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Letter

Polyoxometalate catalysis of dye bleaching by hydrogen peroxide

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Abstract

Ten polyoxo-tungstate and -molybdate complexes have been shown to be stronger catalysts than $[WO_4]^{2-}$ and $[MoO_4]^{2-}$, respectively, for bleaching by hydrogen peroxide of methyl orange and of crocetin in aqueous solutions at pH 10 and at 25°C. This is the first report of kinetics of polyoxometalate-catalysed bleaching of dyestuffs with H_2O_2. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Hydrogen peroxide is increasingly favoured as an environmentally acceptable bleaching agent both in domestic and industrial situations. However, even at its optimum pH of ca. 10, bleaching by H_2O_2 has to be made more effective by adding an activator [1]. We have recently shown that low concentrations of oxometalates, e.g. $[WO_4]^{2-}$ and $[MoO_4]^{2-}$, catalyse the peroxide oxidation of dyes such as phenolphthalein [2] and malvin [3]. It has since been claimed that polyoxometalates also have the potential to act as catalysts in bleaching reactions, and protective patents have been taken out accordingly [4]. However, no kinetic studies of their effects on the bleaching of dyes have been published. We therefore report here a comparative study of the catalytic activity of a representative variety of polyoxometalates on the peroxide bleaching of two typical types of dye, the azo dye methyl orange and the carotenoid crocetin.

2. Experimental

The polyoxometalate complexes listed in Table 1 were made by the literature procedures cited below, and were analysed by ICP: **3** [5], **4** [6], **5** and **6** [7], **7** [8], **8** [9,10], **9** [11], **11** [12], **12** [13].

All experiments were carried out at 25°C in bicarbonate buffer solution at pH 10 in the presence of $10\,\mu M$ ($M = \mathrm{mol\,dm^{-3}}$) CIX (diethylenetriaminepentakismethylenephosphonic acid). This sequestrant removes from the solution traces of impurity transition metal species which might also catalyse the bleaching reaction [3]. Low concentrations of dyes were used to obtain optimum absorbance (A) values (and to avoid dimerisation in the case of methyl orange [14]), together with higher concentrations of

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Table 1
Rate data at 25°C for the catalysed bleaching of the substrates, methyl orange[a] and crocetin[b] by H_2O_2 at pH 10

Catalyst	Methyl orange			Crocetin		
	Catalyst concentration (μM)	Initial k ($10^{-6}\,s^{-1}$)	Final k ($10^{-6}\,s^{-1}$)	Catalyst concentration (μM)	Initial k ($10^{-6}\,s^{-1}$)	Final k ($10^{-6}\,s^{-1}$)
None (**1**)	0	1.4	n.c.[c]	0	3.3	n.c.[c]
$Na_2[WO_4]$ (**2**)	100	12.8	n.c.	35.0	12.0	n.c.
$K_{10}[Mn^{II}_4\{PW_9O_{34}\}_2(H_2O)_2]\cdot 20H_2O$ (**3**)	100	50.7	471	40.9	21.2	49.6
$K_{10}[Co^{II}_4\{PW_9O_{34}\}_2(H_2O)_2]\cdot 22H_2O$ (**4**)	100	69.9	n.c.	45.8	9.65	n.c.
$Na_{12}[Zn_3W\{ZnW_9O_{34}\}_2(H_2O)_2]\cdot 47H_2O$ (**5**)	100	29.0	43.5	38.9	47.7	109
$Na_{12}[Co^{II}_3W\{Co^{II}W_9O_{34}\}_2(H_2O)_2]\cdot 47H_2O$ (**6**)	20	23.9	17.6	21.8	104	1070
$K_6Na_2[Mn^{IV}W_6O_{24}]\cdot 12H_2O$ (**7**)	100	83.2	n.c.	39.3	165	n.c.
$K_{11}[Er^{III}\{PW_{11}O_{39}\}_2]\cdot 20H_2O$ (**8**)	100	116	227	18.8	89.2	103
α,β-$K_6[P_2W_{18}O_{62}]\cdot 14H_2O$ (**9**)	100	21.6	35.1	36.5	19.5	n.c.
$Na_2[MoO_4]$ (**10**)	100	27.8	n.c.	40.0	23.0	n.c.
$(NH_4)_4[Mn^{II}H_6Mo_6O_{24}]\cdot 5H_2O$ (**11**)	100	147	n.c.			
$(NH_4)_6[Mn^{IV}Mo_9O_{32}]\cdot 6H_2O$ (**12**)	100	493	n.c.	49.5	414	n.c.

[a] Concentrations: 34.8 μM of methyl orange with 58 mM of H_2O_2.

[b] 12 μM of crocetin with 9.28 mM of H_2O_2.

[c] n.c.: indicates no change.

oxo- and polyoxo-metalates in order to produce sizeable rate increases. Weighed amounts of the solid catalyst were dissolved in a buffered H_2O_2 solution. These solutions were then added to buffered solution of the dye and CIX in a quartz cuvette and the mixture gently stirred. The reactions were followed by measuring the decrease in optical absorbance of methyl orange at 464 nm and of crocetin at 446 nm.

3. Results and discussion

Plots of $\ln A$ versus time (t) were linear for some catalysts and curved for others. The resulting slopes, either overall or in the initial and final stages, were obtained by polynomial computer fitting to give first-order rate constants k. These are all listed in Table 1.

For the bleaching of methyl orange, the table shows that all the polyoxometalates were better catalysts, mole for mole, than the oxometalates **2** and **10**. The curvatures in some of the $\ln A$ versus t plots are probably caused by the complex breaking up in the high pH environment, e.g. **8** is likely to form $[PW_{11}O_{39}]^{7-}$ in the presence of H_2O_2 and then to react further to form a series of polyperoxophosphotungstates [10]. In other cases, such as **6**, the added CIX appears to have complexed the catalyst and any catalytic fragments in the early stages of the runs. Four polyoxometalates, **4**, **7**, **11** and **12**, as well as the two oxometalates **2** and **10**, gave linear plots throughout.

Complex **3** produced the fastest final rate constant; within 35 min nearly 50% of the methyl orange had been bleached. Complex **12**, with a relatively simple structure of nine molybdenum atoms around a central Mn^{IV} atom [13], was the best catalyst with an overall linear plot. The high oxidation-state manganese centre is likely to have been redox-active under our conditions. Manganese(IV) was also involved in the “Persil Power” detergent activator [15].

The catalytic oxidation of crocetin required milder conditions than in the case of methyl orange. Lower peroxide and catalyst concentrations were therefore used in the 20 min runs. All but one of the polyoxometalates, the cobalt complex **4**, displayed stronger catalytic action per mole than did the corresponding oxometalates **2** and **10**. Most of the kinetic results qualitatively parallel those obtained with methyl orange. The fastest overall rate was achieved with the cobalt complex **6**, with half the crocetin chromophore being destroyed during the run. Complex **12** was again an excellent catalyst, giving a linear first-order plot throughout.

4. Conclusions

Ten tungsten- and molybdenum-based polyoxometalates with a variety of stereochemistries (including sandwich-type with linked Keggin structures for **4** [6] and **5** [7], an Anderson structure for **7** [8] and a Dawson one for **9** [16], respectively) have been shown to be effective catalysts for the peroxide bleaching with an azo dye (methyl orange) and a carotenoid (crocetin). Kinetic data have been presented for these reactions at pH 10 and at 25°C.

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