Mechanism of bleaching by peroxides
Part 5. Kinetics of the peroxide bleaching of crocetin catalysed by $[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2]^{12-}$☆

David M. Gould, Michael Spiro*, William P. Griffith*

Department of Chemistry, Imperial College of Science, Technology and Medicine, London SW7 2AY, UK

Received 15 February 2002; accepted 14 March 2002

Abstract

The kinetics of the bleaching of crocetin (8,8-diapocarotenedioic acid) by hydrogen peroxide catalysed by the triple sandwich polyoxometalate $Na_{12}[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2] \cdot 47H_2O$ have been studied at pH 10 and 25 °C. The effect of the concentration of the added sequestrant CIX (diethylenetriamine*pentakis*methylenephosphonic acid) was particularly investigated. The mechanism which fitted the experimental results involved the formation of an intermediate crocetin–catalyst complex which was then oxidised by the hydrogen peroxide. In the absence of CIX the formation of the intermediate was rate-determining while, in the presence of excess CIX, the oxidation of the intermediate became rate-determining with a Michaelis–Menten-type rate equation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Bleaching; Oxidation catalysis; Polyoxometalate; Hydrogen peroxide; Kinetics

1. Introduction

The bleaching of dyes by hydrogen peroxide at ambient temperatures and at normal domestic bleach pH (*ca* 10) is a matter of considerable industrial concern [1]. Since H_2O_2 is a relatively slow oxidant under such conditions, it is of interest to find efficient and environmentally acceptable catalysts to speed up the bleaching process. In earlier work [2], we have described in detail the bleaching by peroxide at pH 10–12 of *trans*-crocetin (gardenin), a carotenoid dye soluble in alkaline aqueous media by virtue of its two terminal carboxylate groups; at pH 10 it is present as the di-anion. We have also reported the kinetics of bleaching by H_2O_2 of phenolphthalein, both uncatalysed [3] and catalysed by a wide variety of transition metal complexes including molybdate $[MoO_4]^{2-}$ and tungstate $[WO_4]^{2-}$ [4]. We have also studied the uncatalysed peroxide bleaching of the anthraquinonoid dye alizarin [2] and the catalysed bleaching of the anthocyanidin dye malvin [5].

In view of the considerable current interest in isopoly- and heteropolyoxometalates [6] in oxidation catalysis, we have recently compared the catalytic abilities of 10 polyoxometalates and two oxometalates as catalysts for the bleaching of methyl orange and of crocetin by H_2O_2; of the 12 catalysts studied, the salt $Na_{12}[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2] \cdot 47H_2O$ was the most effective [7]. This material, hereafter for convenience called Co_3W, has been structurally characterised and is known to retain its structure in

solution at pH 10 [8]. We report here a fuller investigation of its properties as a potential bleaching catalyst, using crocetin as the dye substrate.

2. Experimental

2.1. Materials and conditions

Starting materials were purchased from Aldrich or BDH and used without further purification. Crocetin was purchased from Sigma–Aldrich, CIX (diethylenetriamine*pentakis*methylenephosphonic acid) and 30% hydrogen peroxide were provided by Solvay Interox. The concentration of H_2O_2 was determined by permanganate titration [9].

The complex $Na_{12}[Co_3^{II}W(H_2O)_2\{Co^{II}W_9O_{34}\}_2] \cdot 47H_2O$ was synthesised according to the literature method of Tourné et al. [8]. The yield of green crystals was 7.80 g (16%). The electronic spectrum of the aqueous solution gave a value for λ_{max} of 611 nm with an extinction coefficient (ε) of 696 dm^3 mol^{-1} cm^{-1}, in excellent agreement with the literature values [8] of $\lambda_{max} \cong 610$ nm and $\varepsilon \cong 700$ dm^3 mol^{-1} cm^{-1}.

2.2. Experimental

Buffered solutions of the dye and CIX were mixed in one flask while H_2O_2 and the catalyst, also in buffered solution, were mixed in another flask. Equal volumes (1.2 cm^3) of these liquids were combined by adding them to a 10 mm quartz cuvette using a Gilson P5000 pipette with a fresh tip. The contents were mixed by stirring with a plastic cuvette stirrer or by capping the cell and carefully inverting it. The cell was then placed into a temperature-controlled cell holder and the optical absorbance at the peak wavelength of 446 nm was measured every 30 or 60 s. For reactions carried out at temperatures other than ambient, the flasks containing buffered solutions of reactants had been immersed in an external temperature-controlled water bath.

Buffer solutions were made by a modification of the method of Bates [10] by diluting 2.1 g of NaHCO$_3$ and 107 cm^3 of aqueous 0.1 M NaOH (M = mol dm^{-3}) solution with triply deionised water to give a total volume of 1000 cm^3. All solutions were stored in polythene bottles which had been soaked for >24 h in a 5% Decon 90 solution and then thoroughly rinsed with deionised water.

2.3. Instrumentation

Electronic spectra were measured on a Perkin Elmer Lambda 2 spectrophotometer fitted with an LKB2219 Multitemp II thermostatic circulator. Values of pH were determined with a RadioSpares 610 540 pH meter. Raman spectra of Co$_3$W as a solid and as a saturated aqueous solution were recorded on a Dilor LabRam Infinity instrument using a He–Ne laser at 632 nm and a frequency doubled Nd-YAG laser at 532 nm. ICP analyses were recorded on a ARL instrument by Mr. B. Coles of the Geology Department, Imperial College.

3. Results and discussion

3.1. Bleaching in the presence of CIX

The rate of peroxide bleaching of crocetin in aqueous buffer solutions at pH 10 and at 25 °C in the absence of added activator has been studied spectroscopically by Thompson et al. [2]. After the addition of low concentrations of the sequestrant Dequest 2060 (cyclohexane-1,2-diamino-N,N′-*tetrakis*methylenephosphonic acid) to overcome the inadvertent effect of an iron impurity in the dye, they found the reaction to be first-order in both crocetin and H_2O_2. In our experiments, we used a fresh sample of crocetin and the stronger sequestrant CIX (diethylenetriamine*pentakis*methylenephosphonic acid) in place of Dequest. With 11.6 mM H_2O_2 and 10 μM CIX, at pH 10 and at 25 °C, we found the first-order rate constant k_{obs} to be 4.2×10^{-6} s^{-1}, ca. 9% lower than the result obtained by Thompson et al. [2].

Addition of Co$_3$W greatly increased the rate of crocetin bleaching by H_2O_2. However, as Fig. 1 shows, plots of ln A (A = absorbance) versus time t were only initially linear and then curved sharply downwards. Only at very low Co$_3$W concentrations were the plots linear throughout a 15 min run. The greater the concentration of Co$_3$W, the shorter and steeper were the initial linear sections. Thus for Co$_3$W concentrations of 5, 10 and 15 μM, the lengths of the linear sections were, respectively, >900, 600 and <400 s, and the
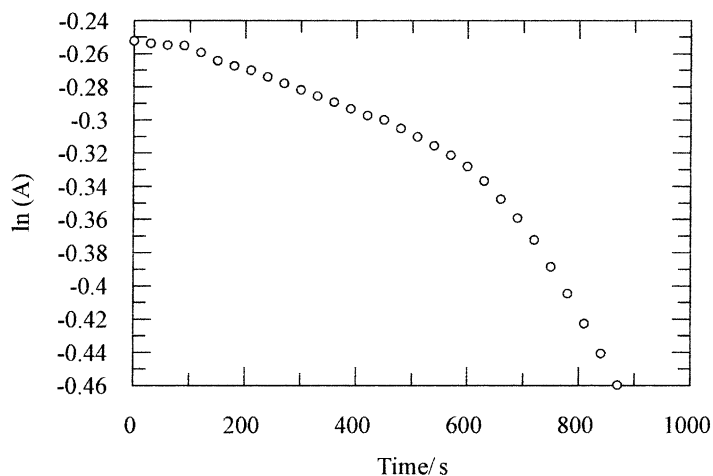
Fig. 1. A typical ln(absorbance) versus time plot for the bleaching of crocetin (12 μM) by H_2O_2 (11.6 mM) and Co_3W catalyst (10 μM) in the presence of CIX (10 μM) at 25 °C in pH 10 bicarbonate buffer.

respective slopes (in $10^{-6} \, s^{-1}$) were 48 ± 4, 97 ± 18 and 180 ± 57. After allowance is made for the poorer reproducibility when the linear sections were short, the initial rate constant appears to be approximately proportional to the Co_3W concentration. When, as a blank, the last experiment with 15 μM Co_3W was repeated without the addition of any peroxide, only a very slow degradation of the crocetin was observed ($k_{obs} = 8 \times 10^{-6} \, s^{-1}$).

The gradient of the second stage in Fig. 1 was $580 \times 10^{-6} \, s^{-1}$, comparable with slopes found in the total absence of CIX. This indicated that by then the CIX had been fully complexed. Further evidence was obtained from a test experiment in which the crocetin, Co_3W and CIX had been left to stand together in the buffered solution for 20 min and then mixed with H_2O_2 to start the reaction. The resulting graph no longer showed two stages but was a gentle curve with a slope, gradually increasing, of the same order of magnitude as in the second stage of Fig. 1. This suggested that the CIX had reacted with the Co_3W prior to the start of the run. However, leaving the

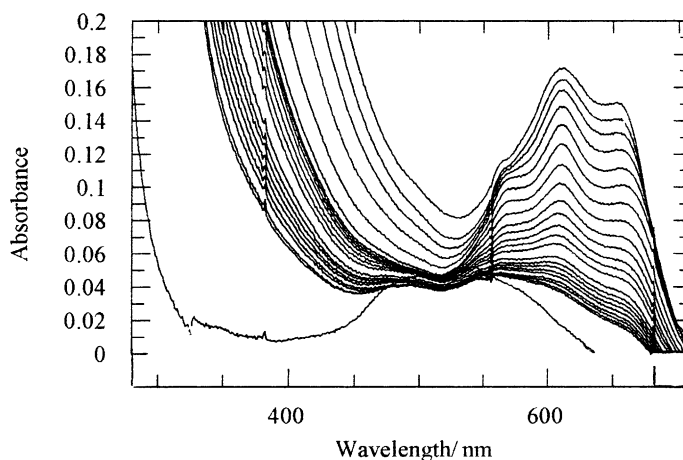Fig. 2. The overlaid spectra for Co_3W (250 μM) showing its decomposition in the presence of CIX (1.5 mM) in pH 10 bicarbonate buffer. A spectrum was measured every 5 min for 2 h. The lowest intensity spectrum was measured the following day.

crocetin, Co$_3$W and buffer together for 20 min and then adding the H$_2$O$_2$ and the CIX produced a plot similar to Fig. 1.

Evidence of a slow interaction between Co$_3$W and CIX at pH 10 is shown in Fig. 2, where its extent has been exaggerated by using much greater concentrations than normal. An estimate was made of the rate of the Co$_3$W–CIX interaction by plotting $\ln(A - A_f)$ against time, where A is the absorbance at 611 nm and A_f its value in the lowest intensity spectrum. The resulting curve gave an initial first-order rate constant of $79 \times 10^{-6}\,\mathrm{s}^{-1}$. The slope gradually increased with time, probably due to easier accessibility for CIX to the cobalt ions as the Co$_3$W was broken up. These results suggest that the Co$_3$W catalyst was only slightly degraded by 60 μM CIX during the 20 min crocetin runs. Nevertheless, the very existence of this interaction is a further reason for focussing on the initial slopes of the crocetin bleaching runs.

Because of the complicated nature of the catalysed bleaching reaction, it was decided to study the system under two extreme conditions: in the absence of CIX and in the presence of an excess of CIX.
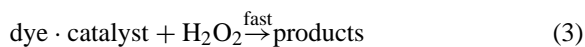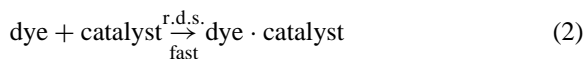
3.2. Bleaching in the absence of CIX

Without the addition of CIX, the bleaching reaction with Co$_3$W was so rapid that the concentrations of the catalyst were reduced to the range 0.2–1.0 μM and those of H$_2$O$_2$ to between 1.16 and 11.6 mM. Plots of $\ln A$ versus t were gentle curves whose slopes gradually increased with time. The initial gradients were determined by fitting second-order polynomials to the experimental data. All reported data are the means of at least two runs.

The standard crocetin concentration employed was 17 μM. Experiments with 4.7 μM crocetin using a 30 mm cuvette and with 106 μM crocetin using a 1 mm cuvette yielded initial k_{obs} values which showed no trend with crocetin concentration. This confirmed that the reaction was first-order in dye. It was also first-order in Co$_3$W since values of k_{obs} increased linearly with [Co$_3$W] with a small intercept equal to the rate constant of a blank run without any Co$_3$W. However, the rate constants were independent of the concentration of H$_2$O$_2$ over the range 1–12 mM. There was even a very slow bleaching reaction in the absence of H$_2$O$_2$ by Co$_3$W alone.

The kinetics of the peroxide bleaching reaction catalysed by Co$_3$W can therefore be represented by the equation

$$-\frac{\mathrm{d[crocetin]}}{\mathrm{d}t} = k[\mathrm{crocetin}][\mathrm{Co_3W}] \tag{1}$$

where $k = 550 \pm 20\,\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ at 25 °C and pH 10. This is consistent with the simple mechanism:

$$\mathrm{dye + catalyst} \overset{\mathrm{r.d.s.}}{\underset{\mathrm{fast}}{\rightarrow}} \mathrm{dye \cdot catalyst} \tag{2}$$

$$\mathrm{dye \cdot catalyst + H_2O_2} \overset{\mathrm{fast}}{\rightarrow} \mathrm{products} \tag{3}$$

The existence of a 1:1 dye·catalyst intermediate has been suggested recently for the bleaching mechanism of the *o,o'*-dihydroxyazo dye calmagite by KHSO$_5$ [11]. In our dye·catalyst complex, it is unlikely on chemical grounds that the alkene linkage in crocetin will coordinate either to Co^{II} or to W^{VI} since back-bonding from the electronegative Co^{II} will be low, and such back-bonding would not be possible for the d^0 W^{VI}. Far more likely is single deprotonation of one of the hydroxy groups at the end of the crocetin and its coordination to one of the octahedral Co^{II} centres as shown in Fig. 3a, possibly by displacement of a water molecule. Attack may then take place by H$_2$O$_2$ or HOO$^-$ on double bonds of the coordinated crocetin via the mechanism suggested in previous work [2]. Alternatively, there may be attack by coordinated η^2-peroxo ligands adjacent to the cobalt centre, as in Fig. 3b.

Kinetic studies on the peroxide bleaching of phenolphthalein catalysed by [MoO$_4$]$^{2-}$ and [WO$_4$]$^{2-}$ [4] have shown that singlet oxygen (^{1}O$_2$) becomes a major contributor to the oxidation of the dye at higher (millimolar) concentrations of H$_2$O$_2$. Moreover, ^{1}O$_2$ is known to react readily with C=C bonds [12] and to be quenched by carotenoids [13]. To test whether ^{1}O$_2$ played a significant role in the present system, kinetic experiments were also carried out with the addition of the singlet oxygen trapping agent 2,5-dimethylfuran (DMFu), which we have previously found [2–5,14] to be an effective trap for this purpose. It was always used at a 3.75 mM concentration, close to its solubility limit in our buffer solutions.

When DMFu was added, the bleaching rates were consistently lower than before. However, the first-order rate constants again rose linearly with the Co$_3$W
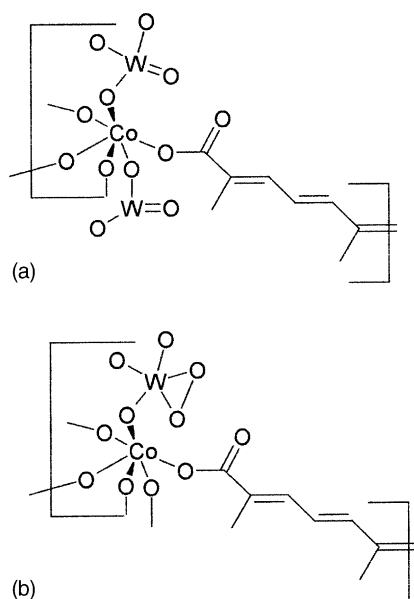
(a)

(b)

Fig. 3. Possible models for the crocetin·catalyst complex: (a) coordination of crocetin to $[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2]^{12-}$ by deprotonation of one of the end groups of crocetin; (b) attack by coordinated η^2-peroxo ligands adjacent to a cobalt centre in $[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2]^{12-}$.

Table 1

Effects of varying the concentrations of crocetin (dye) and Co_3W (catalyst) on the catalytic first-order rate constant in bleaching by H_2O_2 (11.6 mM) in the presence of CIX (60 μM) at 25 °C in pH 10 bicarbonate buffer

[dye]^0 (μM)	[cat]^0 (μM)	k_{cat}[a] $(10^{-6}\,s^{-1})$	[dye·catalyst] (μM)	$k'(10^{-6}\,s^{-1})$
4	6	41.5	1.28	130
12	6	30.4	2.87	127
15	6	18.4	3.24	85
31	6	17.4	4.36	124
4	10	58.3	1.80	130
12	10	42.9 (27.5)[b]	4.34	119 (76)[b]
15	10	36.1 (23.9)	5.00	108 (72)
31	10	24.5 (19.2)	7.05	108 (84)
77	10	18.2	8.72	(160)
15	0.5	1.6$_7$	0.30	84
15	1	4.0$_0$	0.59	102
15	1.5	6.0$_4$	0.88	103
15	2	7.2$_4$ (4.9$_6$)	1.16	94 (64)
15	4	13.0 (10.5)	2.24	87 (70)
15	6	18.4 (15.6)	3.24	85 (72)
15	8	26.7 (18.3)	4.17	96 (66)
15	10	36.1 (23.7)	5.00	108 (71)
15	12	46.1	5.77	120

[a] $k_{cat} = k_{obs} - (k_{obs})_{uncat}$; $(k_{obs})_{uncat} = 4.2 \times 10^{-6}\,s^{-1}$.
[b] Bracketed results were obtained with DMFu (3.75 mM) present.

concentration and were essentially independent of the H_2O_2 concentration, with a mean second-order rate constant of $380 \pm 20\,M^{-1}\,s^{-1}$ at 25 °C and pH 10. This figure has been corrected for the slow bleaching reactions by H_2O_2 alone and also by Co_3W alone. Thus the peroxide oxidation path accounted for approx. 69% of the bleaching process and the singlet oxygen pathway for the remaining 31%. It seems likely that the WO_4 moieties of the Co_3W catalysts (cf. Figs. 3a and b) together with H_2O_2 are largely responsible for the formation of the $^1O_2$; Aubry and coworkers [15] have shown that at pH 10 isopolyoxotungstates are potent generators of $^1O_2$.

3.3. Bleaching with a high concentration of CIX

Reaction mixtures containing 10 μM of CIX produced $\ln A$ versus t plots which were initially linear. When experiments were carried out with a much larger CIX concentration of 60 μM, the resulting first-order plots were linear throughout. There was no change in the slope when the CIX concentration was doubled to 120 μM.

Most experiments were carried out with 15 μM of crocetin and involved the use of 10 mm cuvettes. By using cuvettes ranging from 1 to 30 mm, it was possible to investigate the effect of wide variations in the initial dye concentration. The results listed in Table 1 show that the apparent first-order rate constants decreased monotonically as the dye concentration was raised. The reaction was therefore not simply first-order in crocetin. Table 1 also shows that, with a given crocetin concentration, the value of k_{obs} increased approximately linearly with rising Co_3W concentration. When the concentrations of the crocetin and Co_3W were both kept constant and the concentration of H_2O_2 was increased, k_{obs} rose linearly at low $[H_2O_2]$ and tended to an asymptotic maximum as depicted in Fig. 4.

These results can again be explained by the formation of a dye·catalyst complex which then reacts with H_2O_2. However, in the presence of 60 μM CIX the reaction was two orders of magnitude slower than in its absence. This is likely to have been brought about
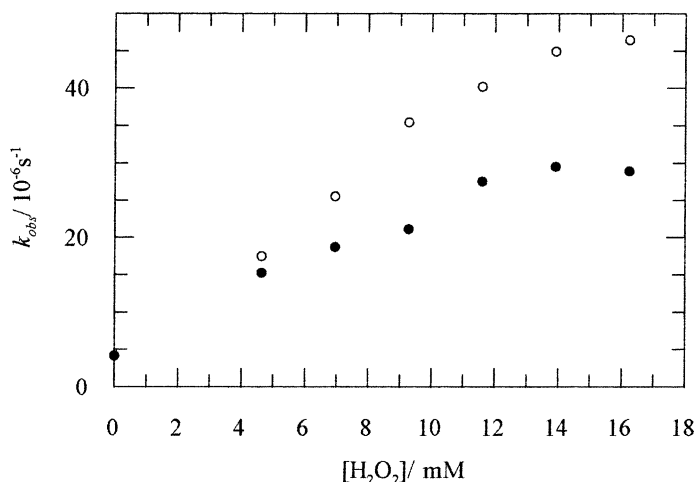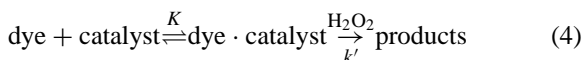
Fig. 4. The effect of varying the concentration of H_2O_2 on the bleaching of crocetin (15 μM) catalysed by Co_3W (10 μM) in the presence of CIX (60 μM) at 25 °C in pH 10 buffer (($\bigcirc$) without DMFu; ($\bullet$) with 3.75 mM DMFu).

by CIX molecules surrounding the Co_3W species, and so slowing down its reaction with crocetin. Moreover, the dye·catalyst complex itself will have been surrounded by CIX molecules, slowing down its oxidation by H_2O_2 and HOO^- (or by $^1O_2$). The mechanism suggested below for the 60 μM CIX experiments therefore includes an equilibrium stage followed by rate-determining attack on the intermediate complex:

$$\text{dye} + \text{catalyst} \underset{}{\overset{K}{\rightleftharpoons}} \text{dye} \cdot \text{catalyst} \overset{H_2O_2}{\underset{k'}{\rightarrow}} \text{products} \qquad (4)$$

where

$$K = \frac{[\text{dye} \cdot \text{catalyst}]}{[\text{dye}][\text{catalyst}]} \qquad (5)$$

Hence at any given excess peroxide concentration

$$\frac{-\mathrm{d}[\text{dye}]^0}{\mathrm{d}t} = k'[\text{dye} \cdot \text{catalyst}] \qquad (6)$$

where k' is a function of the peroxide concentration and

$$[\text{dye}]^0 = [\text{dye}] + [\text{dye} \cdot \text{catalyst}] \qquad (7)$$

as there was no significant spectral shift when catalyst was first added to the dye. Since

$$k_{\text{obs}} = \frac{-\mathrm{d}\ln(A)}{\mathrm{d}t} = \frac{-\mathrm{d}\ln[\text{dye}]^0}{\mathrm{d}t} \qquad (8)$$

it follows that

$$k' = \frac{k_{\text{obs}}[\text{dye}]^0}{[\text{dye} \cdot \text{catalyst}]} \qquad (9)$$

The constancy of k' provides a test of the proposed mechanism. Exploratory calculations indicated that this constancy was not very sensitive to the choice of the equilibrium constant K, and a value of $K = 1.0 \times 10^5 \, \text{dm}^3 \, \text{mol}^{-1}$ was chosen. The concentrations of [dye·catalyst] were then calculated from Eq. (5) for each set of conditions and are listed in Table 1. This allowed the values of k' to be calculated from Eq. (9), correction for the uncatalysed reaction being made by substituting for k_{obs}, the parameter k_{cat} given by

$$k_{\text{cat}} = k_{\text{obs}} - (k_{\text{obs}})_{\text{uncat}} \qquad (10)$$

Table 1 shows that, whether dye or catalyst concentrations are varied the calculated values of k' are far more constant than the experimental values of k_{cat}. Overall, the mean k' value is $108 \times 10^{-6} \, \text{s}^{-1}$ with a standard deviation of the mean of $\pm 4 \times 10^{-6} \, \text{s}^{-1}$. There is also no trend within any of the three sets of tabulated data. The only value which falls outside the normal scatter range is the $160 \times 10^{-6} \, \text{s}^{-1}$ result obtained for the highest dye concentration of 77 μM. This suggests the possibility of the formation of a second complex in which two dye species are associated with each catalyst molecule.
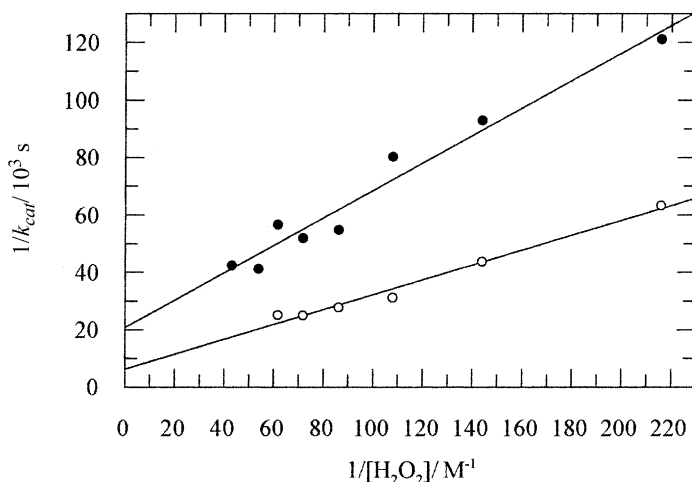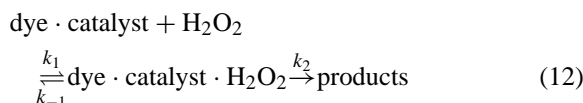
Fig. 5. Variation of $1/k_{cat}$ with $1/[H_2O_2]$ for the bleaching of crocetin (15 μM) catalysed by Co_3W (10 μM) at 25 °C in pH 10 buffer ((○) without DMFu; (●) with 3.75 mM DMFu).

The variation of k_{obs} with the peroxide concentration in Fig. 4 is reminiscent of a Michaelis–Menten plot [16], which has also been noted for the oxidation of the cationic quinaldine red (2-[2-[4-(dimethyl-amino)phenyl]]-1-ethenylquinolinium iodide) by H_2O_2 [17]. Values of k_{cat} were therefore fitted to the equation

$$k_{cat} = \frac{a[H_2O_2]}{1 + b[H_2O_2]} \quad (11)$$

with the small contributions of the uncatalysed reaction in Eq. (10) being taken as proportional to $[H_2O_2]$. Thus $1/k_{cat}$ should vary linearly with $1/[H_2O_2]$, as indeed it did as shown in Fig. 5. The intercept and slope led to $a = 3.86 \times 10^{-3} \, M^{-1} \, s^{-1}$ and $b = 24.4 \, M^{-1}$ for the bleaching reaction with 15 μM crocetin. These findings can be related to the second stage of the overall mechanism (Eq. (12)):

$$dye \cdot catalyst + H_2O_2$$
$$\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} dye \cdot catalyst \cdot H_2O_2 \overset{k_2}{\rightarrow} products \quad (12)$$

Application of the steady-state approximation to the dye·catalyst·H_2O_2 complex, plus use of the Michaelis–Menten procedure [16], leads to

$$k' = \frac{k_1 k_2 [H_2O_2]}{k_{-1} + k_2 + k_1 [H_2O_2]} \quad (13)$$

Thus $1/k_2$ will be the intercept of a plot of $1/k'$ against $1/[H_2O_2]$, just as b/a was the intercept of the plot of $1/k_{cat}$ against $1/[H_2O_2]$. Eqs. (9) and (10) and Table 1 show that, for the bleaching reaction of 15 μM crocetin catalysed by 10 μM Co_3W in the presence of 60 μM CIX at pH 10 and at 25 °C

$$k' = \frac{k_{cat}[dye]^0}{[dye \cdot catalyst]} = 3k_{cat} \quad (14)$$

It follows that

$$k_2 = \frac{3a}{b} = 4.7 \times 10^{-4} \, s^{-1}$$

When similar experiments were carried out in the presence of the $^1O_2$ trap DMFu, the uncatalysed rate constant was unaffected but all the Co_3W catalysed runs were slower. The results obtained are given in brackets in Table 1. Qualitatively, these rate constants k_{cat} decreased with increasing crocetin concentration and rose with increasing concentration of Co_3W. A quantitative analysis, again based on the formation of a 1:1 dye·catalyst complex with a formation constant $K = 1.0 \times 10^5 \, dm^3 \, mol^{-1}$, led to the bracketed k' values in the last column. These showed reasonable constancy, with a mean value of $(72 \pm 2.2) \times 10^{-6} \, s^{-1}$.

The variation of k_{obs} with peroxide concentration in Fig. 4 again showed Michaelis–Menten-type behaviour. The DMFu runs were therefore analysed in

the same way as above, except that in Eq. (10) k_{obs} was also corrected for the slow reaction in a blank run with DMFu but no peroxide. Fig. 5 confirms the linear relationship between $1/k_{cat}$ and $1/[H_2O_2]$. The intercept and slope led to $a = 2.09 \times 10^{-3} M^{-1} s^{-1}$ and $b = 43.9 M^{-1}$. Eq. (14) then yields $k_2 = 1.4 \times 10^{-4} s^{-1}$ for the peroxide bleaching of $15 \mu M$ crocetin catalysed by $10 \mu M$ Co_3W in the presence of $60 \mu M$ CIX and $3.75 mM$ DMFu. For these reactant conditions it follows, on the basis of the postulated mechanism, that $^1O_2$ attacks the dye·catalyst complex more than twice as fast (i.e. $[4.7 - 1.4]/1.4$) as H_2O_2 itself. These proportions were reversed in the absence of CIX.

3.4. Stability of Co_3W

The profiles of the Raman spectra of solid Co_3W and of its solution at pH 10 were found to be very similar, suggesting retention of the structure of the complex anion in solution. Moreover, its electronic spectrum remained the same for many hours, confirming literature evidence [8] that it was stable at pH 10. In solutions of the order of $100 \mu M$, it was best characterised by a peak at 611 nm. Addition of $58 mM$ H_2O_2 at pH 10 produced little spectral change over several hours apart from occasional spikes due to effervescent peroxide decomposition.

When $8 \mu M$ of crocetin was added to $84 \mu M$ of Co_3W at pH 10, the Co_3W absorbance at 611 nm decreased only very slightly over 24 h. The larger crocetin peaks in the 400–450 nm region, however, decreased by around 30% over this period, showing that the dye was slowly bleached by Co_3W alone. Addition of $1500 \mu M$ CIX to $250 \mu M$ of Co_3W, on the other hand, brought about a much faster decline in the Co_3W peak at 611 nm as shown in Fig. 2. The lowest intensity spectrum in the figure had a maximum absorbance at 539 nm while the original Co_3W peak had vanished. By then the colour had turned from green to pale pink, indicative of octahedrally bound Co(II). This points to extraction of cobalt, from either one or both of the two cobalt environments within the Co_3W complex, to form Co–CIX complexes.

Since the lowest intensity spectrum in Fig. 2 differed from that of a simple mixture of $Co(NO_3)_2$ and CIX, it appeared that even after several hours the solution still contained rump Co_3W fragments. The weaker sequestrant EDTA fared no better at breaking

up the Co_3W, but the stronger sequestrant nitroso-R (disodium-1-nitroso-2-naphthol-3,6-disulphonic acid) [18] was found to extract all the cobalt from Co_3W.

4. Conclusion

The polyoxometalate ion $[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2 (H_2O)_2]^{12-}$ was found to be an efficient catalyst for the bleaching of the carotenoid dye crocetin by hydrogen peroxide in an aqueous buffer medium at pH 10 and at $25 \,^{\circ}C$. Kinetic data gathered under a variety of conditions can be fitted to a simple mechanism involving formation of a crocetin·catalyst complex which is then oxidised by peroxide.

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