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Mechanism of bleaching by peroxides Part 7. The pH dependence of the oxometalate catalysed bleaching of methyl orange☆

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

Department of Chemistry, Imperial College, London SW7 2AZ, UK

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Abstract

The kinetics have been studied over the pH range 8.95–11.0 of the bleaching of the azo dye methyl orange (4-[[(4-dimethylamino)phenyl]-azo]benzenesulfonic acid sodium salt) by hydrogen peroxide catalysed by molybdate and tungstate at 25 °C. A plot of the overall rate constants against pH fell on a bell-shaped curve with molybdate catalyst, but with tungstate the rate constant rose to a plateau as the pH increased. The contributory rate constants for both the peroxometalate catalyst and the singlet oxygen pathways were determined by carrying out experiments both without and with the singlet oxygen trap 2,5-dimethylfuran. The singlet oxygen rate constants correlated well with $^1O_2$ generation data in the literature. The results obtained with molybdate were consistent with $MoO(O_2)_3^{2-}$ ion being the active metalate bleaching agent and also the precursor for $^1O_2$ generation, but the tungstate results indicated that our knowledge of the peroxotungstate system is still incomplete.
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Keywords: Bleaching; Catalysis; Methyl orange; Molybdate; Tungstate

1. Introduction

Hydrogen peroxide is a more environmentally acceptable bleaching agent than the chlorine-containing compounds often used elsewhere [1]. However, H_2O_2 oxidises coloured stains much more slowly, and there has been much industrial and academic interest [2–4] in finding suitable catalysts to enhance its activity. In our laboratory it has been shown that the bleaching by H_2O_2 under alkaline conditions of certain dyes (phenolphthalein [5], crocetin [6,7] and methyl orange [7,8]) is catalysed by certain oxometalates and polyoxometalates. Their interaction with H_2O_2 is known [9–17] to form peroxometalate species, and we have found their catalytic mode of action to be twofold. First, certain peroxometalate species oxidised the dyes directly and, secondly, the peroxometalate systems generated singlet oxygen ($^1O_2$) [12,14,17] which also attacked the dyes. These two bleaching routes could be distinguished by carrying out kinetic experiments in the presence of a $^1O_2$ trap such as DMFu (2,5-dimethylfuran) as well as in its absence, as we have shown in earlier work [5,6]. The difference in rates between these two sets of experiments then yielded the rate of bleaching by $^1O_2$ on the assumption that the two catalytic pathways proceeded independently (the additivity hypothesis).

The catalytic work in the experiments above was normally carried out at pH 10. We now present kinetic data over a wider alkaline pH range for the peroxide bleaching of methyl orange (4-[[(4-dimethylamino)phenyl]-azo]benzenesulfonic acid sodium salt) catalysed by molybdate (MoO_4^{2-}) and by tungstate (WO_4^{2-}).

2. Experimental

2.1. Materials and conditions

The starting materials were, as before [8], purchased from Sigma-Aldrich or BDH-Merck and used without further

☆ For Part 6 see Ref. [8].

* Corresponding authors. Tel.: +44 20 7594 5759; fax: +44 20 7594 5804.
E-mail address: w.griffith@imperial.ac.uk (W.P. Griffith).

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purification. Buffer compositions were based on recipes given by Bates [18]. The carbonate buffers were made by dissolving $NaHCO_3$ in appropriate volumes of 0.1 M NaOH (M = mol dm^{-3}) and diluted with triply-deionised water. Phosphate buffers were made by diluting NaH_2PO_4 and 0.1 M NaOH solution, and borax buffers by diluting $Na_2B_4O_7{\cdot}10H_2O$ and 0.1 M NaOH or 0.1 M HCl solutions as required.

The same procedure for runs was used as described previously [8]. Buffered solutions of methyl orange and the sequestrant CIX (diethylenetriamine-*pentakis*methylenephosphonic acid) were mixed in one flask while buffered solutions of the catalyst and H_2O_2 were mixed in another flask. Equal volumes (1.2 cm^3) of these liquids were then pipetted into a 10 mm quartz cuvette, carefully mixed and thermostatically controlled at 25 °C. The optical absorbance A at the broad 464 nm peak of methyl orange was then measured with time on a Perkin-Elmer Lambda 2 spectrophotometer and stored on an Epson AX2 computer. Under the pseudo first-order conditions used, good linear plots were obtained of ln *A* versus time *t*, and their slopes yielded the rate constants k_{obs}.

3. Results and discussion

3.1. Bleaching experiments with and without DMFu

Experiments were carried out in borax buffer of pH 8.95, bicarbonate buffer of pH 9.55 and 10.5, and phosphate buffer of pH 11. Results for bicarbonate buffers of pH 10 were presented in the previous paper [8]. A few runs were also carried out in borax buffers of pH 7.9 and 10 and a phosphate buffer of pH 11.7.

In every medium, at constant concentration of H_2O_2, k_{obs} increased linearly with the concentration of added molybdate or tungstate, both in the absence or the presence of added DMFu. An example is shown in Fig. 1 for the case of pH 11. The respective second-order rate constants k_2 are listed in Table 1. No meaningful data could be obtained with

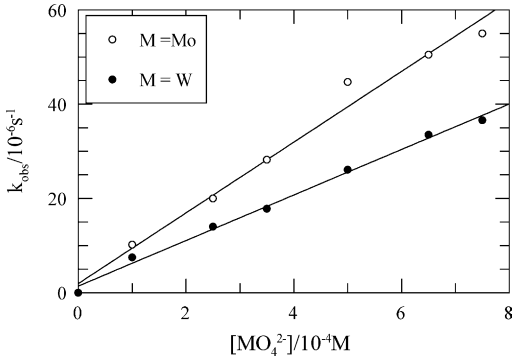

Fig. 1. Variation of k_{obs} with the concentration of MO_4^{2-} for the bleaching of methyl orange (34.8 μM) by H_2O_2 (58 mM) in the presence of DMFu (6.25 mM) and CIX (0.1 mM) in pH 11 phosphate buffer at 25 °C.

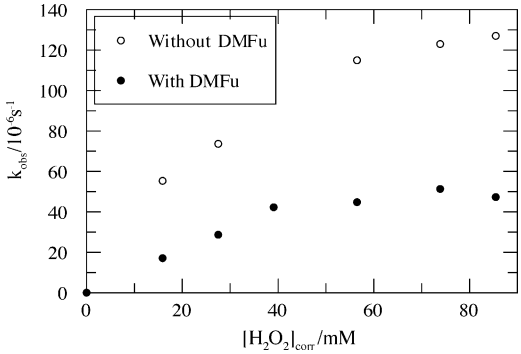

Fig. 2. Dependence of k_{obs} on $[H_2O_2]$ for the bleaching of methyl orange (34.8 μM) catalysed by MoO_4^{2-} (500 μM) in the presence of CIX (0.1 mM) in pH 11 phosphate buffer at 25 °C with and without 6.25 mM DMFu.

DMFu with the pH 8.95 borax buffer, either with molybdate or tungstate catalysts, because k_{obs} here fell progressively on addition of DMFu up to its solubility limit. In the other buffers there was no further significant decrease in k_{obs} after 5 mM of DMFu had been added.

When the catalyst concentration was kept constant, the values of k_{obs} depended in a more complex way on the concentration of "free" H_2O_2 (corrected for its complexation with metalate [8]). In the presence of molybdate, k_{obs} rose with increasing $[H_2O_2]$ and appeared to reach plateau values at around 80 mM H_2O_2. Lower rate constants, which rose more gradually, were obtained from solutions containing at least 5 mM DMFu, as shown in Fig. 2. With the tungstate-catalysed bleaching reaction, in contrast, the plot of k_{obs} versus $[H_2O_2]$ rose to a peak around 40 mM H_2O_2 and then gradually declined as seen in Fig. 3. (For the pH 8.95 borax buffer, however, the shape of the tungstate k_{obs} versus $[H_2O_2]$ plot resembled, but was lower than, that of the molybdate plot.) When at least 5 mM of DMFu had been added to the tungstate-containing solutions, the rate constants were smaller and reached a long plateau from about 30 mM H_2O_2 onwards (Fig. 3). The maximum values attained by k_{obs}, whether in the form of a peak or a plateau, are summarised in Table 2.

Fig. 4 shows how the rate constants of the molybdate-catalysed runs varied with the pH. Under the standard

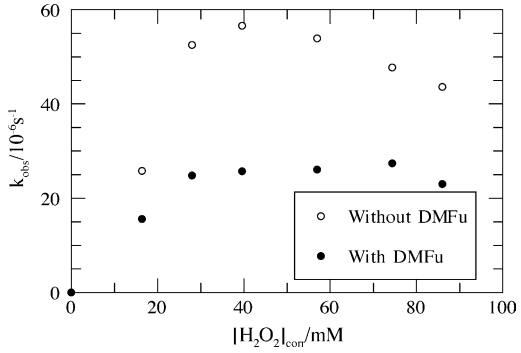

Fig. 3. Dependence of k_{obs} on $[H_2O_2]$ for catalysis by 500 μM WO_4^{2-}. Other conditions and symbols as in Fig. 2.

Table 1
Second-order rate constants for the bleaching of methyl orange (usually 34.8 μM) by H_2O_2 (58 mM) in the presence of CIX (0.1 mM) at 25 °C, both with and without DMFu (≥5 mM) in different buffer solutions

pH and buffer	k_2 (molybdate) ($\times10^{-2}$ M^{-1} s^{-1})	k_2 (molybdate + DMFu) ($\times10^{-2}$ M^{-1} s^{-1})	k_2 (tungstate) ($\times10^{-2}$ M^{-1} s^{-1})	k_2 (tungstate + DMFu) ($\times10^{-2}$ M^{-1} s^{-1})
8.95 (borax)	7.3		4.3	
9.55 (bicarbonate)	21.1	7.2	8.1	4.0
10.0 (bicarbonate)	24.5	7.2	9.8	4.8
10.5 (bicarbonate)	25.8	8.6	9.0	4.6
11.0 (phosphate)	22.3	8.2	9.9	4.8

Table 2
Peak values of k_{obs} in plots against [H_2O_2], at constant (500 μM) concentrations of molybdate or tungstate in the presence of CIX (0.1 mM) at 25 °C, both with and without DMFu (≥5 mM) in different buffer solutions

pH and buffer	k_{obs}^{max} (molybdate) ($\times10^{-6}$ s^{-1})	k_{obs}^{max} (molybdate + DMFu) ($\times10^{-6}$ s^{-1})	k_{obs}^{max} (tungstate) ($\times10^{-6}$ s^{-1})	k_{obs}^{max} (tungstate + DMFu) ($\times10^{-6}$ s^{-1})
8.95 (borax)	51		27	
9.55 (bicarbonate)	116	49	43	25
10.0 (bicarbonate)	138	50	54	27
10.5 (bicarbonate)	138	53	57	26
11.0 (phosphate)	128	45	57	27

conditions used, the k_{obs} values display a bell-shaped curve, passing over a peak at around pH 10.5 and declining at lower and higher pH. With the addition of DMFu the k_{obs} values are all smaller but fall on a similarly shaped plot. At pH 10 the rate constant for the borate buffer was 28% lower than for the bicarbonate buffer.

The pH variation of the tungstate-catalysed rate constants is shown in Fig. 5. Here k_{obs} also rose initially with increasing pH but then reached a plateau. The behaviour of the small DMFu k_{obs} values was similar. In contrast to the molybdate results, the tungstate rate constant at pH 10 obtained for the borax buffer agreed with the results using bicarbonate but, as mentioned above, no meaningful k_{obs} values could be determined for borax buffers containing DMFu.

3.2. Speciation effects

The different behaviour with borax buffers can be attributed to the well-documented [19,20] interactions between borate and H_2O_2. In alkaline solutions borax forms $B(OH)_4^-$ which then complexes with H_2O_2 to form $B(OOH)(OH)_3^-$ and $B(OOH)_2(OH)_2^-$ species. Calculations based on the literature equilibrium data show that, in our pH 10 borax buffer with 58 mM H_2O_2, more than 50% of the peroxide will have formed these peroxoborate species. The resulting decrease in the concentration of ordinary H_2O_2 molecules will then lower the rate of molybdate-catalysed bleaching, as shown in Fig. 2. This explains why the rates with borate buffers in Fig. 4 are so much smaller than expected from the results in the other buffers. However, Fig. 5 shows that in the case of tungstate catalysis, the rates with borate buffers appear to fit in smoothly with those from the other types of buffer. This can be understood from the fact that, with tungstate, k_{obs} passed through a maximum as the H_2O_2 concentration increased (cf. Fig. 3). Borate complexation which halved the effective H_2O_2 concentration from an overall 58 mM would therefore have produced little change in k_{obs}.

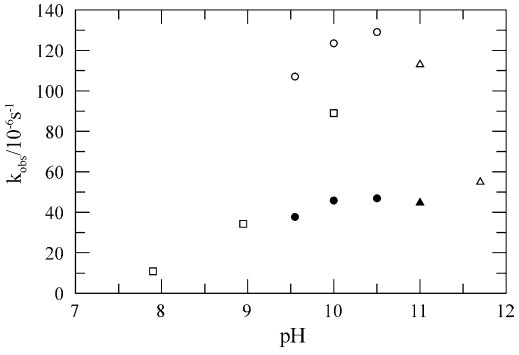

Fig. 4. Variation of k_{obs} with pH for the bleaching of methyl orange (34.8 μM) by H_2O_2 (58 mM) catalysed by MoO_4^{2-} (500 μM) in the presence of CIX (0.1 mM) at 25 °C using borax (□), carbonate (○) and phosphate (△) buffers. Filled symbols refer to systems containing 5 mM of DMFu.

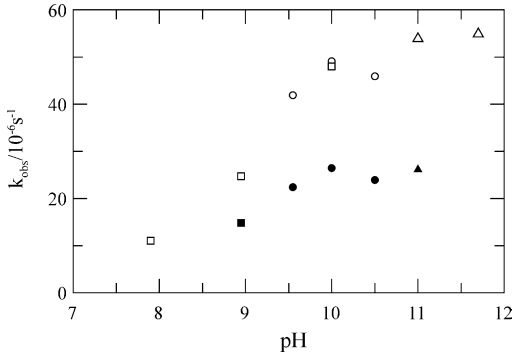

Fig. 5. Variation of k_{obs} with pH for catalysis by WO_4^{2-} (500 μM). Other conditions and symbols as in Fig. 4.

In bicarbonate media too, it is known [21,22] that interaction occurs with H_2O_2 to form hydrogenperoxomonocarbonate HCO_4^-. The literature data [21] show that 1.9% of HCO_3^- would be converted to HCO_4^- with 58 mM H_2O_2 at pH 7.4, and it seems likely that a similar order of conversion would arise at higher pH values. In any given bicarbonate buffer and pH, the ratio of HCO_4^- to free H_2O_2 will have been constant and probably ≤3%.

The experiments with DMFu exclude the contribution from singlet oxygen bleaching and so provide the rate constants due to the catalytic activity of the peroxometalate species in the reaction mixture. To identify the catalysing species responsible, speciation calculations were carried out for the peroxomolybdate species based on the results of Nardello et al. [13]. Although the equilibrium constants they published were derived from experiments using concentrations of H_2O_2 and MoO_4^{2-} in the molar range, we regard them as the best available after certain contradictions with the data of Csányi et al. [16] had been clarified by Thompson et al. [23]. We had concluded previously [8] that the bleaching rates determined with DMFu at pH 10 could best be accounted for if the major triperoxo species $MoO(O_2)_3^{2-}$ was the agent responsible for the catalysis. This also seems to hold for the DMFu bleaching experiments at the other pH values in Fig. 4. At a given H_2O_2 concentration of around 0.05 M, $MoO(O_2)_3^{2-}$ is the only ion whose concentration decreases at lower pH, due mainly to the increased percentage of $HMoO_2(O_2)_2^-$ in the more acid conditions. At pH 9, for example, this lowers $[MoO(O_2)_3^{2-}]$ by 10% and at pH 8 by over 50%. At pH values of 11 and above, $[MoO(O_2)_3^{2-}]$ declines slightly due to the dissociation of H_2O_2 ($pK_a = 11.6_5$ [24]) and of $HMoO_2(O_2)_2^-$.

In the case of the tungstate-catalysed bleaching experiments with DMFu, the behaviour at pH 10 could be partly explained by the presence of the $WO_2(O_2)_2^{2-}$ ion [8] using speciation calculations based on the work of Nardello et al. [12]. For pH values below 10, Fig. 5 shows that the k_{obs} values are lower. This could be related to the decrease in the concentrations either of $WO_2(O_2)_2^{2-}$ or of $W(O_2)_4^{2-}$, both caused by a large percentage rise in the concentration of $HWO_2(O_2)_2^-$. The approximate constancy of k_{obs} above pH 10 is closer to the behaviour expected from $[W(O_2)_4^{2-}]$ than from that of $[WO_2(O_2)_2^{2-}]$ which would be expected to rise somewhat. However, as already observed elsewhere [8,12], speciation knowledge of the peroxotungstate system in this pH range is still incomplete. New data on peroxomolybdates [9] and peroxotungstates [10] in H_2O_2 have recently appeared but do not extend beyond pH 9.

3.3. Bleaching by singlet oxygen

According to the additivity hypothesis, the contribution to the bleaching reaction by singlet oxygen, k_{sing}, can be obtained from the equation

$$k_{sing} = k_{obs}\,(\text{overall}) - k_{obs}\,(\text{with DMFu}) \quad (1)$$

Table 3
Variation with pH at 25 °C of k_{sing} (for the bleaching of methyl orange in solutions containing 58 mM H_2O_2 and 500 μM MO_4^{2-} with 0.1 mM CIX) compared with the rates $v(^1O_2)$ of $^1O_2$ evolution (from solutions of 50 mM H_2O_2 and 1000 μM MO_4^{2-} with 0.1 mM EDTA), interpolated from the curves in Fig. 2 of Ref. [12]

MO_4^{2-}	Parameter	pH					
		8.95	9.55	10.0	10.5	11.0	11.5
MoO_4^{2-}	k_{sing} ($\times10^{-6}$ s^{-1})		69	86	85	70	
MoO_4^{2-}	$v(^1O_2)$ ($\times10^{-6}$ M^{-1} s^{-1})	1.8	3.0	3.5	3.7	3.6	2.8
WO_4^{2-}	k_{sing} ($\times10^{-6}$ s^{-1})		21	25	22	25	
WO_4^{2-}	$v(^1O_2)$ ($\times10^{-6}$ M^{-1} s^{-1})	0.6_3	1.0_0	1.1_9	1.2_6	1.2_8	1.2_4

The values so calculated are given in Table 3. With molybdate as catalyst, k_{sing} is seen to pass through a maximum around pH 10–10.5. A closely similar trend is observed from data of Nardello et al. [12], where rates $v(^1O_2)$ of evolution from peroxomolybdate mixtures of comparable composition fall on a bell-shaped curve with a maximum near pH 10.5. With tungstate as catalyst there is little variation with pH of the k_{sing} values. This behaviour resembles the $^1O_2$ evolution rates for peroxotungstate solutions [12] which display a broad maximum from pH 10–11.5. Moreover, the k_{sing} values as well as the $v(^1O_2)$ rates are some three times greater in peroxide solutions containing molybdate than in ones containing tungstate. Bearing in mind the uncertainties in both the k_{sing} data (calculated from rate constant differences) and the $v(^1O_2)$ figures (interpolated from published curves), these correlations offer further support for the existence of a singlet oxygen pathway for methyl orange bleaching acting in parallel with a metalate ion-catalysed pathway.

Aubry's group concluded that the main precursor for $^1O_2$ generation in the molybdate system was $MoO(O_2)_3^{2-}$ [13], and later proposed that $WO_2(O_2)_2^{2-}$ was the precursor of $^1O_2$ in the tungstate system [12]. It is interesting that the former, and in part the latter, are also the peroxo species which appear to have been responsible for the metalate catalytic pathway in the bleaching reaction.

3.4. Representation of the kinetics

The plots of the first-order rate constants versus $[H_2O_2]$ in Figs. 2 and 6, and similar plots for molybdate catalysis for the other pH media, are reminiscent of Michaelis–Menten plots [25]. Taken together with the above evidence that the $MoO(O_2)_3^{2-}$ ion is ultimately responsible for both catalytic pathways, it follows that rate equations of the type

$$k_1 = \frac{k'[MoO(O_2)_3^{2-}][H_2O_2]}{1 + k''[H_2O_2]} \quad (2)$$

should describe each of the two kinetic contributions, with k_1 representing either k_{obs} (with DMFu) for the metalate catalysis or k_{sing} for catalysis by $^1O_2$.

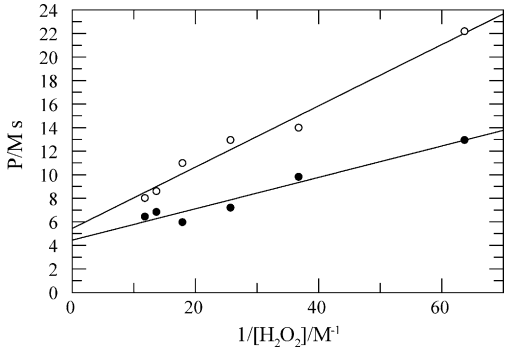

Fig. 6. Plot of P vs. $1/[H_2O_2]$ for solutions containing 500 μM MoO_4^{2-} at pH 9.55, for bleaching by peroxomolybdate (○) and by $^1O_2$ (●).

Rearrangement leads to

$$P = \frac{[MoO(O_2)_3{}^{2-}]}{k_1} = \frac{1 + k''[H_2O_2]}{k'[H_2O_2]} = \frac{1}{k'[H_2O_2]} + \frac{k''}{k'} \quad (3)$$

Plots of the parameter P versus $1/[H_2O_2]$ should therefore be straight lines at any given pH, with $[H_2O_2]$ corrected for the amount of peroxide removed by complexation with molybdate and $[MoO(O_2)_3{}^{2-}]$ calculated from the speciation equilibria. A good example is shown in Fig. 6. At other pH values, too, the points fitted linear plots though with some significant scatter.

For catalysis by $MoO(O_2)_3{}^{2-}$ the slope was $0.26 \pm 0.02\,M^2\,s$ at pH 9.55; it averaged $0.14\,M^2\,s$ from pH 10 to 11 and was independent of the molybdate concentration used. The intercepts were fairly constant over the pH range with a mean of $6.1 \pm 0.6\,M\,s$, leading to $k' = 7(\pm1)\,M^{-2}\,s^{-1}$, and $k'' = 44(\pm7)\,M^{-1}$ from pH 10 to 11. For catalysis by $^1O_2$ the slopes were constant over the pH range with a mean of $0.13 \pm 0.02\,M^2\,s$, while the intercepts appeared to vary randomly with pH giving an average of $3.6 \pm 0.7\,M\,s$. Hence $k' = 8(\pm1)\,M^{-2}\,s^{-1}$ and $k'' = 28(\pm7)\,M^{-1}$ at 25 °C.

As might be anticipated from inspection of Figs. 3 and 6, the corresponding points for $[WO_2(O_2)_2{}^{2-}]/k_1$ plotted against $1/[H_2O_2]$ fitted less well as straight lines. The tungstate k_{sing} data points, in particular, fell on pronounced curves. This is consistent with the evidence above about our current incomplete knowledge of speciation of the peroxotungstate system.

4. Conclusions

The kinetics of bleaching of methyl orange by H_2O_2 catalysed by MoO_4^{2-} and WO_4^{2-} have been measured in borax, bicarbonate and phosphate buffers from pH 8.95 to 11.0 at 25 °C. In all buffers, the pseudo first-order rate constants were first-order in catalyst concentration but showed more complex behaviour with varying peroxide concentrations. With catalysis by MoO_4^{2-} the peroxide dependences fitted Michaelis–Menten type equations. In all media, the rate constants were much smaller in the presence of the $^1O_2$ trap DMFu, showing that at every pH bleaching occurred via two catalytic pathways, by peroxometalates and by $^1O_2$. Rate constants for the latter varied with pH in a similar way to published rates of $^1O_2$ evolution by peroxomolybdates. Effects of the different peroxo species formed by MoO_4^{2-} and WO_4^{2-} as well as by the buffer borate and bicarbonate ions were discussed.

Acknowledgements

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