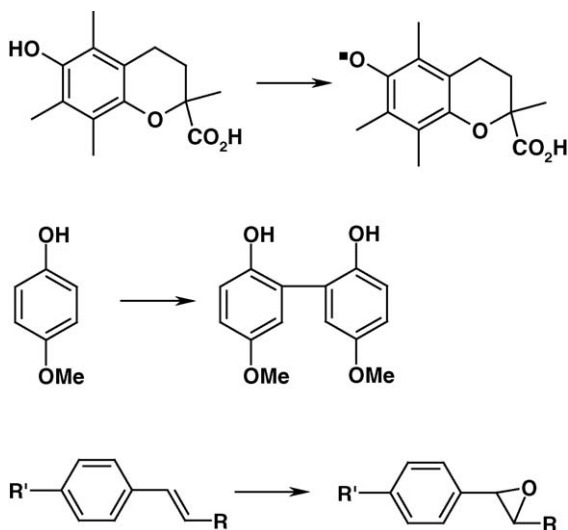


Fig. 3. Model substrates employed in aqueous media for reactivity studies: Trolox, *p*-MeOH-phenol and substituted styrenes.

bridging oxygen atoms stays intact [36]. Protonation of one of the oxygen bridges (species (B)) may lead to further reactivity with hydrogen peroxide after cleavage of one of the Mn-oxo bonds. When reducing (1) electrochemically in citrate buffer, carboxylate-bridged dinuclear $\text{Mn}^{\text{III}}\text{Mn}^{\text{III}}$ species were formed (species (C) in Scheme 1) [36]. This may link to the buffer effects noted for stain bleaching by (1) (*vide supra*).

The formation of mononuclear species, on the other hand, was corroborated using electrospray mass spectrometry (ES-MS) measurements [35,37]. Reacting the catalyst with 4-methoxyphenol with H_2O_2 at pH 10 revealed the formation of [(2,2-bisphenolate)-(Me₃tacn)Mn^V=O]⁺ (species (H) in Scheme 1) based on ES-MS [35,37]. Also signals assigned to mononuclear Mn^{III} (F) and Mn^{IV} species (G) were observed. Based on the ES-MS data Gilbert et al. suggested that mononuclear species are involved in the bleaching [38]. A reaction scheme derived for azo dye oxidation involved $\text{Mn}^{\text{V}}=\text{O}$ and $\text{Mn}^{\text{IV}}=\text{O}$ species yielding two times one-electron-transfer reactions, similarly to the reaction cycle postulated for peroxidase enzymes (Scheme 1: cycle involving species (G), (H), (I)) [38]. Such scheme is also likely to be valid for *p*-MeO-phenol oxidation, where mainly phenol-coupling products were observed (Fig. 3) [35,37,39].

As (2) exhibited a clear benefit at pH > 9 and remains dinuclear during the bleaching processes, it is inferred that also dinuclear species could be active to bleach stains or lignin. This suggests that dinuclear species may also be operative when using compound (1). Although no spectroscopic measurements were published, it was suggested that a dinuclear Mn-hydroperoxo species yields lignin oxidation (species (D) in Scheme 1) [25–31], quite different from the above-mentioned mononuclear (Me₃tacn)Mn=O species. It should be noted that Wieghardt and co-workers published the X-ray structure of a dinuclear Mn(Me₃tacn) complex containing a peroxo bridge between the Mn centers [40]. Studies on lignin-model substrate oxidations made by Chen and co-workers suggest that electron-transfer reactions are operative, followed by reaction

with hydroxyl radicals [28,29]. This conclusion is somewhat surprising as hydroxyl radicals are strongly oxidizing species and react unselectively with substrates. Therefore one would expect that also cellulose degradation takes place, as observed previously using unstabilized hydrogen peroxide at high temperatures [41,42]. Although (1) has been shown to give cellulose degradation [24], no indications for hydroxyl radicals were found using EPR sensitive radical spin traps [38]. This contrasts the conclusion made by Meunier and co-workers that hydroxyl radicals are responsible for the oxidation using (1). When adding mannitol to (1) and H_2O_2 an inhibition of quinone degradation (formed upon catechol oxidation) was found [43]. Unfortunately, no radical trapping EPR experiments were done under these conditions and therefore also other explanations may be valid. For example binding of mannitol to the active species giving substrate inhibition may explain the observations. As the lignin reaction products observed using (1) and (2) were quite similar it was suggested that similar bleaching mechanisms are operative [31]. A difference noted was that (1) showed a faster pulp bleaching and model-lignin substrate oxidation reaction than (2) [31].

A different type of reactivity obtained for the manganese-triazacyclononane complexes is oxygen transfer. Styrene and 4-vinylbenzoic acid were epoxidized selectively by manganese complexes containing the triazacyclononane moiety and H_2O_2 (Fig. 3). Apart from the aforementioned compounds (1) and (2), also the mononuclear complexes $[\text{Mn}^{\text{IV}}(\text{Me}_3\text{tacn})(\text{CH}_3\text{O})_3]^+$ (3) and $[\text{Mn}^{\text{IV}}(\text{L})]^+$ ((4); H_3L = 1,4,7-tris(hydroxyethyl)-1,4,7-triazacyclononane; Fig. 1) were studied in some more detail towards their epoxidation activity on these substrates [6,44–46]. A catalyst to substrate to oxidant ratio of 1:100:10,000 was used to mimic the laundry solution where also a large excess of H_2O_2 is present with respect to the stain. At pH 8 both mononuclear complexes (3) and (4) have total turnovers of at least 400 yielding the epoxide selectively, concomitant with decomposition of the H_2O_2 present in large excess in solution. Compound (4) did not show any epoxidation activity at pH 10, unlike compounds (1)–(3). Similarly, this closed-shell compound is inactive at pH 10 as bleaching catalyst [6]. As $[\text{Mn}^{\text{IV}}(\text{L})]^+$ is a kinetically inert d^3 species, it is conceivable that protonation of one of the alkoxide M–O bonds is needed to facilitate the formation of the putative Mn–OOH species. UV–vis titration experiments showed between pH 7 and 9 shifts in the spectra of (4), in agreement with the suggested protonation step [46]. This may suggest that the absence of epoxidation and bleaching activity can be understood by lack of reactivity of the complex with hydrogen peroxide at alkaline pHs. Using $\text{H}_2^{18}\text{O}_2$ and (4) revealed that the epoxide is fully ¹⁸O labelled, showing that oxygen transfer takes place from the co-ordinated hydroperoxide species or a species derived thereof [45]. As discussed by Que for Fe-based catalysts, a high-valent metal-oxo species, derived from the metal-hydroperoxo species, may exchange with unlabelled water. As a consequence partly unlabelled product is formed [47]. Therefore, the formation of the labelled epoxide suggests that if high-valent manganese-oxo species, such as species (H) or (I) from Scheme 1, were involved in the oxidation reaction, then it reacts quicker with the alkene than exchanging with water. No

hydroxylation of the aromatic group of styrene was observed and thus hydroxyl radicals are unlikely to form under these conditions, similarly to what was concluded from EPR trapping experiments [38].

Epoxidation of cinnamic acid by (1)/H₂O₂ at pH 9.5 was studied as well by Gilbert and co-workers. It should be noted that similar amounts of (1) and substrate were employed rather than just catalytic amounts of (1). Electron-poor olefins react very slowly with (1)/H₂O₂, suggesting the involvement of an electrophilic oxidation. The electrophilic character of the active oxidant is in agreement with the involvement of a Mn^V=O species (species (H) in Scheme 1). As observed for (4), labelled epoxide is mostly found when H₂¹⁸O₂ was employed [48]. Electropray MS indicated the presence of mononuclear species in solution and these species, similarly to the ones described for phenol oxidations, were implicated to be involved in the epoxidation reactions (species (H) in Scheme 1).

4. Oxidations in non-aqueous media

Compound (1) activates hydrogen peroxide also in non-aqueous media and catalyzes oxygen transfer reactions, like epoxidation, *cis*-dihydroxylation of alkenes, and sulfide oxidations, as well as electron/H^{*} transfer reactions such as alkane oxidations. These reactivities are discussed below. Like found for the stain bleaching studies, catalysis was also reported using mixtures of Me₃tacn ligand and Mn(II) salts.

4.1. Epoxidation of alkenes

De Vos and Bein revealed that a mixture of Mn(II) salts and Me₃tacn ligand in the presence of H₂O₂ gives efficient and selective epoxidation reactions in acetone. For example styrene was converted into the epoxide with a total turnover of 1000 and a selectivity of more than 98% (Fig. 4) [49]. The efficiency and selectivity depends on the conditions applied. One important factor is the solvent. In acetonitrile or isopropyl alcohol the yields and selectivities are much poorer compared to acetone, whilst concomitantly excessive H₂O₂ decomposition was observed. It is known that H₂O₂ can bind to acetone, to yield the peroxy-acetal intermediate [50]. This led to the suggestion that an equilibrium between free and bound H₂O₂ exists in acetone, yielding low concentrations of H₂O₂ and thus less of the undesired catalase activity takes place [51]. However, it is also possible that different peroxy-species are formed when acetone is used as a solvent, as shown by Que and co-workers using an Fe(trispyridylmethylamine) complex [52].

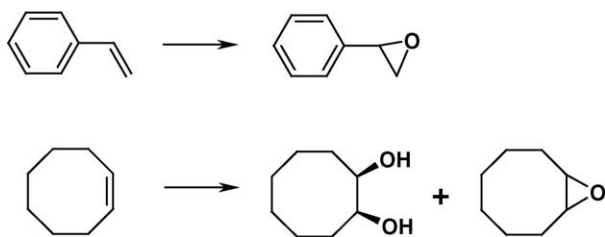


Fig. 4. Alkene epoxidation and *cis*-dihydroxylation.

Adding oxalate or ascorbic acid to acetonitrile also suppresses the catalase reaction [53,54]. Moreover, the selectivity of the epoxidation reaction was altered; (1) and H₂O₂ in acetonitrile containing oxalate as additive furnished solely the *cis*-epoxide from *cis*-alkene whilst in acetone without additive also significant amounts of *trans*-epoxide were formed [53]. The formation of *trans*-epoxide suggests that the O-transfer reactions operate via radical addition processes. Using ascorbic acid as co-catalyst, up to 3000 total turnovers could be obtained as shown by Berkessel and Sklorz [54]. In both papers, no information on the nature of the active species was given. Also zeolites containing Mn(Me₃tacn) species were studied as epoxidation catalysts [55]. These systems yield selective epoxidation reactions as well, although the rates of conversion were diminished with respect to the homogeneous systems. EPR spectroscopy revealed the presence of dinuclear [LMn^{III}(X)Mn^{IV}L] species under reaction conditions (A in Scheme 1) [55,56]. Other means to obtain a heterogeneous Mn-Me₃tacn catalyst was achieved by attaching the triazacyclononane backbone on a polymer. By attaching a trimethoxysilane moiety to the triazacyclononane and then immobilizing it onto silica an efficient epoxidation catalyst was obtained. Apart from epoxidation also *cis*-dihydroxylation reactions were observed (*vide infra*) [57]. The use of heterogenized triazacyclononane-based manganese complexes for epoxidation and *cis*-dihydroxylation was patented as well by the same group [58]. Efficient and selective epoxidation reactions were reported for polymerized norbornene moieties containing manganese(II) bound to triazacyclononane ligands [59]. A related ligand 1,4,7-tris(2-propanol)-1,4,7-triazacyclononane was also linked to a glycidylated silica surface and this system gives, in the presence of manganese and hydrogen peroxide, efficient epoxidation reactions [60].

Enantioselective olefin epoxidations was achieved by employing Mn(II) salts with S,S,S-tris(2-propanol)-tacn in methanol as reported by Bolm et al. [61]. Up to 43% ee of R-styrene oxide from styrene was obtained. Mostly *trans* epoxide with 55% ee was formed from *cis*- β -methylstyrene with this catalytic system (*vide supra*). Epoxidation of olefins including natural terpenes by [Mn^{IV}₂(μ -O)₃(Me₃tacn)₂]²⁺ in acetonitrile containing acetic acid was described by Shul'pin et al. [62]. Although not corroborated by spectroscopic measurements, the involvement of dinuclear high-valent Mn species was suggested in the epoxidation reactions (species (E) in Scheme 1). When rose bengal was added to (1) (only 10% with respect to the catalyst) a good reactivity was observed in acetone [63]. Using electron-rich alkenes, often based on cholesterol derivatives, epoxidation was obtained, as well as allylic CH oxidations. Linear alkenes were found to be epoxidized exclusively [64]. Electron-poor olefins did not react, as observed for cinnamic acid derivatives [48].

4.2. *Cis*-dihydroxylation of alkenes

Three papers describe the *cis*-dihydroxylation activity using [Mn^{IV}₂(μ -O)₃(Me₃tacn)₂]²⁺ and depending on the conditions and co-catalysts applied, different ratios between *cis*-diols and epoxides were found. Initially, De Vos et al. observed that signi-

ficant amounts of *cis*-diol were formed together with the epoxide by reacting alkenes using the 1,4,7-triazacyclononane ligand anchored to a solid support in acetonitrile with oxalate [57,58]. Using glyoxylic acid methylester hemiacetal (gmha) as additive, (1) yields a good conversion of a series of alkenes into their corresponding *cis*-diols and epoxides [64]. For example cyclooctene was converted into the *cis*-diol and epoxide with total turnover numbers for each product of 400 (Fig. 4). Mononuclear Mn-oxo species were suggested to yield the epoxides and the diols (species (H) or (I) in Scheme 1). A further improvement on diol versus epoxide ratio and turnover numbers was made by adding Cl₃COOH or 2,6-Cl₂PhCOOH to (1)/H₂O₂ in acetonitrile [65]. A selectivity of more than 80% towards *cis*-diol and total turnover numbers of 2000 were reached under certain conditions, showing the high reactivity of this system. The activity is significantly higher than any other osmium-free based catalyst for diol formation. Interestingly changing to salicylic acid as additive under the same conditions yielded about 90% epoxide. Compound (1) shows a considerable lag-phase before the oxidation reaction commences. X-ray analyses and spectroscopic measurements revealed that during the lag-phase [Mn^{III}₂(μ-O)(μ-Cl₃COO)₂(Me₃tacn)₂]²⁺ is formed (species (C) in Scheme 1) and this may be the immediate precursor of the active species. It was suggested that dinuclear Mn species are involved in these oxidation processes. The exact nature of the active species towards *cis*-dihydroxylation is not known.

4.3. Oxidation of alkanes

The first paper on cyclohexene oxidation by a Mn(II) complex with a polyfluorinated 1,4,7-triazacyclononane derivative was published by Fish and co-workers [66]. Using ^tBuOOH in an O₂ atmosphere in perfluoroheptane a good conversion of cyclohexene into cyclohexenol and cyclohexenone was observed (Fig. 5). The authors proposed an auto-oxidation mechanism in which manganese dimers are involved [67]. EPR spectroscopy showed the presence of a [LMn^{III}(X)Mn^{IV}L] species (A) in the perfluoroheptane phase under oxidative conditions.

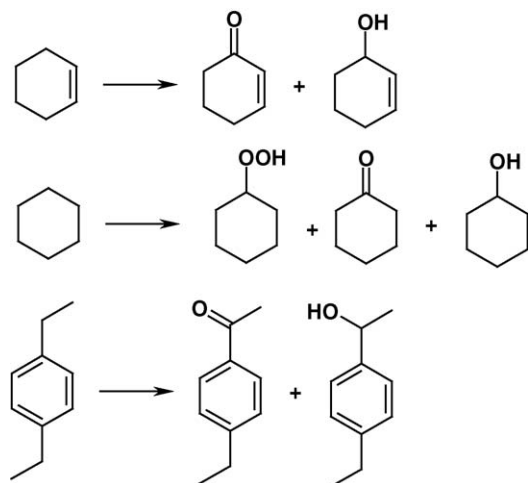


Fig. 5. Allylic CH-activation/oxidation.

Shul'pin and co-workers described the functionalization of alkanes into hydroperoxides, alcohols and ketones using (1)/H₂O₂ in acetonitrile and acetic acid (Fig. 5) [68–70]. Without addition of acetic acid, excessive H₂O₂ decomposition was observed. Various substrates react with (1) and H₂O₂ in acetonitrile/acetic acid, like cyclohexane, ethane, hexane, adamantane. Based on kinetic analyses, it was suggested that a dinuclear high-valent Mn-species, such as species (E), is involved in the alkane oxidation processes. It was proposed that alkyl radicals are formed upon interaction of the alkane with the active species, which then in a second step react with Mn–OOH such as species (D) to furnish the alkylhydroperoxide [70]. This mechanistic scheme is very different from the autoxidation mechanisms that are typically proposed, where the alkyl radicals react extremely rapidly with dioxygen, in most cases diffusion controlled [67]. The residual catalase (H₂O₂ decomposition) activity observed was thought to originate from the participation of dinuclear bis-hydroperoxide species. Unfortunately, no spectroscopic evidence for the presence of these species was given. The same polymer bound Me₂tacn ligand as discussed above [60] was shown to give the same type of alkane conversion upon addition of manganese salt and hydrogen peroxide [71].

Also Kim and co-workers described alkane oxidation, like cyclohexane conversion into cyclohexanol and cyclohexanone [72]. In these studies acetone was employed in combination with various carboxylate-containing additives. Oxalate has been found to give the most efficient conversions. Interestingly, Kim et al. suggested that radicals/autoxidation processes are not involved when acetone/oxalate is used. A high alcohol to ketone ratio was formed, even though (1)/H₂O₂ was shown to convert the alcohol into the ketone as well. For an autoxidation process both reaction products in more or less equal amounts would be expected. The absence of auto-oxidation processes was supported by stereoselective hydroxylation of *cis*- and *trans*-1,2-dimethylcyclohexane by (1)/H₂O₂.

Benzylic oxidations were described by Srinivas and co-workers in water/acetonitrile mixtures using Mn(II)SO₄ and Me₃tacn with various additives, such as acetate, tartrate, oxalate and ascorbate [73]. Especially in the presence of oxalate or citrate an efficient conversion of ethylbenzene into alcohol and ketone was observed in the presence of hydrogen peroxide (Fig. 5). Based on UV–vis and EPR studies mononuclear Mn-oxo species were suggested to participate in the catalysis (species (H) or (I) in Scheme 1). Also Shen and co-workers described the benzylic oxidation activity of (1)/H₂O₂ containing rose bengal as additive (vide supra).

4.4. Oxidation of alcohols

Feringa and co-workers reported the conversion of various benzyl alcohols into benzaldehydes by (1)/H₂O₂ and [(Me₃tacn)Mn^{III}(acac)(H₂O)]²⁺/H₂O₂ (acac = acetyl acetonate) (Fig. 6) [74]. Moderate total turnover numbers were obtained (280) when reacting the substrate with the catalyst and H₂O₂ in acetone. The efficiency could be significantly improved by pretreating the catalyst with excess of hydrogen peroxide (8000 equivalents) and then adding the substrate with H₂O₂ or

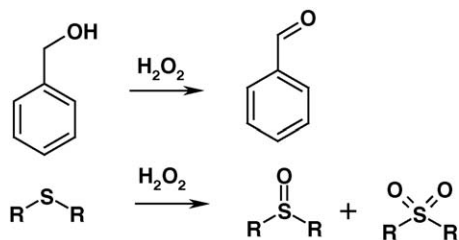


Fig. 6. Benzyl alcohol oxidation to benzaldehyde (top) and oxidation of dialkylsulfides (bottom) to sulfoxides and sulfones, respectively.

^tBuOOH under inert atmosphere. This furnished selectively the aldehydes in high turnovers. It was noted that when benzoic acid was formed, the oxidation reaction was inhibited. $[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{tacn})_2]^{2+}/\text{H}_2\text{O}_2$ is inactive towards benzyl alcohol oxidation and it is assumed that binding of benzoate to the manganese centers inactivates the catalyst. No details on the possible mechanism of these processes were given, however.

Catalyzed oxidation of alcohols by (1) has also been patented. Lonza claimed the use of (1)/ H_2O_2 in acetonitrile containing an additive, such as acetic acid for conversion of secondary alcohols into ketones [79]. Oxidation of primary alcohols using a dicarboxylate-containing additives was claimed by BASF [80].

4.5. Oxidation of sulfide

Brinksma et al. showed that (1)/ H_2O_2 in acetone reacts with methylphenylsulfide to yield mixtures of the sulfoxide and sulfones, with again very high turnover numbers (Fig. 6) [75]. As the selectivity was poor, no additional studies were carried out by this group. In further studies by Barker and Ren mainly sulfone as oxidation products were formed [76]. High turnover numbers (up till 5300) using similar substrates in acetonitrile containing sodium oxalate was reported. Both (1) and $[\text{Mn}^{\text{III}}_2(\mu\text{-O})(\mu\text{-CH}_3\text{COO})_2(\text{Me}_3\text{tacn})_2]^{2+}$ were shown to be very efficient catalysts provided that oxalate was present. Various mononuclear and dinuclear manganese (hydro)peroxo species were considered to be of relevance for the electrophilic activation of H_2O_2 [76].

Barton et al. investigated the reactivity of (1)/periodic acid in pyridine as solvent with a variety of substrates [77,78]. Various dialkylsulfides were shown to yield the sulfoxides and sulfones in high yields. Depending on the substrate, different sulfoxide/sulfone ratios could be observed. Additionally substrates such as di-*t*-butylphenol and terpinenes were converted into the bisphenol dimer and cumenes, respectively. Based on the similar reactivities of permanganate salts, the involvement of dinuclear $\text{Mn}^{\text{IV}}\text{Mn}^{\text{V}}=\text{O}$ species similar to species (E) in Scheme 1 was proposed [77] (Fig. 6).

5. Concluding remarks

The different publications and patents show that manganese complexes containing 1,4,7-triazacyclononane-based ligands

are efficient catalysts to remove certain stains and lignin. For both processes the conditions chosen determine the efficiency of the bleaching reactions, which is correlated to suppression of hydrogen peroxide decomposition and/or manganese species formed in solution. In alkaline aqueous solutions both oxygen transfer reactions (epoxidation) as well as electron-transfer reactions are accelerated. No conclusions can be made concerning the nature of the heterogeneous stain/pulp bleaching reactions, although Chen et al. indicated that electron-transfer processes are of relevance for the lignin bleaching processes catalyzed by (2) and (1).

Also in organic solvents the manganese complexes containing 1,4,7-trimethyl-1,4,7-triazacyclononane are potent catalysts for various types of oxidation reactions, like epoxidation, alcohol oxidation, alkene *cis*-dihydroxylation, alkane functionalization, and sulfide oxidation. Again the reaction conditions like solvent and/or additive used to catalyze determine the efficiency and selectivity of the reaction. For example using CCl_3COOH leads to formation of nearly exclusively *cis*-diol instead of epoxides upon reacting (1)/ H_2O_2 with alkenes in acetonitrile. Further, it was recognized that this catalyst may give excessive H_2O_2 decomposition, which was largely reduced by using acetone as solvent. As mixtures of acetone and H_2O_2 may lead to formation of explosive systems, acetone is clearly not a preferred solvent for any large-scale industrial application. De Vos and co-workers were the first to develop an efficient catalytic system in acetonitrile or methanol with oxalate or other additives. Also acetic acid or other substituted acids were found to give desired substrate conversions, due to suppression of the H_2O_2 decomposition. In some papers the involvement of dinuclear species in the H_2O_2 decomposition reaction was suggested, largely based on kinetic experiments and the presence of a dinuclear Mn species in the active site of certain catalase enzymes [46,52]. It is thought that the addition of oxalate may generate exclusively mononuclear species thereby reducing the rate of hydrogen peroxide decomposition.

It is still unknown which species are involved in the different oxidation reactions. Whilst (2) appears to give stain and lignin bleaching as a dinuclear species, spectroscopic measurements on (1) under model bleaching conditions suggested that both mononuclear and dinuclear species are formed. Based on the pH-dependent bleaching studies on both (1) and (2), it was proposed that at pH 10 dinuclear species are involved, whilst at pH < 9 mainly mononuclear species are operative as (2) is then virtually inactive [6]. However, electrospray MS measurements showed at pH 10 that also mononuclear species are formed using (1) under bleaching conditions, which may be active as well. A wide variety of mononuclear and dinuclear species has been proposed to participate in the oxidation reactions, largely without any spectroscopic or kinetic evidence. However, based on the often selective substrate oxidation processes, the involvement of unselective hydroxyl radicals is very unlikely. A variety of manganese-(hydro)peroxo and/or high-valent manganese-oxo species may be key in these oxidation processes, but detailed mechanistic and spectroscopic studies are required to understand this interesting catalytic system in more detail. These studies

may then in turn lead to the development of even more active and/or selective oxidation processes based on this or other novel oxidation catalysts.

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