Mechanism of bleaching by peroxides[☆]
Part 6. Kinetics of the peroxide bleaching of methyl orange catalysed by MoO_4^{2-} and WO_4^{2-} at pH 10

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Abstract

The kinetics of bleaching of the azo dye methyl orange (4-[[(4-dimethylamino)phenyl]-azo]benzenesulfonic acid sodium salt) by hydrogen peroxide both alone and catalysed by $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ have been studied at 25 °C at pH 10. The effects of adding the sequestrant CIX (diethylenetriamine*pentakis*-methylenephosphonic acid), free radical and singlet oxygen traps were investigated. It was established that two parallel catalytic pathways were involved: bleaching by peroxomolybdate or peroxotungstate species and oxidation by singlet oxygen, the latter being generated by peroxo species.
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1. Introduction

We have reported in earlier work the catalytic effects of molybdate and tungstate ions, MoO_4^{2-} and WO_4^{2-}, for the bleaching of phenolphthalein [1] and of malvin chloride [2] by hydrogen peroxide. The conditions used were those applicable to domestic laundry bleaching, i.e., at ambient temperatures and at normal domestic bleach pH (ca. 10). In later work [3], we compared the efficacies of these catalysts with those of a series of polyoxomolybdate and polyoxotungstate complexes for the bleaching by H_2O_2 of the azo dye methyl orange and of the carotenoid dye crocetin. The kinetics and mechanism of the bleaching by H_2O_2 catalysed by the triple sandwich polyoxometalate $Na_{12}[Co_3^{II}W\{Co^{II}W_9O_{34}\}_2(H_2O)_2]\cdot47H_2O$ were then studied in more detail [4].

Here we report a fuller study of the kinetics of bleaching of methyl orange $Na(Me_2NC_6H_4N{=}NC_6H_4SO_3)$ by hydrogen peroxide using MoO_4^{2-} and WO_4^{2-} as catalysts. Methyl orange may be taken as a typical azo dye. The kinetics and mechanism of its uncatalysed bleaching by peroxosulfate and by several organic peracids have recently been studied by Oakes and Gratton [5] who have also studied the oxidation of several related arylazo dyes [6,7].

2. Experimental

2.1. Materials and conditions

Starting materials were purchased from Aldrich or BDH and used without further purification. Methyl orange was obtained from Sigma–Aldrich while CIX (diethylenetriamine-*pentakis*methylenephosphonic acid) and 30% stabilised hydrogen peroxide were provided by Solvay Interox. Buffer components were purchased from Merck. The concentration of H_2O_2 was determined by permanganate titration [8]. Triply de-ionised water (18 MΩ cm) was used throughout.

The methyl orange was twice recrystallised from water and then analysed (found C, 42.6; H, 4.6; N, 10.5%. Calc. for $C_{14}H_{20}N_3O_6Na$ C, 43.0; H, 4.1; N, 10.7%).

2.2. Experimental procedures

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 appropriate wavelength 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 modifications of the procedures given by Bates [9]. For the pH 10 buffer, $4.2\,g$ of $NaHCO_3$ and $276\,cm^3$ of aqueous 0.1 M NaOH ($M = mol\,dm^{-3}$) solution were diluted with triply de-ionised water to give a total volume of $1000\,cm^3$. Buffer solutions were stored in polythene bottles which had been soaked for >24 h in a 5% Decon 90 solution and then thoroughly rinsed with de-ionised water.

2.3. Instrumentation

Electronic spectra were measured on a Perkin-Elmer Lambda 2 spectrophotometer fitted with an LKB2219 Multitemp II thermostatic circulator and controlled by an Epson AX2 computer. Values of pH were determined with a RadioSpares 610 540 pH meter. ICP analyses were recorded on an ARL instrument by Mr. B. Coles of the Geology Department, Imperial College.

3. Results and discussion

3.1. General conditions

In aqueous solution methyl orange is almost completely dimerised above 2×10^{-4} M and undergoes further aggregation at millimolar and higher concentrations [10]. We therefore used a dye concentration in the 10^{-5} M range, typically $34.8\,\mu M$, where the Beer–Lambert law is obeyed. Reactions at pH 10 were followed at the broad peak at 464 nm in the electronic absorption spectrum $\varepsilon = 2.68 \times 10^4\,M^{-1}\,cm^{-1}$ [5]. To avoid adventitious catalysis by traces of transition metal impurities, runs were carried out with 0.1 mM of the sequestrant CIX, used by us in earlier work [3,4], which greatly improved the kinetic reproducibility.

Good linear plots of $\ln A$ (A is the absorbance) versus time t were obtained under the pseudo first-order conditions used, with hydrogen peroxide concentrations usually in the range 20–120 mM. As partial dissociation of H_2O_2 (pK_a 11.65 [11]) in the alkaline solution produced a small decrease in the pH,
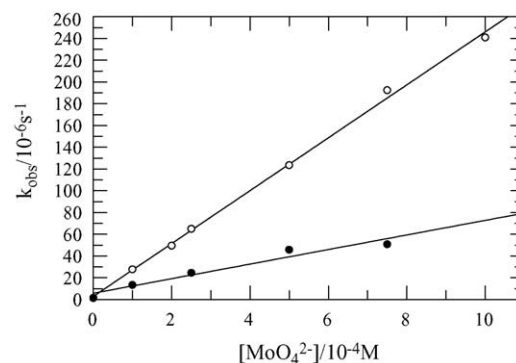

Fig. 1. Variation of k_{obs} with $[MoO_4^{2-}]$ with ($\bullet$) and without ($\bigcirc$) 5 mM DMFu for the bleaching of methyl orange ($34.8\,\mu M$) by H_2O_2 (58 mM) in the presence of CIX (0.1 mM) at 25 °C in pH 10 bicarbonate buffer.

the concentrations of the buffer components were adjusted to keep the pH constant.

The uncatalysed reaction was very slow. The pseudo first-order rate constant k_{obs} was proportional to the H_2O_2 concentration, giving a second-order rate constant k_{uncat} of $2.5 \times 10^{-5}\,M^{-1}\,s^{-1}$ at 25 °C and pH 10.

3.2. Catalysed bleaching

3.2.1. Bleaching catalysed by MoO_4^{2-}

Addition of quite small concentrations of MoO_4^{2-} greatly increased the rate of bleaching by H_2O_2. The electronic spectrum of the methyl orange from 190 to 1100 nm was not affected by the presence of the molybdate or any of the products of the reaction, and in the absence of H_2O_2 k_{obs} was zero. At a fixed H_2O_2 concentration, k_{obs} rose linearly with $[MoO_4^{2-}]$ as shown in Fig. 1, so that the catalytic reaction was first-order with respect to molybdate.

In all our experiments the large excess of H_2O_2 would have converted most of the MoO_4^{2-} to the oxotriperoxo species $MoO(O_2)_3^{2-}$ [12,13] and the values of the "free" H_2O_2 concentrations were corrected accordingly. When $[MoO_4^{2-}]$ was kept constant, k_{obs} rose in a non-linear fashion at low $[H_2O_2]$ and then approached an asymptotic maximum as seen in Fig. 2. Similarly shaped plots were obtained at other MoO_4^{2-} concentrations up to 750 μM. The asymptotic maximum was found to increase proportionally to the MoO_4^{2-} concentration with a gradient of $0.265\,M^{-1}\,s^{-1}$.

3.2.2. Bleaching catalysed by WO_4^{2-}

As with molybdate, the electronic spectrum of methyl orange (190–1100 nm) was unaffected by addition of tungstate. However, WO_4^{2-} had a lower catalytic activity than MoO_4^{2-} under the same conditions, as we had found earlier for the peroxide bleaching of phenolphthalein [1] and of malvin chloride [2] catalysed by these two ions. A plot of k_{obs} versus $[WO_4^{2-}]$ was linear at any given H_2O_2 concentration. In experiments with fixed tungstate concentrations and variable $[H_2O_2]$, the latter were corrected to "free" H_2O_2 by allowing for the formation of the predominant [14,15] diperoxo

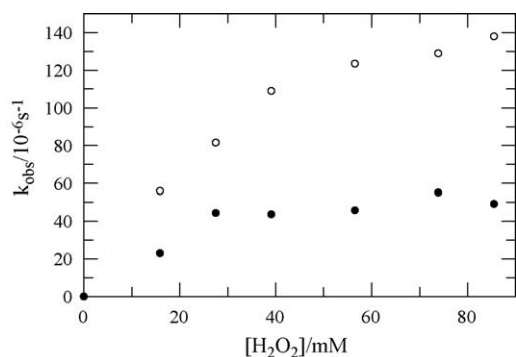Fig. 2. Plots of k_{obs} vs. [H_2O_2] for the bleaching of methyl orange (34.8 μM) catalysed by 500 μM $MoO_4{}^{2-}$ with (●) and without (○) 5 mM DMFu in the presence of 0.1 mM CIX at 25 °C in pH 10 bicarbonate buffer.

species $WO_2(O_2)_2{}^{2-}$ at pH 10. Fig. 3 shows that the resulting graphs possess an unusual shape: the k_{obs} values increase rapidly with increasing [H_2O_2] and then pass through a peak near 35 mM of the latter before gently decreasing. The maximum values for k_{obs} are approximately $55 \times 10^{-6}\,\mathrm{s}^{-1}$ for 0.5 mM $WO_4{}^{2-}$ and $105 \times 10^{-6}\,\mathrm{s}^{-1}$ for 1 mM $WO_4{}^{2-}$.

3.2.3. Bleaching by other catalysts

Brief studies were made with two other potential catalysts. Potassium chromate had previously been shown to be a moderately effective catalyst for the bleaching by H_2O_2 of phenolphthalein [1] and of malvin chloride [2], but with methyl orange the rate was only slightly increased by addition of K_2CrO_4. Addition of $[Co(NH_3)_5Cl]Cl_2$, particularly at the higher concentration of 1 mM, was actually found to inhibit the peroxide bleaching of methyl orange.

3.2.4. Effect of varying the dye concentration

In the above experiments the catalyst concentration exceeded that of methyl orange because of the large extinction coefficient of the latter and the high concentration of catalyst needed to achieve a reasonably fast rate. Work was therefore carried out with higher concentrations of dye (34.8, 69.6, 104 and 176 μM), with and without each catalyst, by using quartz
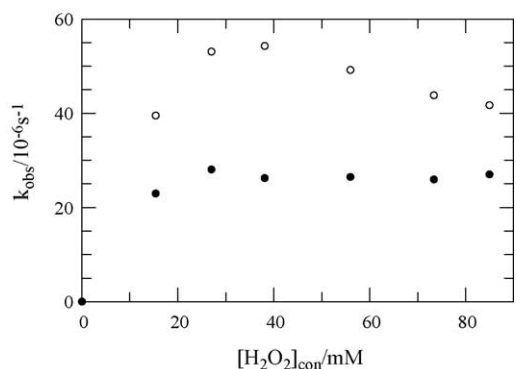

Fig. 3. Plots of k_{obs} vs. [H_2O_2] for the bleaching of methyl orange (34.8 μM) catalysed by 500 μM $WO_4{}^{2-}$, with (●) and without (○) 5 mM DMFu in the presence of 0.1 mM CIX at 25 °C at pH 10.

cells of 1, 5 and 10 mm widths, in order to keep the initial absorbances at 464 nm close to the optimal 0.8. The values obtained for k_{obs} varied slightly but displayed no trend with rising dye concentrations, confirming that the reaction was first-order with respect to methyl orange.

3.2.5. Effect of light and of free radical trapping agents

Experiments were carried out to establish whether the spectrophotometer radiation at 464 nm affected the rate of bleaching by blocking out the light for periods between measurements. There was no discernible effect on k_{obs} for either $MoO_4{}^{2-}$- or $WO_4{}^{2-}$-catalysed bleaching.

Addition of 0.5 mM N-tert-butyl-α-phenylnitrone, an effective trap for free-radicals in alkaline solutions [1,2,16], to reaction mixtures of 34.8 μM methyl orange, 58 mM H_2O_2, 0.1 mM CIX, and 1 mM $MoO_4{}^{2-}$ or $WO_4{}^{2-}$, in pH 10 aqueous bicarbonate buffer at 25 °C, gave values of k_{obs} of $235 \times 10^{-6}\,\mathrm{s}^{-1}$ for $MoO_4{}^{2-}$ and $104 \times 10^{-6}\,\mathrm{s}^{-1}$ for $WO_4{}^{2-}$. These are very close to those found in the absence of trapping agent ($241 \times 10^{-6}\,\mathrm{s}^{-1}$ and $98.4 \times 10^{-6}\,\mathrm{s}^{-1}$, respectively), indicating that free radicals do not play a significant role under these conditions.

3.2.6. Effect of a singlet oxygen trapping agent

As in our earlier work [1,2,16], the possible involvement of singlet oxygen ($^1O_2$) was detected by the $^1O_2$ trap 2,5-dimethyfuran (DMFu). In initial experiments at pH 10 and at 58 mM H_2O_2, DMFu at concentrations between 1 and 7.5 mM was added to reactions catalysed by 0.5 mM $MO_4{}^{2-}$ (M = Mo, W) so that it was in excess of both dye and catalyst concentrations. The values of k_{obs} then decreased markedly, suggesting that $^1O_2$ did indeed play a significant role. With $MoO_4{}^{2-}$ k_{obs} decreased from $123 \times 10^{-6}\,\mathrm{s}^{-1}$ to a minimum of ca. $43 \times 10^{-6}\,\mathrm{s}^{-1}$ when the concentration of DMFu reached 5 mM: at higher DMFu concentrations the value of k_{obs} did not decrease further. For $WO_4{}^{2-}$ a concentration of 4 mM DMFu was needed for k_{obs} to fall from $49 \times 10^{-6}\,\mathrm{s}^{-1}$ to a minimum of $25 \times 10^{-6}\,\mathrm{s}^{-1}$. It is likely that tungstate needed less DMFu than molybdate because $WO_4{}^{2-}$ produces less $^1O_2$ than does $MoO_4{}^{2-}$ in alkaline solutions [13,14]. In all subsequent experiments we used at least 5 mM of DMFu.

It follows that $^1O_2$ is an active oxidant in the bleaching of methyl orange, contributing some 70% of k_{obs} for $MoO_4{}^{2-}$ and 50% for $WO_4{}^{2-}$. Additional evidence for the involvement of $^1O_2$ in these systems was provided by comparing reaction rates carried out in ^2H_2O buffer solutions. The short lifetime of $^1O_2$ arises from the efficiency of H_2O as a quenching agent; ^2H_2O is much less efficient in this respect, and the corresponding lifetime of $^1O_2$ is 14 ± 1 times longer in ^2H_2O [17]. It follows that if the bleaching of methyl orange involves substantial participation of $^1O_2$, k_{obs} should increase in deuteriated buffer solutions. In agreement with this, k_{obs} values for 0.5 mM $MoO_4{}^{2-}$ and $WO_4{}^{2-}$ in pH 10 aqueous bicarbonate buffer at 25 °C were $123 \times 10^{-6}\,\mathrm{s}^{-1}$ and $49 \times 10^{-6}\,\mathrm{s}^{-1}$, respectively, while in a 50% by volume deuteriated buffer

solution the corresponding values were $194 \times 10^{-6}\,\text{s}^{-1}$ and $72 \times 10^{-6}\,\text{s}^{-1}$. The larger rise in k_{obs} of 58% for $MoO_4{}^{2-}$ than of 47% for $WO_4{}^{2-}$ in the partially deuterated buffer again reflects the greater ability of molybdate to generate singlet oxygen [13].

3.2.7. Reaction paths in molybdate catalysed bleaching

As Fig. 1 shows, k_{obs} increased linearly with added sodium molybdate in the presence of 5 mM DMFu as well as in its absence. However, the resulting second-order rate constant was much reduced by adding DMFu, from $24.5 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1}$ to $6.5 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1}$. The directly measured uncatalysed rate constant was not affected by addition of DMFu.

At given molybdate concentrations in the presence of DMFu, k_{obs} initially rose with increasing $[H_2O_2]$ and then gradually levelled off to an apparent plateau. The plateau values were approximately proportional to the molybdate concentrations used. As seen in Fig. 2, although the general pattern was fairly similar to that found in the absence of DMFu, the rate constants were all much smaller when DMFu was present to trap singlet oxygen.

We now postulate the additivity hypothesis that bleaching catalysis by the peroxomolybdate species (represented by the DMFu results) and bleaching catalysis by singlet oxygen (generated by the peroxomolybdate system) proceed side by side, independently of each other. It follows that subtraction of the k_{obs} values obtained with DMFu (which suppressed the $^1O_2$ path) from the overall k_{obs} values obtained in the absence of DMFu, leads to rate constants (called k_{sing}) due to bleaching by singlet oxygen alone.

The resultant values of k_{sing} have been plotted in Fig. 4 against the corrected concentrations of free H_2O_2 at 0.25 and 0.5 mM molybdate concentrations. Superimposed have been the rates of generation of $^1O_2$ published by Aubry and Cazin [17] for 1 mM molybdate in otherwise very similar conditions. A closely similar plot for $^1O_2$ formation at 1 mM molybdate was obtained by Böhme and Brauer [18]. The agreement between the shape of the $^1O_2$ curve and our k_{sing} data supports the additivity hypothesis and underpins the evi-
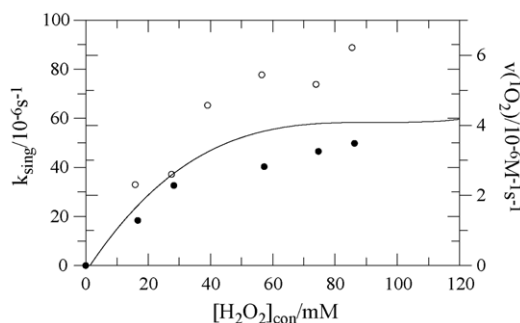
Fig. 4. Variation of k_{sing} with $[H_2O_2]$ in the presence of 250 μM (●) and 500 μM (○) $MoO_4{}^{2-}$ and 0.1 mM CIX in pH 10 bicarbonate buffer at 25 °C, compared with the rate of evolution v of $^1O_2$ in the presence of 1000 μM $MoO_4{}^{2-}$ and 0.1 mM EDTA in pH 10.5 phosphate buffer at 25 °C reported by Aubry and Cazin [17].
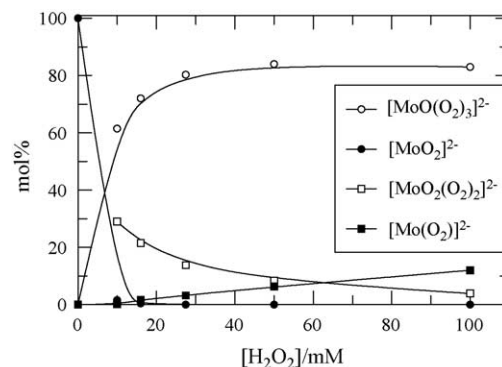
Fig. 5. Speciation diagram for peroxomolybdates at pH 10 calculated from the data of Nardello et al. [13].

dence for a singlet oxygen pathway in the catalysed bleaching of methyl orange.

The experiments involving DMFu provide the rate constants of the other catalytic pathway. To identify the relevant catalytic agent the results need to be compared with the behaviour of the various peroxomolybdate species. Several research groups [12,13,15,19,20] have investigated the peroxomolybdate system by a variety of spectroscopic and kinetic techniques. Although the work of Nardello et al. [13] used concentrations of $MoO_4{}^{2-}$ and H_2O_2 in the molar range, their equilibrium constants seem to be the most reliable (after Thompson et al. [1] clarified certain contradictions between some of their data and those of Csányi et al. [12]). We have therefore based our speciation calculations on them. The resultant speciation diagram in Fig. 5 applies to molybdate concentrations sufficiently low for dimeric species such as $Mo_2O_3(O_2)_4{}^{2-}$ to be almost fully dissociated. Comparison with the DMFu runs in Fig. 2 clearly points to $MoO(O_2)_3{}^{2-}$ as the most likely species responsible for catalysing the bleaching reaction. Nardello et al. [13] concluded that it was also the main precursor of molecular oxygen formation.

3.2.8. Reaction paths in tungstate catalysed bleaching

Plots of k_{obs} against the concentration of added sodium tungstate were linear in the presence of 58 mM H_2O_2 and 5 mM DMFu, but with a smaller slope of $4.3 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1}$ than without DMFu ($9.8 \times 10^{-2}\,\text{M}^{-1}\,\text{s}^{-1}$). However, when the tungstate concentrations were kept constant, Fig. 3 shows that k_{obs} passed over a peak at around 40 mM H_2O_2 and then declined. With the addition of DMFu, k_{obs} became almost independent of the concentration of H_2O_2 after an initial rise. All the rate constants were lowered by addition of DMFu because it eliminated the $^1O_2$ catalytic pathway.

Application of the additivity equation

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

leads to the rate constants for bleaching by singlet oxygen alone.

In Fig. 6 k_{sing} is seen to rise with increasing $[H_2O_2]$ to a marked peak near 40 mM H_2O_2, and then to decline. This lat-
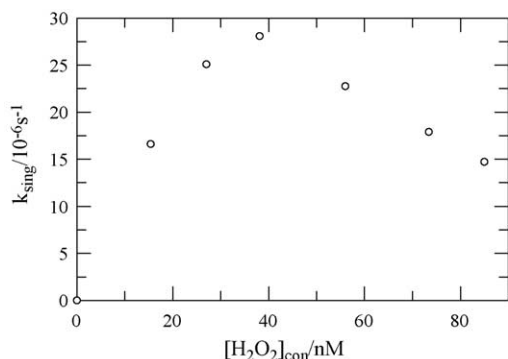
Fig. 6. A plot of k_{sing} vs. [H_2O_2] in the presence of 500 μM WO_4^{2-} and 0.1 mM CIX at pH 10 and 25 °C.

ter behaviour parallels that of the concentration of the diperoxotungstate species $WO_2(O_2)_2^{2-}$ in the speciation diagram (Fig. 7) calculated from the data of Nardello et al. [14] for the peroxotungstate system. However, the diperoxo curve in Fig. 7 fails to explain the steep rise in the k_{sing} values at low H_2O_2 concentrations. This suggests that the diperoxo species may not be the precursor of $^1O_2$ as proposed by Nardello et al. [14].

The bleaching rate constants by the other catalytic pathway are given by the DMFu runs in Fig. 3. The dependence of the k_{obs}(DMFu) results on [H_2O_2] is quite different from the [H_2O_2] variation of either the diperoxo $WO_2(O_2)_2^{2-}$ or the tetraperoxo $W(O_2)_4^{2-}$ species in Fig. 7. Although no evidence for a triperoxotungstate $WO(O_2)_3^{2-}$ species was provided by the ^{183}W NMR spectra of 1 M WO_4^{2-} solutions in H_2O_2, Nardello et al. stated that formation of such a species could not be completely ruled out [14]. It is just such a triperoxo ion, $MoO(O_2)_3^{2-}$, which fitted the kinetic results in the analogous molybdate system discussed above.

3.2.9. Reaction products

There seem to be no reports in the literature concerning the nature of the products formed on oxidation of methyl orange by H_2O_2 catalysed by molybdate or tungstate, or oxidised by $^1O_2$. We found that oxidation of methyl orange on a preparative scale by excess H_2O_2 at pH 10 in the presence of sodium
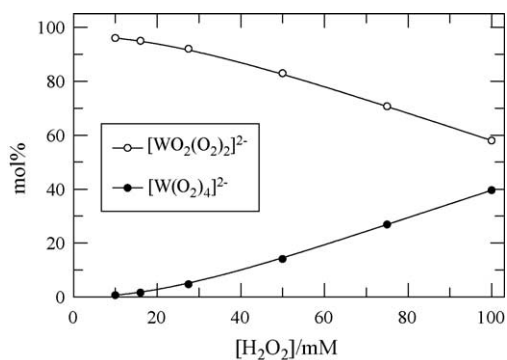

Fig. 7. Speciation diagram for peroxotungstates at pH 10 calculated from the data of Nardello et al. [14].

molybdate over a period of 2 weeks gave a clear pale orange solution. Its electronic spectrum had a peak at 319 nm and a profile which, as in the work of Oates and Gratton using peroxysulfate as co-oxidant [5], closely matched that of the amine oxide $Me_2N^+O^-C_6H_4N_2C_6H_5$ reported by Pentimalli [21]. Electron-spray mass spectroscopy and HPLC analyses were also used on solutions near pH 10 containing H_2O_2, MoO_4^{2-}, CIX and dye, but although at least five fragments were observed in HPLC none could be identified with certainty by mass spectroscopy.

Recent work has shown that the oxidation products of methyl orange by H_2O_2 catalysed by $[Mn_2(\mu-O)_3(TMTACN)]^{2+}$ (TMTACN = 1,4,7-trimethyl-1,4,7-triazacyclononane) include its N-oxide, the azoxy-N-oxide and monodemethylated methyl orange [22].

4. Conclusions

The bleaching of methyl orange by H_2O_2 is strongly catalysed by molybdate and tungstate at pH 10. Both catalysed reactions are first-order with respect to dye and catalyst concentrations with a more complex peroxide dependence. The bleaching consists of two parts: metal-catalysed, which does not involve free radicals, and by singlet oxygen, generated by the peroxomolybdate and peroxotungstate systems.

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