

Calmagite dye oxidation using *in situ* generated hydrogen peroxide catalysed by manganese(II) ions

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Hydrogen peroxide (H₂O₂) generated from the manganese(II) catalysed reduction of dioxygen has been shown to efficiently oxidize Calmagite (3-hydroxy-4-(2-hydroxy-5-methylphenylazo)naphthalene-1-sulfonic acid) in aqueous solution at pH 8.0 and 20 ± 1 °C with de-protonated Tiron (1,2-dihydroxybenzene-3,5-disulfonate, disodium salt) acting as an essential co-ligand.

Introduction

The kinetics and mechanism of the peroxosulfate oxidation of Calmagite (3-hydroxy-4-(2-hydroxy-5-methylphenylazo)naphthalene-1-sulfonic acid) catalysed by manganese(II) ions at pH 10.0 and 40 °C has been reported previously.¹ This paper also addressed the slower oxidation observed when peroxosulfate was replaced with hydrogen peroxide as oxidant. It was proposed that oxidation occurs *via* coordination of Calmagite to manganese(II), followed by nucleophilic attack on the metal centre by oxidant leading to peroxide-bond scission and formation of manganese(III) or -(IV) species which oxidize the coordinated dye molecule. When Calmagite (Fig. 1) was replaced by the related Orange G (3-hydroxy-4-(phenylazo)naphthalene-1,5-disulfonate, disodium salt), no oxidation occurred and this was explained by the much lower binding capacity of Orange G as it lacks an additional *o*-hydroxy group.

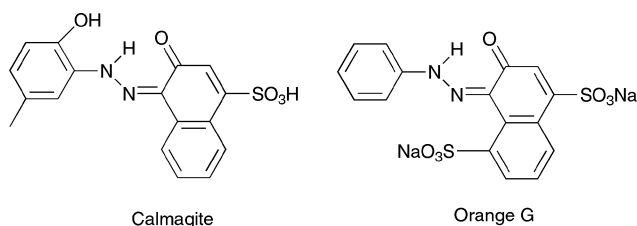


Fig. 1 Structures of Calmagite and Orange G in their more stable hydrazone forms.

The manganese(II) catalysed reduction of dioxygen to hydrogen peroxide using either hydroxylamine or hydrazine as substrates has been described previously.² Electron deficient catechols such as Tiron (1,2-dihydroxybenzene-3,5-disulfonate, disodium salt) were found to be essential ligand requirements for this system. We were interested to investigate whether this catalytic system could also

oxidize Calmagite, thus providing a model system that can not only generate hydrogen peroxide, but also activate the *in situ* generated peroxide to perform useful chemical work.

Hydrogen peroxide is one of the cleanest and most environmentally safe oxidants available because it has high atom efficiency and the by-product in its use is usually water.³ The treatment of wastewaters from dye manufacturers and the textile processing industries is a growing problem⁴ with azo dyes which contain the –N=N– moiety being particularly problematic as they not only account for 70% of textile dyestuffs but are also chemically stable.⁵ The metal-catalysed decolourization of dyes using hydrogen peroxide has shown some positive results in overcoming the sluggish reaction kinetics of H₂O₂ with the recent publication of Lenoir *et al.* using Fe^{III}–TAML (tetra amido macrocyclic ligands) for the oxidation of Orange II using (added) peroxides being particularly relevant to this work.⁶ There are many examples of published work in the area of low temperature bleaching using manganese-based catalysts, but in all of these cases the H₂O₂ was added separately.⁷ Thus while hydrogen peroxide may be viewed as an ideal, green, oxidant, the current method of industrial production and the transport, storage and handling of bulk H₂O₂ impacts negatively on these favourable environmental characteristics.⁸ For laundry and other applications, bleaching based on activation of atmospheric O₂ would lead to an even more desirable reduction in chemical loading and costs.⁹ An alternative strategy that is described in this paper involves the catalytic reduction of O₂ to H₂O₂ to generate an *in situ* activated hydrogen peroxide molecule that can perform selective bleaching under mild conditions. In this case it would be useful if the catalysts and substrates used to generate the H₂O₂ are cheap and non-toxic. While an ultimate goal this is not realized in the current system, in part, due to the hazards and cost in the use of hydroxylamine as substrate.

Results and discussion

Fig. 2 depicts the disappearance of Calmagite (0.100 mM) as it is oxidized by *in situ* generated hydrogen peroxide at 20 ± 1 °C and pH 8.0 (using the non-coordinating EPPS buffer) in the presence of manganese(II) ions (50.0 μM) and Tiron (1.50 mM) with an O₂ flow rate of 0.6 L min⁻¹. †

With 100 mM NH₂OH, as reducing substrate, the oxidation was complete in less than 10 min. The TOF (turnover frequency = moles of dye oxidised per mole of catalyst per hour) is calculated to be 42 h⁻¹ (Table 1).

During this time, no hydrogen peroxide was detected in solution presumably because it was consumed as soon as it was formed. Thereafter, a slow increase in the concentration of hydrogen peroxide was observed. In the absence of added manganese(II)

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Table 1 Summary of initial rates and turnover frequencies for dye oxidation and hydrogen peroxide formation or decomposition using *in situ* generated H₂O₂ (except where indicated) at 20 ± 1 °C. In all cases initial [NH₃OH⁺Cl⁻] was 100 mM and the pH was 8.0 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O₂ flow rate 0.6 L min⁻¹

Fig. no.	Dye/0.10 mM	Catalyst/0.050 mM	10 ⁷ Initial rate of dye oxidation/mol dm ⁻³ s ⁻¹		10 ⁴ Initial rate of H ₂ O ₂ formation or decomposition/mol dm ⁻³ s ⁻¹	
			No Tiron (TOF/h ⁻¹) ^a	Tiron added/1.50 mM (TOF/h ⁻¹) ^a	No Tiron	Tiron added/1.50 mM
2	Calmagite	Aqueous MnCl ₃ ·4H ₂ O	0.32	5.8 (42)	1.4 (formation)	—
3	Orange G	Aqueous MnCl ₃ ·4H ₂ O	Neg.	—	0.18 (formation)	—
4	Calmagite	[Na ₅][Mn ^{III} (3,5-(SO ₃) ₂ Cat) ₂]·10H ₂ O	1.9 (14)	2.9 (21)	—	0.34 (formation) ^b
5	Calmagite	Aqueous MnCl ₃ ·4H ₂ O	—	1.9	0.082 (formation)	0.16 (decomposition)
6	Calmagite	Aqueous MnCl ₃ ·4H ₂ O (with added H ₂ O ₂)	Neg.	10 (72)	Neg.	1.1 (decomposition)

^a TOF = turnover frequency (moles of dye oxidised per mole of catalyst per hour. ^b After dye oxidation.

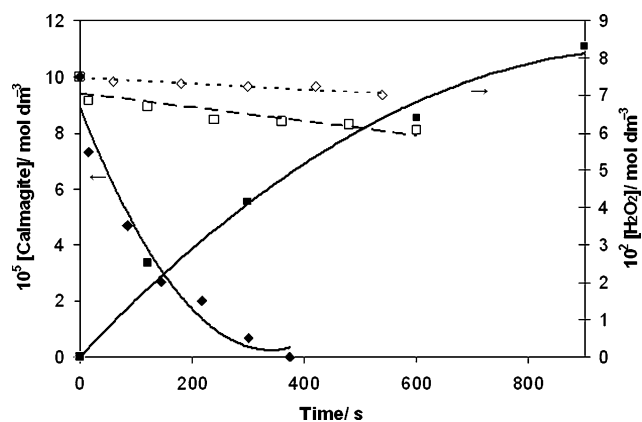


Fig. 2 The change in [Calmagite] with time monitored at 544 nm and the formation of hydrogen peroxide (in the absence of Tiron) at 20 ± 1 °C. Initial [Calmagite] and [NH₃OH⁺Cl⁻] were 0.100 mM and 100 mM respectively. [MnCl₃·4H₂O] was 0.0500 mM (□, ◆) or zero (◇), Tiron was 1.50 mM (□, ◆) or zero (◇) and the pH was 8.0 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O₂ flow rate 0.6 L min⁻¹. Secondary y-axis: The formation of H₂O₂ (■) with Calmagite in the absence of Tiron (all conditions as above).

and Tiron, very slow dye oxidation was observed which could be effectively stopped by the addition of edta²⁻ (0.100 mM).

In the presence of Mn(II) but with no added Tiron, slow oxidation of Calmagite was observed. This was shown to be due to the slow formation of hydrogen peroxide (Fig. 2, secondary y-axis) generated by Calmagite substituting for Tiron in the manganese(II) catalysed reduction of dioxygen to hydrogen peroxide using hydroxylamine as substrate. Under these conditions (*i.e.* the absence of Tiron) an accumulation of H₂O₂ in the reaction solution was observed (despite the presence of un-reacted Calmagite). This sequence of reactions shows that both manganese(II) ions and hydrogen peroxide are essential components in the oxidation of Calmagite and that the manganese catalysed reduction of dioxygen to hydrogen peroxide with de-protonated Tiron (or less effectively Calmagite) can generate the *in situ* hydrogen peroxide needed. No oxidation of Orange G (Fig. 3) was observed under these conditions, despite the presence of *in situ* generated H₂O₂ which is in line with results previously reported by Oakes *et al.*,¹ *i.e.* that effective coordination to manganese(II) is an essential pre-requisite for dye oxidation and this is not achieved with an *o*-monohydroxy azo dye.

When Mn(II) ions are replaced with an equimolar amount of aqueous [Na₅][Mn^{III}(3,5-(SO₃)₂Cat)₂]·10H₂O (50.0 μM), which contains the de-protonated Tiron anion, a similar decomposition curve for Calmagite was observed (Fig. 4) with again no hydrogen peroxide detected in the reaction solution until essentially all of the Calmagite had been destroyed (secondary y-axis).

In the absence of added Tiron, a slower Calmagite decomposition was observed presumably because of the importance of the de-protonated Tiron anion being coordinated to the manganese atom. With [Na₅][Mn^{III}(3,5-(SO₃)₂Cat)₂]·10H₂O an initial reduction of Mn(III) to Mn(II) by NH₂OH is probable.¹⁰

Fig. 5 depicts the oxidation of Calmagite by *in situ* generated H₂O₂ with Tiron added during the experiment. After an initial small loss of Calmagite, the [Calmagite] remains constant, despite

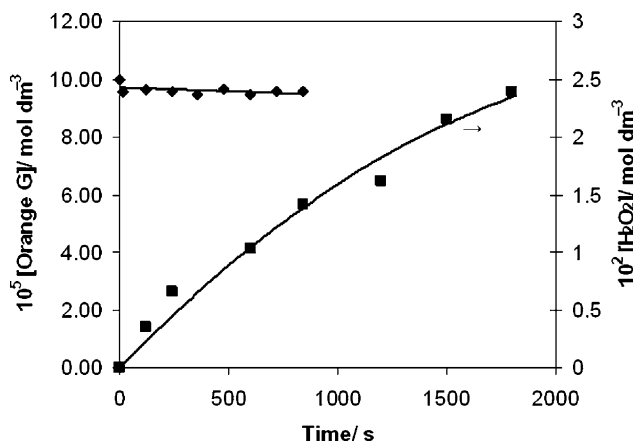


Fig. 3 The change in [Orange G] with time monitored at 478 nm (◆) and the formation of hydrogen peroxide (■) at 20 ± 1 °C. Initial [Orange G] and $[\text{NH}_3\text{OH}^+\text{Cl}^-]$ were 0.10 mM and 100 mM respectively. $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$ and [Tiron] were 0.0500 mM and 1.50 mM respectively and the pH was 8.0 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O_2 flow rate 0.6 L min^{-1} .

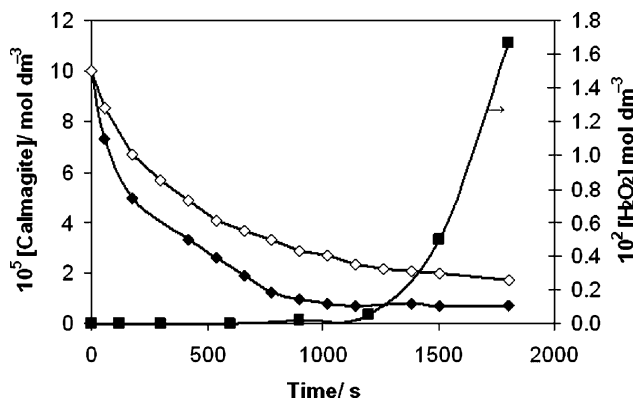


Fig. 4 The change in [Calmagite] with time monitored at 544 nm at 20 ± 1 °C and the formation of hydrogen peroxide. Initial [Calmagite] and $[\text{NH}_3\text{OH}^+\text{Cl}^-]$ were 0.100 mM and 100 mM respectively. $[\text{Na}_5[\text{Mn}^{\text{III}}(3,5\text{-}(\text{SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}]$ was 0.050 mM and Tiron was 1.50 mM (◆) or zero (◇) and the pH was 8.0 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O_2 flow rate 0.6 L min^{-1} . Secondary y-axis: The formation of H_2O_2 (■) with Calmagite in the presence of Tiron (all conditions as above).

the *in situ* formation of H_2O_2 which rises to a concentration of $\sim 4.5 \text{ mM}$ ($[\text{H}_2\text{O}_2]/[\text{Calmagite}] \sim 50$) over a 10 min period.

When Tiron (150 mM, 1.00 mL) was then added (at $t = 10$ min), rapid decomposition of Calmagite was observed which was accompanied by a rapid loss of H_2O_2 in solution. The frothing of the solution at this time suggests that at least partial mineralization of Calmagite may be occurring with the evolution of CO and CO_2 . Initial experiments obtained by bubbling the exhaust gases through a known excess of aqueous sodium hydroxide and back titrating with acid suggest that ~ 5 mole equivalents of CO_2 (to Calmagite decomposed) were evolved. When this solution was left stirring in air over-night, H_2O_2 was detected in the reaction solution and the addition of another portion of Calmagite resulted in the rapid disappearance of the purple colour indicating that the catalytic system (specifically the Tiron anion) is robust to chemical

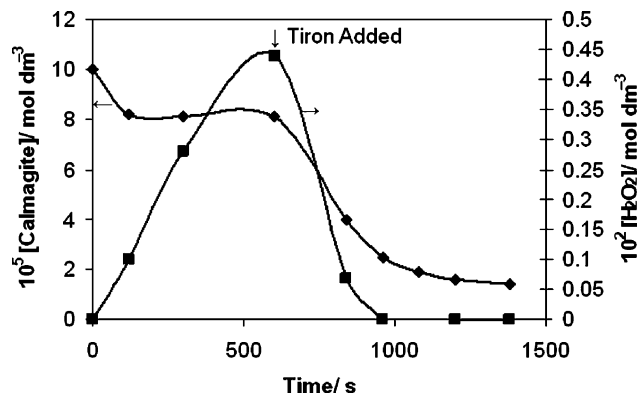


Fig. 5 The effect of added Tiron on the oxidation of Calmagite (◆) with time monitored at 544 nm and the change in $[\text{H}_2\text{O}_2]$ (■) at 20 ± 1 °C. Initial [Calmagite] and $[\text{NH}_3\text{OH}^+\text{Cl}^-]$ were 0.100 mM and 100 mM respectively. $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$ was 0.0500 mM. Tiron was 1.50 mM (added at $t = 10$ min) and the pH was 8.00 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O_2 flow rate 0.6 L min^{-1} .

oxidation and further portions of dye can be oxidised. In a separate experiment, H_2O_2 ($\sim 10 \text{ mM}$) was added to a solution of Calmagite, initially in the absence of added Tiron. Very little loss of Calmagite occurred over a 10 min period (Fig. 6).

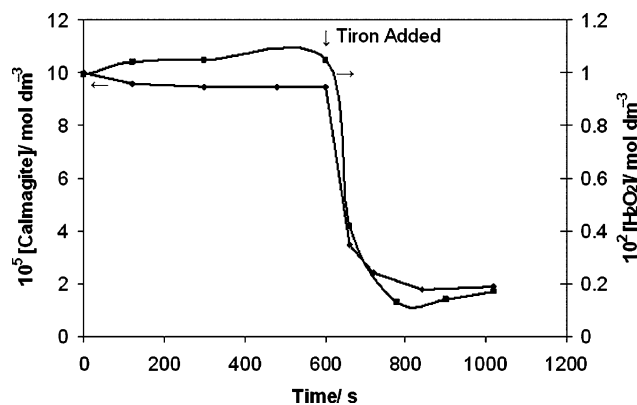
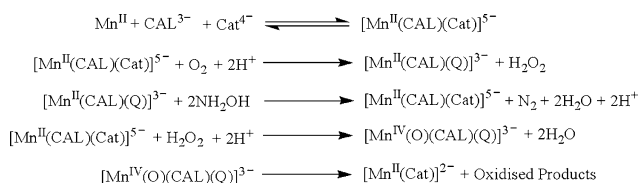


Fig. 6 The effect of added Tiron on the oxidation of Calmagite (◆) with time monitored at 544 nm and the change in $[\text{H}_2\text{O}_2]$ (■) at 20 ± 1 °C. Initial [Calmagite], $[\text{NH}_3\text{OH}^+\text{Cl}^-]$ and $[\text{H}_2\text{O}_2]$ were 0.100 mM, 100 mM and $\sim 10 \text{ mM}$ respectively. $[\text{MnCl}_2 \cdot 4\text{H}_2\text{O}]$ was 0.0500 mM. Tiron was 1.50 mM (added at $t = 10$ min) and the pH was 8.00 (20 mM, *N*-2-hydroxyethylpiperazine-*N'*-3-propanesulfonic acid, EPPS, buffer) with O_2 flow rate 0.6 L min^{-1} .

When Tiron (150 mM, 1.00 mL) was added (at $t = 10$ min), rapid decomposition of Calmagite was observed ($\text{TOF} = 72 \text{ h}^{-1}$, Table 1), which was accompanied by a rapid loss of H_2O_2 . Thereafter the $[\text{H}_2\text{O}_2]$ was observed to rise in solution. Thus despite an excess of H_2O_2 in the reaction solution, the catalytic system, in the absence of Tiron, cannot effectively utilise the H_2O_2 present for the rapid oxidation of Calmagite. These results provide evidence for the strong preference of the oxidising system for deprotonated Tiron as a co-ligand in a mixed manganese(II) deprotonated Calmagite/Tiron complex. The slower oxidation of Calmagite observed with $[\text{Na}_5[\text{Mn}^{\text{III}}(3,5\text{-}(\text{SO}_3)_2\text{Cat})_2] \cdot 10\text{H}_2\text{O}]$ in the absence of added Tiron suggests that the system works most

efficiently in the presence of excess Tiron as this may be needed for it to be successful in competing for coordination sites around the manganese atom. The experiment with added H₂O₂ indicates that the importance of the Tiron anion is not only due to its efficiency of *in situ* H₂O₂ generation but crucially its ability to utilise the *in situ* H₂O₂ generated for the oxidation of Calmagite. The efficacy of de-protonated Tiron in this may be related to its redox, non-innocent, properties that enable it to exist as a catechol, semi-quinone or quinone species while still bound to the manganese centre. The H₂O₂ formed presumably oxidises the Tiron-catechol to its semi-quinone or quinone forms and/or binds to a vacant site on the Mn atom to form a Mn(III), Mn(IV)–oxo (or possibly Mn(V)–oxo) species which is then responsible for the oxidation of bound Calmagite (Scheme 1).



Scheme 1 General mechanism for the catalytic *in situ* generation of H₂O₂ and oxidation of Calmagite. CAL = de-protonated Calmagite anion; Cat = de-protonated Tiron catechol anion and Q = Tiron quinone anion.

Similar mechanisms have been proposed by both Oakes *et al.*¹ and Lenoir *et al.*⁶ in the oxidation of azo dyes by peroxides catalysed by Mn(II) and Fe(III)–TAML complexes respectively.

Conclusions

This study provides, to the best of our knowledge, the first example of a system that can, not only catalytically generate hydrogen peroxide *in situ* from dioxygen in aqueous solution under mild conditions, but also utilize this hydrogen peroxide to perform a model oxidation reaction using the same catalytic system under the same ambient conditions. The mixed manganese(II) de-protonated Calmagite/Tiron complex is able to efficiently utilise the *in situ* H₂O₂ generated for the rapid decomposition of Calmagite and this only occurs slowly in the absence of Tiron. The importance of de-protonated Tiron as a co-ligand for efficient Calmagite destruction in this work is an interesting, if perhaps not un-surprising result, given the non-innocent redox properties of catechols.¹¹ Future studies, including the use of EPR, will help provide further information on the nature of the oxidising species in this system. The generation of hydrogen peroxide with Calmagite provides the first example of a non-catechol molecule that can generate hydrogen peroxide from the catalytic reduction of dioxygen using hydroxylamine and this provides an important additional insight into the mechanism of hydrogen peroxide generation. The current system provides an interesting example of the ability of manganese–catecholate complexes to effectively activate small molecules to perform useful chemical work which has importance in the modelling of natural systems. The tailoring of the decomposition of specific dyes with the catalytic system

used in relation to this work (with Calmagite) and the work of Lenoir *et al.* using Fe^{III}–TAML (with Orange II) has important implications in terms of the treatment of wastewaters.

Acknowledgements

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Notes and references

† *N*-2-Hydroxyethylpiperazine-*N'*-3-propanesulfonic acid (EPPS) buffer (200 mM, 10.0 mL), hydroxylamine hydrochloride (NH₂OH⁺Cl⁻ 1.00 M, 10.0 mL), Tiron (1,2-dihydroxybenzene-3,5-disulfonate, disodium salt (15.0 mM, 10.0 mL) and sodium hydroxide pellets (semi-conductor grade, 0.40 g, 1.0 mM) were added to de-ionised water (~20 mL). When all of the NaOH had dissolved, the pH was adjusted to 8.0 using freshly prepared (CO₂-free) NaOH(aq). To this solution were added Calmagite (1.00 mM, 10.0 mL) and MnCl₂·4H₂O (0.0500 mM, 1.00 mL) to produce a purple coloured solution which was transferred to a volumetric flask (100.0 mL) and made up with de-ionised water. The pH was checked again and if necessary adjusted to 8.0 and the solution transferred to a dreschel bottle equipped with a glass inlet. The dreschel bottle was placed in a water bath at 20 ± 1 °C and dioxygen gas at a rate of 0.6 L min⁻¹ was passed through the rapidly stirred solution. The absorbance of the solution at 544 nm ($\epsilon = 10\,500 \text{ L mol}^{-1} \text{ cm}^{-1}$) was monitored at regular intervals using a 0.10 cm glass cuvette. As the Calmagite dye was oxidized it changed colour from a deep purple to a pale yellow. Where appropriate, aqueous Mn(II) solution was replaced with [Na₃[Mn^{III}(3,5-(SO₃)₂Cat)₂]:10H₂O (0.0500 mM, 1.00 mL), where H₂Cat = 1,2-dihydroxybenzene. [Na₃[Mn^{III}(3,5-(SO₃)₂Cat)₂]:10H₂O was prepared as described previously.¹² The oxidation of Orange G (1.00 mM, 10.0 cm³) when used in place of Calmagite was monitored at 478 nm ($\epsilon = 11\,600 \text{ L mol}^{-1} \text{ cm}^{-1}$). Analysis for hydrogen peroxide was achieved by removing aliquots (0.50 mL) of reaction solution which were added to titanium(IV) solution (3.00 mL) and the absorbance of the samples measured at λ_{max} of 407 nm ($t = 0 \text{ min}$ as blank) using a 0.10 cm glass cuvette.¹³

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