DALTON

Kinetic investigations into the mechanism of peroxosulfate oxidation of Calmagite dye catalysed by manganese(II) ions

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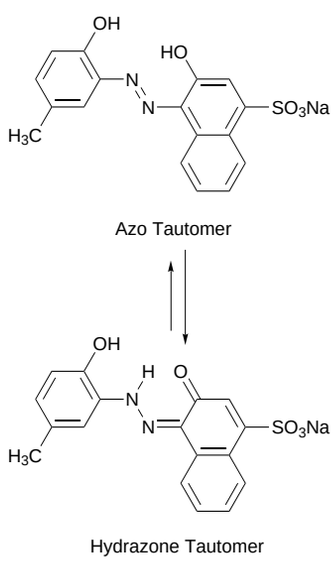
Manganese(II) ions were found to be capable of catalysing the peroxosulfate ($KHSO_5$) oxidation of Calmagite, a dye containing the *o*,*o*′-dihydroxy azo structural motif at pH 10 but not the more common monohydroxy azo dyes or those that contain no *o*-hydroxy group. The catalysed decomposition of Calmagite results in decomposition profiles that resemble an autocatalytic process, *i.e.* the reaction rate increases as dye concentration decreases. Spectroscopic investigations indicated that two complexes are formed between Mn^{II} and Calmagite (D), having 1:1 and 1:2 stoichiometries, *i.e.* [MnD] and [MnD_2]. Under experimental conditions [$KHSO_5$] ⩾ [D] ⩾ [Mn^{II}] so the catalyst exists in the form [MnD_2] and it is shown that the unusual kinetics are due to a reaction of order -1 in [D]. This negative order is explained by attributing [MnD] as the active catalyst, formed from the inert [MnD_2], with which it is in equilibrium, by the loss of one dye molecule. The experimental data were found to conform to the rate expression $-d[D]/dt = k_0[Mn^{II}][KHSO_5]/[D]$ and the rate constant k_0 can be determined from plots of $[D]^2$ against time. It is concluded that a key factor for promoting catalysis is specific complexation of Mn^{II} to the dye substrate, and that the *o*,*o*′-dihydroxy azo structural unit is specifically required for efficient manganese catalysis. Some insight into the mechanism of catalysis was obtained by investigating Mn^{III} as catalyst and from studies where H_2O_2 was employed as the oxidant. It is proposed that the mechanism involves nucleophilic attack by oxidant on the metal centre followed by peroxide-bond scission, leading to formation of manganese-(III) or -(IV) species which subsequently initiate dye oxidation *via* an inner-sphere reaction mechanism.

This paper addresses the interesting and unusual kinetic profiles obtained during the catalysed oxidation of the azo dye Calmagite (Scheme 1) in alkaline media using manganese(II) ions as catalyst. A comprehensive kinetic analysis is presented and some insights generated into the mechanism of reaction.

Although there has been some recent work on bleaching of dyes in solution,[1] and on the use of dimeric manganese complexes,[2] comparatively little has appeared on catalysed dye bleaching in alkaline media using Mn^{II}. Earlier work[3] used Mn^{II} but concentrated upon the use of its complexes (*e.g.* acetylacetonate, hydrogencarbonate) with peroxide as the oxidant around neutral pH. The authors[3] invoked two mechanisms, which were intimately associated with the affinity of the dye for Mn. Where the binding affinity was high an inner-sphere mechanism was proposed, which implicated high-oxidation-state manganese intermediates as active oxidant species; on the other hand, an outer-sphere process involving radicals as active oxidant species was proposed when the dye binding affinity was low. A more recent study[4] noted that the peroxide oxidation of 3-(2-hydroxyphenylazo)pyridine-2,6-diol was extremely sensitive to trace manganese(II) ions in alkaline media and proposed that the system be used as an analytical method for the estimation of Mn^{II}.

This work focuses upon the Mn^{II}-catalysed oxidation of dyes using the inorganic peracid potassium hydrogenperoxosulfate ($KHSO_5$) as oxidant. As the studies progressed, they were extended to include Mn^{III} as catalyst and hydrogen peroxide as oxidant, to develop an understanding of the mechanism.

Three types of azo dyes were chosen for this study, functioning as tri-, bi- and mono-dentate ligands. Two of the three types contain an hydroxy group conjugated with the azo group. Such dyes can exist in either one of two tautomeric forms, an azo form or a hydrazone form,[5] or an equilibrium mixture of the two (Scheme 1). Calmagite is an *o*,*o*′-dihydroxy azo dye existing predominantly as the hydrazone tautomer and was selected as it is known to exhibit strong metal binding.[6] Orange G exemplifies azo dyes having one *o*-hydroxy group. It, too, exists



Scheme 1 Azo–hydrazone tautomerism of Calmagite dye in solution

primarily as the hydrazone tautomer but exhibits lower metal-binding constants[6] as it can act only as a bidentate ligand. Otherwise, it has a similar structural motif to Calmagite, the extra sulfonate simply reducing its tendency to aggregate. Altering the position of the sulfonate (provided it is not *ortho* to the azo group) or adding a second sulfonate has little effect on metal binding or oxidative destruction of the dye. Model dyes I and II are monohydroxyazo dyes which are structurally similar to Orange G but are substituted with an *o*-carboxy or sulfonate group. These were selected to probe the influence of extra *ortho* substituents on metal binding/catalysis. Methyl Orange is a dye which exists exclusively in the azo form and contains no *ortho* substituents. As it acts as a monodentate ligand, this dye has very low affinity for metal binding.

Upon ionisation of these hydroxyazo dyes, or on metal

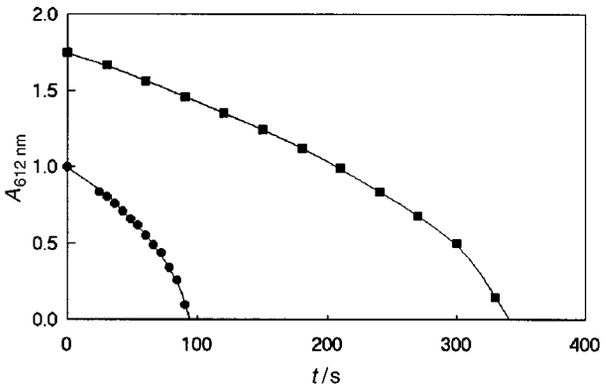
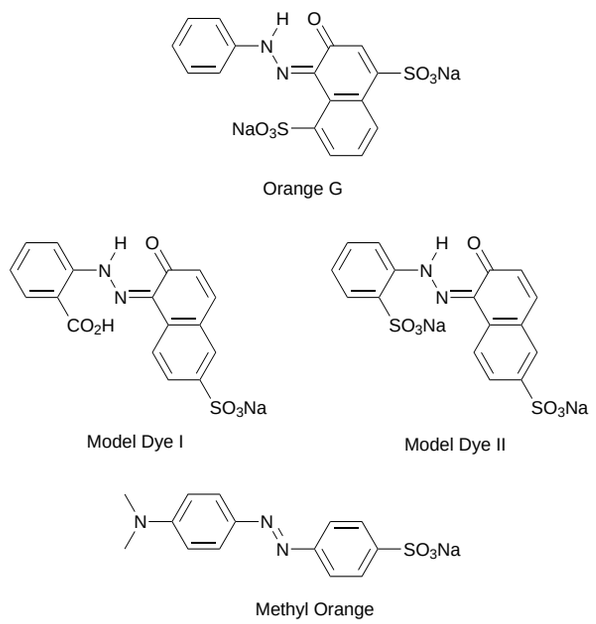


Fig. 1 Change in absorbance of 4.9×10^{-5} (●) and 9.1×10^{-5} M (■) Calmagite at 612 nm with time due to catalysed oxidation using 1 mM $KHSO_5$ with 10^{-6} M Mn^{II} at pH 10 and 40 °C



binding, there is extensive electron delocalisation over the whole molecule and they tend to exhibit azo character, with electron density concentrated upon the oxygen atom.[7]

Results and Discussion

Experimental observations

The decomposition profiles for the Mn^{II}-catalysed peroxosulfate oxidation of Calmagite are unusual (Fig. 1). As the reaction proceeds and dye concentration decreases, the reaction accelerates. Furthermore, the initial reaction rate is slower when $[D]_0$ (D = dye) is increased. Both observations are contrary to those normally found and have characteristics usually associated with autocatalytic processes. If Mn^{II} is substituted by Mn^{III} the decomposition profiles are unchanged. When Calmagite is substituted by other dyes (Orange G, Model dyes I and II and Methyl Orange) oxidation by peroxosulfate is not catalysed by addition of Mn^{II} or Mn^{III}.

Since the observed reaction with Calmagite is suppressed by increase in initial dye concentration, it was conceivable that the dye could be aggregating. This possibility was eliminated since the absorbance *vs.* [D] plots obeyed the Beer–Lambert law over the range of concentrations studied. In the next section another possible explanation is explored, namely complexation between manganese and dye.

Complexation of Mn^{II} with Calmagite

Changes in the UV/VIS spectrum of 5×10^{-5} M Calmagite at

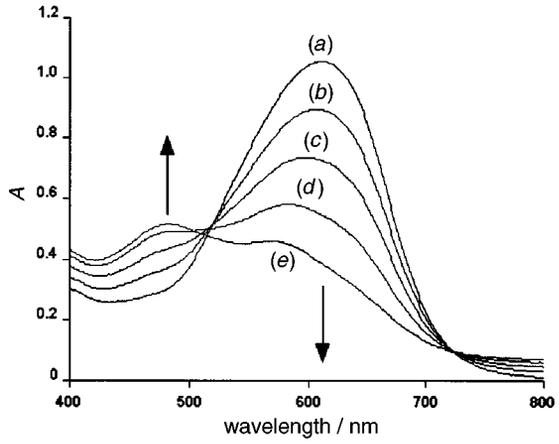


Fig. 2 Influence of Mn^{II} on the UV/VIS spectrum of 5×10^{-5} M Calmagite at pH 10 and 40 °C. Spectra (*a*) to (*e*) comprise a titration with aliquots of 7×10^{-6} M Mn^{II} from zero to 2.8×10^{-5} M inclusive

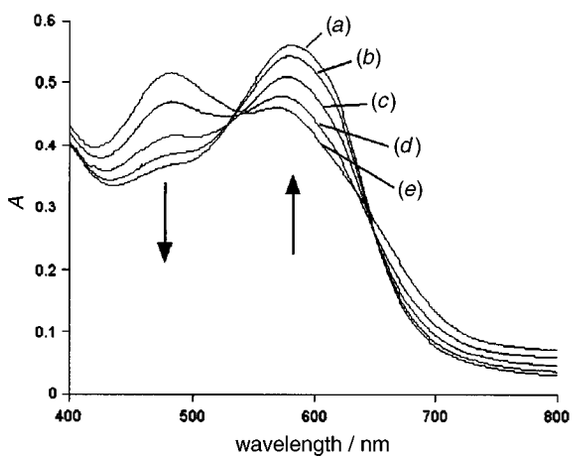


Fig. 3 Influence of Mn^{II} on the UV/VIS spectrum of 5×10^{-5} M Calmagite at pH 10 and 40 °C. Spectra (*a*) to (*e*) correspond to titration with aliquots of 7×10^{-6} M Mn^{II} from 2.8×10^{-5} to 5.6×10^{-5} M inclusive.

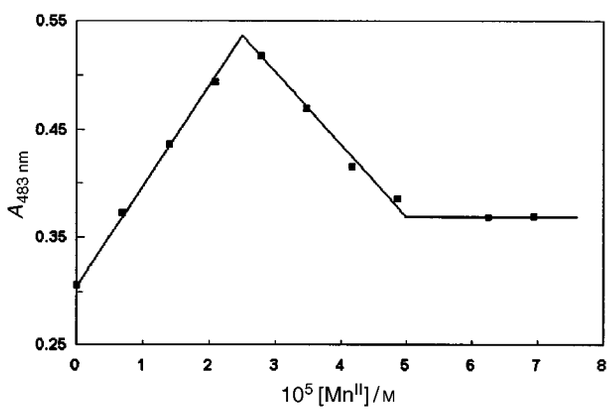


Fig. 4 Changes in the absorbance of 5×10^{-5} M Calmagite at 483 nm due to complexation with added Mn^{II} at pH 10 and 40 °C

40 °C and pH 10 upon titration with manganese(II) ions are depicted in Figs. 2 and 3. Upon addition of Mn^{II} the absorption maximum A_{max} shifts progressively from 612 to 483 nm (Fig. 2) but on further addition of Mn^{II} it shifts back to 582 nm (Fig. 3). No further spectral shifts occur beyond a 1:1 molecular ratio. The formation of a 1:2 complex (MnD_2) is illustrated in Fig. 4, where absorbance at 483 nm is plotted as a function of $[Mn^{II}]$. Thus electronic absorption spectra provide convincing evidence that Mn^{II} forms 1:1 and 1:2 complexes with Calmagite.

Clearly, equilibria (1) and (2) need to be considered for

$$Mn + D \overset{K_1}{\rightleftharpoons} [MnD] \quad (1)$$

$$[MnD] + D \overset{K_2}{\rightleftharpoons} [MnD_2] \quad (2)$$

kinetic analysis. Under the conditions of catalysis, where $[Mn^{II}] \ll [D]$, effectively all the Mn^{II} is tied up as MnD_2.

If Mn^{II} is replaced by Mn^{III} then direct oxidation of Calmagite is induced, even in the absence of $KHSO_5$. In particular, there is a considerable reduction in intensity of the spectral peak at 612 nm in the UV/VIS spectrum if Mn^{III} is added to Calmagite up to and beyond a 2:1 stroichiometric Mn:D ratio and there remains a comparatively weak spectrum, identical to those for the Mn^{II}–Calmagite complexes. On the other hand, when Calmagite is replaced by Orange G, Model Dyes I and II, and Methyl Orange no corresponding changes are observed in their UV/VIS spectra upon addition of Mn^{II} or Mn^{III}. Indeed, with these dyes there are visible signs of formation of insoluble manganese oxides at pH 10, particularly with Mn^{III}; this does not occur with Calmagite, except at high $[Mn^{II}]$ at pH > 12. Clearly, Calmagite, like other sequestrants, suppresses alkaline hydrolysis of Mn^{II} and subsequent oxidation to Mn^{III} by molecular oxygen.

Knowledge of the structure and stoichiometry of complexes formed is important for analysis of the kinetic behaviour and to establish the rate law for the reaction. Moreover, since two complexes form with Calmagite, we are provided with a mechanism for explaining the unusual kinetic behaviour and it is now explored whether the catalytic behaviour can be understood in terms of catalysis by complexes formed from pre-equilibrium mixtures of reactants, *i.e.* Mn^{II} and dye. In order to understand the unusual kinetic profiles, it is necessary to examine potential decomposition pathways and relevant equilibria.

Kinetics of dye destruction

Reaction scheme. The simplified reaction sheme in equations (3)–(6) needs to be considered. Reaction (5) represents 'free'

$$[MnD_2] + KHSO_5 \xrightarrow{k_1} \text{Products} \quad (3)$$

$$[MnD] + KHSO_5 \xrightarrow{k_2} \text{Products} \quad (4)$$

$$D + Mn + KHSO_5 \xrightarrow{k_3} \text{Products} \quad (5)$$

$$D + KHSO_5 \xrightarrow{k_4} \text{Products} \quad (6)$$

Mn^{II} or, more precisely, catalysed dye destruction *via* an attack on the dye by a manganese complex with peroxosulfate. 'Free' manganese species in higher oxidation states are not considered, for reasons given later.

Analysis of kinetics. As the dye is related to the various manganese species by a set of equilibria, and total [D] is given by the relationship (7), then rate of loss of dye is given by equation (8).

$$[D]_T = [D] + [MnD] + 2[MnD_2] \quad (7)$$

$$-d[D]/dt = 2k_1[MnD_2][KHSO_5] + k_2[MnD][KHSO_5] + k_3[Mn][D][KHSO_5] + k_4[D][KHSO_5] \quad (8)$$

Clearly, these are a set of parallel reactions, so the fastest will control the rate, unlike a set of consecutive reactions where the slowest step is rate determining. At the outset, it is clear that certain reactions can be eliminated as the fast reaction. For example, (3) may be ignored since $[MnD_2] \approx [Mn]_T \approx [Mn]_0$, the initial manganese concentration under the conditions studied, so the rate expression should be zero order in [D] and evidently is not. Similarly, the uncatalysed reaction (6) can be discounted because, apart from being slow, it is first order[8] in [D]. The active catalyst must be either [MnD] or 'free' Mn^{II}. To examine further, let us consider the mass balance in manganese species, equation (9), and equilibrium expressions (10) between species in equations (1) and (2). The three equations (9) and (10) can be

$$[Mn]_0 = [Mn] + [MnD] + [MnD_2] \quad (9)$$

$$K_1 = [MnD]/[Mn][D]; \quad K_2 = [MnD_2]/[MnD][D] \quad (10)$$

rearranged to derive the concentrations of manganese species, equations (11)–(13). As 1:2 complexes form under experimental conditions, then $K_2[D]$ (the ratio $[MnD_2]/[MnD]$) and $K_1K_2[D]^2$ (the ratio $[MnD_2]/[Mn]$) must both be $\gg 1$. Thus equations (11)–(13) can be simplified as (14)–(16) where $[Mn]_0$, the total manganese concentration, is a constant.

$$[Mn] = [Mn]_0/\{K_1[D](K_2[D] + 1) + 1\} \quad (11)$$

$$[MnD] = K_1[D][Mn]_0/\{K_1[D](K_2[D] + 1) + 1\} \quad (12)$$

$$[MnD_2] = K_1K_2[D]^2[Mn]_0/\{K_1[D](K_2[D] + 1) + 1\} \quad (13)$$

$$[Mn] = [Mn]_0/K_1K_2[D]^2 \quad (14)$$

$$[MnD] = [Mn]_0/K_2[D] \quad (15)$$

$$[MnD_2] = [Mn]_0 \quad (16)$$

Substitution for [MnD] and [Mn] in the reduced rate expression, from (8), gives equations (17) and (18). Thus either [MnD]

$$-d[D]/dt = k_2[MnD][KHSO_5] + k_3[Mn][D][KHSO_5] \quad (17)$$

$$-d[D]/dt = (k_2[Mn]_0[KHSO_5]/K_2[D]) + (k_3[Mn]_0[KHSO_5]/K_1K_2[D]) \quad (18)$$

or 'free' Mn^{II} as catalyst would lead to a negative order in [D], *i.e.* an order of −1, but first order in $[KHSO_5]$ and $[Mn^{II}]$.

Under conditions where little binding of Mn^{II} occurs, for example with the monohydroxy azo dyes, there was no evidence for any catalysis. This suggests that Mn^{II} is not catalytically active towards such bleach-sensitive dyes. Secondly, its concentration is extremely low under the experimental conditions. For similar reasons, the presence in the system of 'free' manganese species in higher oxidation states is unlikely. It is thus concluded that the active catalyst is [MnD]. Thus equation (18) reduces to (19).

$$-d[D]/dt = k_2[Mn]_0[KHSO_5]/K_2[D] \quad (19)$$

Experimental determination of rate constants/confirmation of kinetic analysis. As $[Mn]_0$ and $[KHSO_5]$ are effectively constant, then from equation (19) the generalised or experimental rate expression becomes (20). Integration yields expression (21).

$$-d[D]/dt = k_{obs}/[D] \quad (20)$$

$$[D_0]^2 - [D]^2 = 2k_{obs}t \quad (21)$$

This suggests that a plot of $[D]^2$ *versus* time should be linear, with the gradient giving a convenient measure of k_{obs}.

Fig. 5 is a plot of the square of the dye absorbance, A^2, *versus* time for the reactions in Fig. 2. The analysis predicts two parallel lines, from either of which k_{obs} can be obtained. The fit is excellent at the lower initial dye concentration, but not so good at higher [D]. Since there is insignificant catalysed oxidant

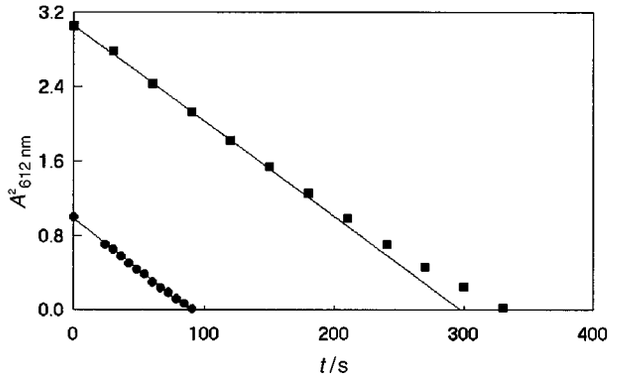


Fig. 5 Plot of square of absorbance of Calmagite at 612 nm (from Fig. 1) *versus* reaction time

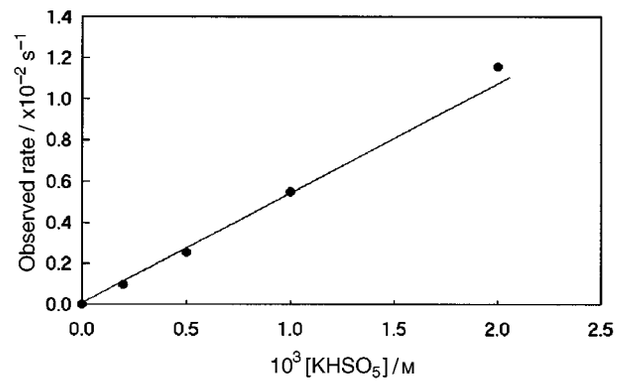


Fig. 6 Plot of observed rate, k_{obs}, *versus* [$KHSO_5$] for the catalysed oxidation of 4.9×10^{-5} M Calmagite using 10^{-6} M Mn^{II} at pH 10 and 40 °C

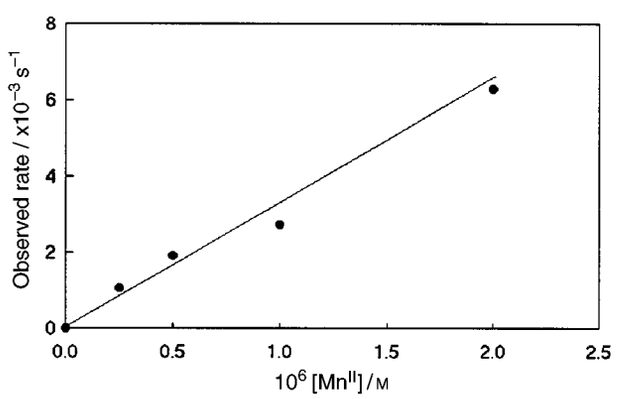


Fig. 7 Plot of observed rate, k_{obs}, *versus* [Mn^{II}] for the catalysed oxidation of 4.9×10^{-5} M Calmagite using 0.5 mM $KHSO_5$ at pH 10 and 40 °C

decomposition under the experimental conditions, this deviation is attributed to contributions becoming more significant from a parallel reaction involving direct reaction of Calmagite with $KHSO_5$.

Furthermore, the analysis suggests that if the dye concentration is increased by n, then the half-life should increase by n^2. Examination of Figs. 1 and 5 suggests that this is indeed the case; an increase in [D] of 1.85 times has led to an increase in the half-life of ≈3.4 times.

The analysis also predicts that k_{obs} should give linear plots against initial concentrations of reactants and this is confirmed experimentally (Figs. 6 and 7). The experimentally derived rate contains the constant, k_0, equation (22), which is related to k_2 [equation (19)] *via* the relationship (23).

$$d[D]/dt = k_0[Mn]_0[KHSO_5]/[D] \quad (22)$$

$$k_0 = k_2/K_2 \quad (23)$$

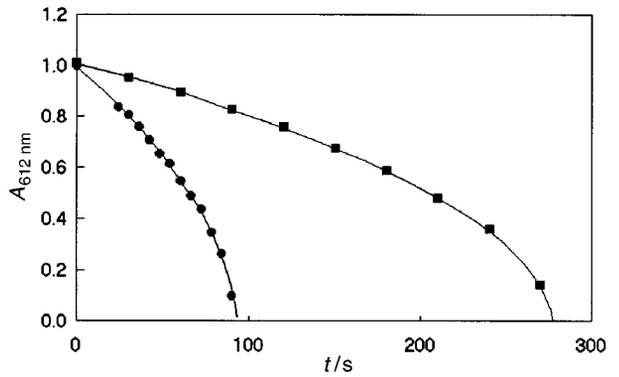


Fig. 8 Changes in absorbance of 4.9×10^{-5} M Calmagite at 612 nm with time due to catalysed oxidation using 1 mM $KHSO_5$ (●) and 1 mM H_2O_2 (■) with 10^{-6} M Mn^{II} at pH 10 and 40 °C

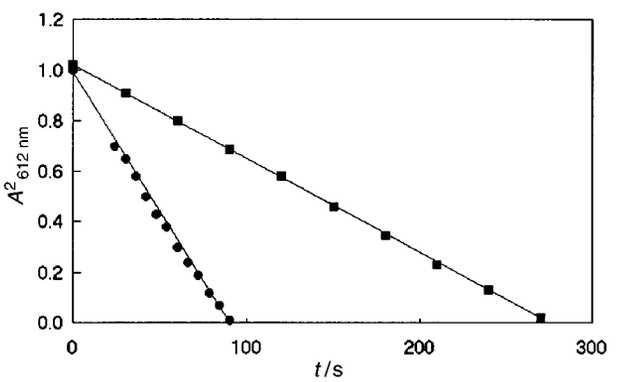


Fig. 9 Square of absorbance of Calmagite at 612 nm (from Fig. 8) *versus* reaction time

To check whether the deviation from linearity in Fig. 5 is due to an uncatalysed reaction, $KHSO_5$ was replaced by H_2O_2 since the uncatalysed direct reaction of Calmagite with H_2O_2 is known to be very much slower[8] than with $KHSO_5$. The experimental data and plots of A^2 *vs.* time are given in Figs. 8 and 9 for both oxidants at pH 10 and 40 °C. As anticipated, peroxide gives much better straight-line plots than $KHSO_5$ over all conditions studied.

Mechanism of Mn^{II} catalysed oxidation of Calmagite

Role of complexation. The UV/VIS studies of Calmagite have shown that its spectrum is extremely sensitive to complexation with Mn^{II} and that two complexes can be clearly identified. On the other hand, corresponding studies with monohydroxy azo dyes or with a non-*ortho*-substituted azo dye, Methyl Orange, did not produce any evidence of manganese(II) binding. Indeed, incorporation of *ortho* substituents like *o'*-carboxy, *o'*-sulfonate into this monohydroxy unit failed to promote significant evidence of binding at pH 10. This suggests not only that specific complexation of Mn^{II} is essential for catalysed bleaching but that the *o*,*o'*-dihydroxy azo unit of the dye is the key unit in binding.

Role of Mn^{III} in catalysis. Replacement of Mn^{II} by Mn^{III} results in direct oxidation of Calmagite in the absence of oxidant, but not with the other dyes investigated. This suggests manganese(III) complexes with Calmagite and induces direct oxidation of the dye *via* a one-electron pathway. Consistent with this view, direct oxidation did not occur when Mn^{III} was pre-complexed with an excess of ethylenedinitrilotetraacetate (edta). These observations indicate that specific complexation is a precursor to oxidative electron transfer and have important implications for the inner-sphere mechanism of Mn-catalysed dye destruction.

Although peroxide ($pK_a = 11.6$) gives a lower observed rate

constant than $KHSO_5$ ($pK_a = 9.5$) for Mn-catalysed Calmagite oxidation at pH 10 (Fig. 9) it becomes higher than that of $KHSO_5$ as the pH is increased above 10. This suggests that the active oxidant species is the oxidant anion, *i.e.* the peracid acts as a nucleophile. The nucleophilic rate constants for H_2O_2 and $KHSO_5$ at 40 °C are $k_0 = 1.6 \times 10^7$ and 0.8×10^7 s^{-1} respectively. The inertness of the 1:2 [MnD_2] complex suggests that dye bleaching occurs *via* ligation of the oxidant anion with the metal centre, followed by subsequent nucleophilic reaction.

Mechanistic insights. Two mechanisms can be considered: as illustrated in equations (24) and (25). In the first case catalysed

$$Mn^{II} + D \rightleftharpoons Mn^{II}D \xrightarrow{SO_5^{2-}} Mn^{III}D \longrightarrow \text{Oxidised Dye} + Mn^{II} \quad (24)$$

$$Mn^{II}D \xrightarrow{SO_5^{2-}} O{=}Mn^{IV}D \longrightarrow \text{Oxidised Dye} + Mn^{II} \quad (25)$$

bleaching of Calmagite is attributable to a one-electron-transfer process whereby bound Mn^{II} becomes oxidised to Mn^{III} which, in turn, induces direct oxidation of Calmagite *via* one-electron oxidation. The oxidised dye is a radical species and its fate will be discussed in a later publication. In the second case catalysed bleaching results from oxygen-atom transfer to produce an active manganese(IV) species.

However, there is no need to invoke higher oxidation states than III, *i.e.* the second mechanism, since dye oxidation by Mn^{III} is spontaneous; in that case, the rate-controlling step may be one-electron oxidation of Mn^{II} to Mn^{III}.

Conclusion

(*a*) Specific complexation between Mn^{II} and dye is prerequisite for efficient Mn-catalysed dye bleaching.

(*b*) Specific complexation occurs with *o*,*o*′-dihydroxy azo dyes, *e.g.* Calmagite, but not with *o*-monohydroxy dyes or dyes not having an *o*-hydroxy group.

(*c*) Manganese(II) forms 1:1 and 1:2 complexes with Calmagite, but only the 1:1 complex is catalytically active.

(*d*) The reaction follows the rate law $-d[D]/dt = k_0[Mn][KHSO_5]/[D]$, *i.e.* order is −1 in [D]. This arises because the active catalyst [MnD] is formed from [MnD_2] by loss of a dye molecule.

Experimental

Manganese(II) nitrate and manganese(III) acetate (99.5%, BDH; >99%, Aldrich, respectively) were used as the sources of Mn^{II} and Mn^{III}. Calmagite and Orange G (C.I. Acid Orange 10) were used as received from Aldrich. Methyl Orange (C.I. Acid Orange 52) was 96% (Sigma). Dyes I and II were synthesized in-house using standard procedures.[5] Further details of syntheses, purification procedures and analysis will be reported later.[9] Potassium hydrogenperoxosulfate (triple salt: $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) was from Interox Chem. Co. and contained 47% $KHSO_5$. Hydrogen peroxide solution was from Aldrich. Water was doubly distilled from deionised water using a Fisons 'Fi-Streem' 4BD Still.

Catalytic oxidations of dye were carried out at pH 10 and 40 °C in the presence of an excess of peracid over dye (≈20-fold) so that rates were not influenced by changes in peracid concentration. The dye:Mn ratio was high (≈50:1) in order that absorbance readings reflected the concentration of uncomplexed dye, simplifying the analysis. Kinetic measurements were carried out by monitoring the Calmagite absorbance maximum at 612 nm as a function of time. Absorbances obeyed the Beer–Lambert law over the experimental range of interest (up to 1×10^{-4} M dye). There was no interference from product absorbances. All experiments were conducted at low ionic strength to minimise dye aggregation and/or effects on other solution equilibria. Accordingly, the pH was maintained by automatic addition of KOH(aq) from a pH-stat rather than with buffer solutions, which have the potential to complicate the system by introducing unwanted trace metal catalysts.

The reactions were carried out in a double-walled glass water jacket, thermostatted with a digital reading circulator. A small overhead stirrer was used to achieve homogeneity. The pH was controlled by a VIT90 titration system in conjunction with a ABU93 autoburette and pH electrodes PHG 201 and REF 401, all from Radiometer.

The reaction liquor was circulated with a peristaltic pump *via* silicone rubber tubing through a quartz flow cell (path length 10 mm) mounted in a double-beam Perkin-Elmer Lambda 14 spectrophotometer. The flow was maintained at such a rate that no significant temperature losses occurred between the reaction vessel and the flow cell.

In a typical reaction sequence, appropriate volumes of dye and manganese stock solutions were diluted to 200 cm^3 total volume in the reaction vessel. The solution was brought to 40 °C (±1 °C) and pH 10 (±0.05) and the spectrometer was made ready to run at 612 nm, with a 2 s sampling interval. With the reaction liquor circulating, the oxidant was added, dissolving instantly, and measurement was initiated. Any gross changes in pH at this point were corrected by immediate addition of small aliquots of KOH(aq) or HNO_3(aq).

In between runs, the reaction circuit was flushed with edta(aq) to remove any trace metals and at least three more times with distilled water. Adsorption of contaminants on the silicone tubing or other hydrophobic surfaces occasionally necessitated the use of polar solvents such as ethanol or acetic acid. All parts (except electrodes) were soaked in alkaline detergent solution containing an excess of edta when not in use.

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