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Oxidation of thioanisole by peroxomolybdate ions: direct oxygen transfer from tetraperoxomolybdate ion

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ABSTRACT: Addition of thioanisole (PhSMe) to Na_2MoO_4 in dilute hydrogen peroxide at pH 9.4 rapidly quenches the absorbance of the tetraperoxo complex, $Mo(O_2)_4^{2-}$, which gradually regenerates as the PhSMe is oxidized to the sulfoxide. This direct oxygen transfer is followed by the decreasing absorbance of $Mo(O_2)_4^{2-}$ at 452 nm. In dilute H_2O_2 the $Mo(O_2)_4^{2-}$ becomes a steady-state intermediate, and kinetics monitored by ^1H NMR spectroscopy allow estimation of the second-order rate constant for oxidation of PhSMe by $MoO(O_2)_3^{2-}$ and rate constants for interconversion of $MoO(O_2)_3^{2-}$ and $MoO(O_2)_4^{2-}$. The steady-state approximation breaks down at higher $[H_2O_2]$, and with $[H_2O_2] = 2$ M the $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ are approximately in equilibrium; based on the rate constants of oxidation of PhSMe by $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ and the related association equilibrium constant, the observed and predicted rate constants for the overall oxidation of PhSMe are similar. Copyright © 2001 John Wiley & Sons, Ltd.

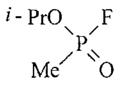
KEYWORDS: sulfide oxidation; thioanisole; peroxomolybdates; direct oxygen transfer; kinetics

INTRODUCTION

Decontamination of chemical weapons under mild conditions is complex because phosphonofluoridate nerve agents, e.g. **GB** (Sarin), react readily with nucleophiles, but not with oxidants,[1,2] and the blister agent **HD** (Mustard Gas) is readily oxidized, but, except in forcing conditions, is relatively unreactive towards nucleophiles and bases. The spontaneous hydrolysis of **HD** is rapid but is limited by its very low solubility. The phosphonothioate nerve agent **VX**[1,2] reacts with anionic nucleophiles, but with OH^- there is a side reaction with P—O cleavage to give the toxic phosphonothioate anion **EA2192**, which reacts slowly with nucleophiles. However, **VX** reacts with oxidants to give nontoxic products.[2]

Concentrated hypochlorite ion and *N*-chloramines can react as oxidants and nucleophiles, and concentrated NaOH in apolar organic media decomposes **HD** in an E2 reaction and reacts nucleophilically with the phosphonyl derivatives.[1] However, these decontaminants are very aggressive reagents.

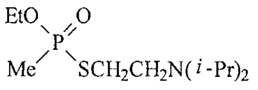
The combination of a nucleophile and an oxidant in mildly alkaline conditions should be a mild broad-spectrum decontaminant. For example, peroxyanions are effective nucleophiles, especially towards phosphonyl derivatives,[1,3] and peroxyacids readily oxidize sulfides,[1,2,4] but their mixtures are unstable and their decomposition generates oxygen.[5] Therefore, their general use requires adjustment of pH, depending on the threat.



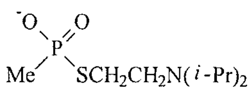
GB

$(ClCH_2CH_2)_2S$

HD



VX



EA2192

Iodoso- and iodoxy-benzoates are effective turn-over nucleophiles towards phosphonofluoridates and related compounds.[1b,6] They react with **VX**, but reduction by the thiolate product makes the reaction noncatalytic.[7] The possibility of regenerating the iodoso- or iodoxy-benzoate by *in situ* oxidation has been examined,[7,8] but this approach does not seem to be practically useful.

Another approach involves the use of hydrogen peroxide, which is not a very effective oxidant, but can be 'activated' by conversion into a peroxyacid, e.g. by reaction with tetraacetyl ethylenediamine,[9] or into a peroxocarbonate by reaction with hydrogen carbonate ions.[4] Another possibility is formation of a peroxocom-

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plex of a transition metal ion. In principle these conversions can be carried out in mildly alkaline solution, which allows formation of nucleophilic HO_2^-.

Aqueous molybdate ions and H_2O_2 form a series of peroxomolybdates whose compositions depend on concentrations and pH,[10] but with dilute molybdate ion and mildly alkaline pH mononuclear complexes have been characterized.[11,12] With $[H_2O_2]$ >0.08 M the tri- and tetra-peroxo molybdates coexist[12] and the association equilibrium constant is 1.58 M^{-1} in water at pH ≈ 9.4.[11] The pK_a of H_2O_2 is *ca* 11.5,[13] and the high nucleophilicity of HO_2^- should permit its reaction with toxic phosphonyl derivatives in these conditions.

Peroxomolybdates at surfaces,[14] or in colloidal dispersions,[15] oxidize sulfides, and their complexes with organic ligands react with sulfides in organic solvents in reactions that are overall second-order.[16] However, decomposition of peroxomolybdates generates $^1O_2$,[12] which also oxidizes sulfides.[17] Aubry and Bouttemy used $MoO_4^{2-} + H_2O_2$ in reverse micelles and concluded that $^1O_2$ generated in the 'water-pool' interior diffused out of the micelles into the organic solvent where it reacted with the hydrophobic organic substrates.[18]

We examined the oxidation of thioanisole (PhSMe) by $Na_2MoO_4 + H_2O_2$ in H_2O:*t*-BuOH 7:3 v/v under conditions in which $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ coexist at a nominal pH of *ca* 9.4. This solvent was selected to allow [PhSMe] to be such that the reaction could be followed by ^{1}H NMR spectroscopy, although in some conditions we followed the decreasing absorbance of $Mo(O_2)_4^{2-}$ due to direct oxygen transfer to PhSMe. Very little sulfone is formed in this reaction (Scheme 1).

$$\text{PhSMe} \xrightarrow{\text{O}} \text{PhSO.Me} \dashrightarrow \text{PhSO}_2\text{.Me}$$

Scheme 1

We used PhSMe as substrate because the ^{1}H NMR signal in the aromatic region can be followed without overlap with those of other species in the reaction mixture. However, oxidation of **HD** is rapid in conditions such that the peroxomolybdate is largely $Mo(O_2)_4^{2-}$.[19]

RESULTS

Equilibrium between tri- and tetra-peroxomolybdates

We can neglect formation of binuclear complexes in dilute Na_2MoO_4 (*ca* 10^{-3} M),[10–12] and with $[H_2O_2]$ >0.05 M the equilibria between the peroxocomplexes are such that we need to consider only $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ at pH 9.4.[11,12] This assumption was verified by observation of a clean isosbestic point between $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ (Experimental). The equilibrium can be monitored spectrophotometrically[11] because λ_{max} for $Mo(O_2)_4^{2-}$ is 452 nm in water and $MoO(O_2)_3^{2-}$ absorbs very weakly at this wavelength. The original measurement of the association equilibrium constant was in water where $K = 1.58$[11] or 1.4[12] M^{-1} and $\epsilon = 440\ \text{M}^{-1}\ \text{cm}^{-1}$. We used H_2O:*t*-BuOH 7:3 v/v at a nominal pH of 9.4.

The equilibrium association constant between $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$

$$MoO(O_2)_3^{2-} + H_2O_2 \overset{K}{\rightleftarrows} Mo(O_2)_4^{2-} \qquad (1)$$

is given by Eqn. (2):

$$\frac{[Mo(O_2)_4^{2-}]}{[Mo_T]} = \frac{K[H_2O_2]}{1 + K[H_2O_2]} \qquad (2)$$

where T denotes total concentration.

Values of K and ε were calculated by using the reciprocal form, Eqn. (3), where A is absorbance:

$$\frac{1}{A} = \frac{1}{\varepsilon[Mo_T]} + \frac{1}{\varepsilon[Mo_T]K[H_2O_2]} \qquad (3)$$

The plot of $1/A$ against $1/[H_2O_2]$ is linear except in very dilute H_2O_2, where there is some $MoO_2(O_2)_2^{2-}$,[11,12] and we allow for depletion of $[H_2O_2]$ in terms of the formation of $[MoO(O_2)_3^{2-}]$. From the slope and intercept we estimate $K = 1.9\ \text{M}^{-1}$, which is slightly higher than the value in water,[11] and $\epsilon = 592\ \text{M}^{-1}\ \text{cm}^{-1}$. Although the equilibrium in Eqn. (1) formally includes water, its concentration is not included in the calculation of K [Eqn. (2)].[11,12]

Initial sulfide oxidation

When excess PhSMe is added to the red–brown solution of Na_2MoO_4 (*ca* 10^{-3} M)[11] in H_2O:*t*-BuOH containing H_2O_2 (0.05–0.4 M) the color of $Mo(O_2)_4^{2-}$ is quenched within a few seconds. The solution remains transparent by eye for a time depending on $[H_2O_2]$ and added PhSMe, and the color gradually returns.

The initial decrease and subsequent recovery of absorbance (Fig. 1) shows that after the initial reaction with PhSMe the concentration of $Mo(O_2)_4^{2-}$ does not change for *ca* 10 min, and within that time it can be regarded as in steady state. The absorbance does not go to zero, possibly because there is a low steady-state concentration of $Mo(O_2)_4^{2-}$, but there was some bubbling in these conditions and light-scattering by small bubbles would reduce transmittance. After the initial decrease the absorbance increases as the formation of $Mo(O_2)_4^{2-}$, by reaction of $MoO(O_2)_3^{2-}$ with H_2O_2, becomes faster than reduction by PhSMe, whose rate decreases with decreasing [PhSMe]. The absorbance levels off as [PhSMe] → 0,

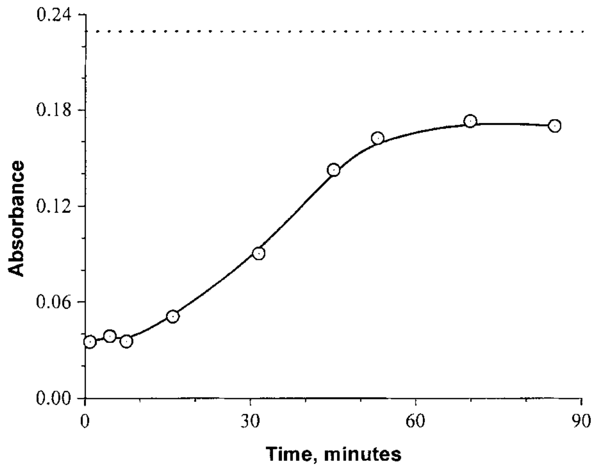


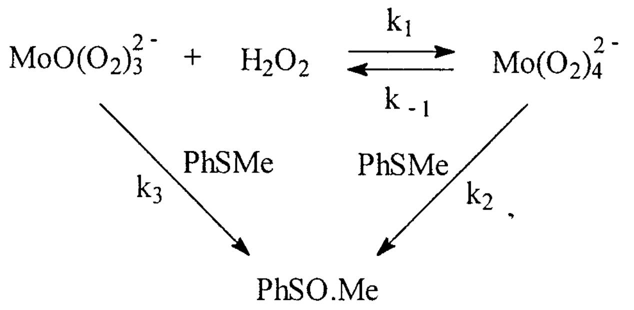
Figure 1. Decrease and recovery of the absorbance of $Mo(O_2)_4^{2-}$ on addition of PhSMe. The broken line indicates absorbance before addition of PhSMe. The solid line is to guide the eye. Conditions are $[H_2O_2] = 0.42$ M, $[Na_2MoO_4] = 10^{-3}$ M and [PhSMe] = 0.02 M

although it does not regain the initial value because $[H_2O_2]$ has decreased due to oxidation of PhSMe and decomposition.[12] After the leveling off of absorbance it is again rapidly quenched by a second addition of PhSMe. The half-life for the initial reaction of $Mo(O_2)_4^{2-}$ with 0.02 M PhSMe is *ca* 3 s. With $[H_2O_2] > 1$ M the absorbance of $Mo(O_2)_4^{2-}$ decreases rapidly, but some color remains and its recovery is much faster than in dilute H_2O_2.

These qualitative observations show that this rapid reaction is a direct oxygen transfer from $Mo(O_2)_4^{2-}$, which, in dilute H_2O_2, is faster than interconversion of $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$. We could follow the reaction in dilute H_2O_2 and lower [PhSMe] and obtained reasonably good first-order kinetics (Experimental). These first-order rate constants are given in Table 1. However, with dilute PhSMe its reaction with $Mo(O_2)_4^{2-}$ may not be very much faster than interconversion of the complexes, and we consider this problem later.

Overall reaction in dilute H_2O_2

The rapid quenching of the color of $Mo(O_2)_4^{2-}$ by PhSMe in dilute H_2O_2 (Table 1 and Fig. 1) shows that after this step we can use the steady-state approximation. Oxidation can involve $MoO(O_2)_3^{2-}$ as well as $Mo(O_2)_4^{2-}$ (Scheme 2).



Scheme 2

In these conditions we can neglect the contributions of other peroxomolybdates[11,12] and $[MoO(O_2)_3^{2-}] \approx [Mo_T]$, where $[Mo_T]$ is the stoichiometric concentration of the various molybdates. (The association constant for formation of $MoO(O_2)_3^{2-}$ is 210 M^{-1} in water at 0 °C and the monoperoxo complex can be neglected[12]).

There is a contribution from direct oxidation by H_2O_2 that is relatively unimportant in dilute H_2O_2, and the cited first-order rate constants k_c, with respect to [PhSMe], are corrected for this reaction (Experimental).

These relatively slow oxidations of PhSMe were followed by ^1H NMR spectroscopy with very dilute Na_2MoO_4 and H_2O_2 in considerable excess over PhSMe.

The first-order rate constant is given by:

$$k_c = k_3[MoO(O_2)_3^{2-}] + k_2[Mo(O_2)_4^{2-}] \tag{4}$$

and with $Mo(O_2)_4^{2-}$ in steady state:

$$[Mo(O_2)_4^{2-}] = \frac{k_1[H_2O_2][Mo_T]}{k_{-1} + k_2[PhSMe]} \tag{5}$$

To a first approximation with $k_2[PhSMe] >> k_{-1}$

$$\frac{k_c}{[Mo_T]} = k_3 + \frac{k_1[H_2O_2]}{[PhSMe]} \tag{6}$$

This simple treatment fails at high $[H_2O_2]$, due to the accelerated interconversion of $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$, but in dilute H_2O_2 it fits the data reasonably well in view of the problems in following reactions by NMR spectroscopy. Concentrations are corrected for the amount of reaction that occurs between mixing the reactants and spectral acquisition, based on relative concentrations of sulfide and sulfoxide.

Values of the rate constants calculated using Eqn. (6) are: $k_1 = 0.032\ M^{-1}\ s^{-1}$, $k_2 \approx 10\ M^{-1}\ s^{-1}$, $k_3 = 0.40\ M^{-1}\ s^{-1}$; and $k_{-1} = 0.017\ s^{-1}$. The value of k_2 is from direct measurement (Table 1) and that of k_{-1} is calculated from k_1 and K.

Table 1. Reaction of $Mo(O_2)_4^{2-}$ with PhSMe[a]

$[H_2O_2]$ (M)	[PhSMe] (M)	k_{obs} (s^{-1})	k_{obs}/[PhSMe] ($M^{-1}\ s^{-1}$)	k_2 ($M^{-1}\ s^{-1}$)[b]
0.20	0.00205	0.0190	9.3	9.5
0.20	0.0041	0.0361	8.8	8.9
0.42	0.02	0.22	11	

[a] At 25.0 °C with 1.12×10^{-3} M Na_2MoO_4.
[b] Calculated by using Eqn. (11).

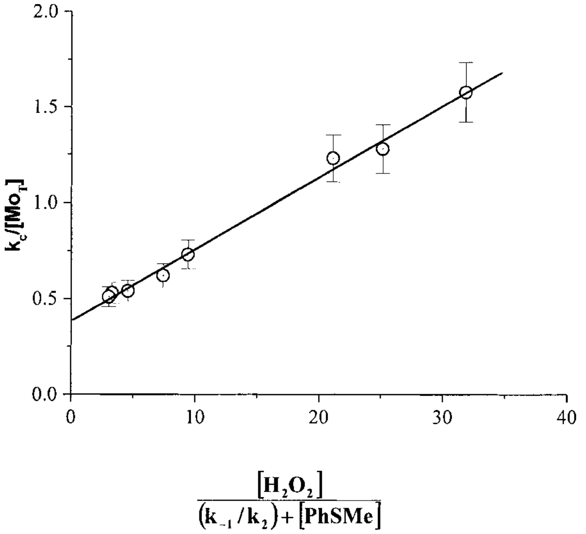


Figure 2. Fit of the rate data to Eqn. (7) under steady-state conditions in 0.084–0.659 M H_2O_2 (Table 2)

In a second approximation we include k_{-1} in the steady-state treatment:

$$\frac{k_c}{[Mo_T]} = k_3 + \frac{k_1[H_2O_2]}{(k_{-1}/k_2) + [PhSMe]} \tag{7}$$

The initial value of k_{-1} is that calculated by using Eqn. (6). The plot of $k_c/[Mo_T]$ against $[H_2O_2]/((k_{-1}/k_2) + [PhSMe])$ is shown in Fig. 2 and is linear up to 0.66 M H_2O_2. The estimated rate constants, $k_1 = 0.037\ M^{-1}\ s^{-1}$, $k_{-1} = 0.020\ s^{-1}$, and $k_3 = 0.38\ M^{-1}\ s^{-1}$, are similar to those from the simpler treatment, and probably within the experimental limits in the accuracy of the kinetic data, and the fit is not very sensitive to the value of k_2. The line in Fig. 2 is from a linear regression, although some data points are at 21.4 °C rather than 25 °C (Table 2); the inherent errors in the use of NMR spectroscopy in monitoring the reaction are covered under Experimental. The error bars in Fig. 2 correspond to ±10%.

Reaction of $Mo(O_2)_4^{2-}$ with PhSMe

It is difficult to obtain good kinetics on the initial reaction in conditions similar to those illustrated in Fig. 1. We cannot use a stopped-flow spectrophotometer, because bubbles form. Also, in order to observe first-order kinetics with respect to $Mo(O_2)_4^{2-}$, its concentration has to be low relative to [PhSMe] and $[H_2O_2]$, but high enough to give a reasonable absorbance change during reaction. With 0.020 M H_2O_2 and dilute PhSMe, we had to separate the reduction of $Mo(O_2)_4^{2-}$ by PhSMe from interconversion of $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ (Table 2).

The decrease in the concentration of $Mo(O_2)_4^{2-}$ by reaction with PhSMe and return to $MoO(O_2)_3^{2-}$ is offset by its formation from H_2O_2 and $MoO(O_2)_3^{2-}$ and, therefore, at any given time:

$$\frac{-d[Mo(O_2)_4^{2-}]}{dt} = [Mo(O_2)_4^{2-}](k_2[PhSMe] + k_{-1}) - k_1[MoO(O_2)_3^{2-}][H_2O_2] \tag{8}$$

$$\frac{-d[Mo(O_2)_4^{2-}]}{dt} = [Mo(O_2)_4^{2-}](k_2[PhSMe] + k_{-1}) - k_1[H_2O_2]([Mo_T] - [Mo(O_2)_4^{2-}]) \tag{9}$$

The rate constants k_1 and k_{-1} are known from independent measurements (Fig. 2), and [PhSMe] and $[H_2O_2]$ are initial values.

The observed first-order rate constants k_{obs} (Table 1) give:

$$\frac{-d[Mo(O_2)_4^{2-}]}{dt} = k_{obs}[Mo(O_2)_4^{2-}] \tag{10}$$

and

$$k_{obs} = k_2[PhSMe] + k_{-1} - k_1[H_2O_2]\left(\frac{[Mo_T]}{[Mo(O_2)_4^{2-}]} - 1\right) \tag{11}$$

In fitting the data to Eqn. (11) we use initial concentrations of H_2O_2 and PhSMe that are considerably larger than that of $Mo(O_2)_4^{2-}$ calculated by using the value of $K = 1.9\ M^{-1}$, the observed first-order rate constants (Table 1) and $k_1 = 0.037\ M^{-1}\ s^{-1}$ and $k_{-1} = 0.020\ s^{-1}$. Values of k_2 in dilute H_2O_2 (Table 1) are slightly higher than the apparent second-order rate constants calculated without correction for interconversion of the peroxo-complexes. These differences depend upon values of k_1 and k_{-1} estimated from NMR data, but an increase of k_1 and k_{-1} by factors of 1.5 decreases calculated values of k_2 by *ca* 10%. The similarities in values of k_2 from both approximations show that the steady-state treatment is reasonably satisfactory. We give values of rate constants to two significant figures because of the limitations in the kinetic use of NMR spectroscopy.

Failure of the steady-state approximation

The kinetic treatment based on Eqns (6) and (7) and

Table 2. Oxidation of PhSMe[a]

$[H_2O_2]$ (M)[b]	$10^4[Mo_T]$ (M)	[PhSMe] (M)[b]	$10^4 k_c$ (s^{-1})	$k_c/[Mo_T]$ (M^{-1} s^{-1})[c]
0.084 (0.082)	3.03	0.0254 (0.0234)	1.6	0.53 (0.51)
0.084 (0.078)	10.1	0.0300 (0.024)	5.1	0.51 (0.50)
0.088 (0.082)	10.1	0.0204 (0.0163)	5.4[d]	0.54 (0.55)
0.088 (0.079)	20.2	0.0217 (0.0091)	12.5[d]	0.62 (0.66)
0.176 (0.167)	10.1	0.0253 (0.0162)	7.4[d]	0.73 (0.74)
0.404 (0.399)[e]	3.17	0.0202 (0.0174)	3.9	1.23 (1.18)
0.423 (0.417)	3.03	0.0257 (0.0193)	5.3	1.75 (1.14)
0.423 (0.415)	10.1	0.0227 (0.015)	12.9	1.28 (1.33)
0.659 (0.548)	3.04	0.0206 (0.0157)	4.8	1.58 (1.59)
1.11 (1.10)	3.04	0.0206 (0.0115)	8.9	2.93 (3.58)
1.56 (1.55)	3.04	0.0206 (0.0097)	15.8	5.20 (5.62)[f]
1.89 (1.87)[e]	3.17	0.0202 (0.0045)	27	8.6 (12.1)[f]
2.14 (2.13)	3.03	0.0191 (0.0059)	26	8.5 (11.2)[f]

[a] At 25.0°C unless specified.
[b] Concentrations in parentheses are at the time of acquisition of the first NMR spectrum.
[c] Unless specified, values in parentheses are calculated by using Eqn. (7).
[d] At 21.4°C;
[e] Unstabilized H_2O_2.
[f] Calculated with the equilibrium approximation, Eqn. (12).

illustrated in Fig. 2 breaks down with increasing $[H_2O_2]$ and faster interconversion of $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$. With $[H_2O_2] \approx 2$ M the addition of PhSMe to the reaction mixture does not quench the color of $Mo(O_2)_4^{2-}$ and, in the limit of high $[H_2O_2]$, $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ should be in equilibrium, with $K = k_1/k_{-1}$ (Scheme 2), which gives:

$$\frac{k_c}{[Mo_T]} = \frac{k_3 + k_2K[H_2O_2]}{1 + K[H_2O_2]} \qquad (12)$$

Predicted and observed values of $k_c/[Mo_T]$ obtained by using Eqn. (12) and values of k_2, k_3 and K are in Table 1. These experimental values are probably too low because the reaction is becoming too fast to be followed conveniently by NMR spectroscopy (the half-life is approximately 3 min). Within these limitations the equilibrium approximation (Scheme 2 and Table 2) is reasonably satisfactory at high $[H_2O_2]$. However, it fails at lower $[H_2O_2]$, where rate constants are over predicted. We cannot test the equilibrium approximation by working with higher $[H_2O_2]$ because the reaction would be too fast to follow in these conditions. Our rate data are inadequate to test the more complicated rate equations that apply to reactions at $[H_2O_2]$ for which neither of our simple treatments apply.

Reactivities of the peroxomolybdates

The tetraperoxomolybdate $[Mo(O_2)_4^{2-}]$ is much more reactive than the triperoxo species $[MoO(O_2)_3^{2-}]$, but in dilute H_2O_2 the latter is the dominant complex,[11,12] and is responsible for much of the reaction. For example, in *ca* 0.08 M H_2O_2, where $k_c/[Mo_T] \approx 0.55$ M^{-1} s^{-1} (Table 2), we estimate that only *ca* 25% of the reaction involves $Mo(O_2)_4^{2-}$, but in *ca* 0.4 M H_2O_2, where $k_c/[Mo_T] \approx 1.25$ M^{-1} s^{-1}, 67% of the reaction involves $Mo(O_2)_4^{2-}$ and in 2 M H_2O_2 there is only a minor contribution of reaction with $MoO(O_2)_3^{2-}$.

The kinetic form of the quenching of $MoO(O_2)_4^{2-}$ by PhSMe shows that this reaction is a direct oxygen transfer, as for oxidations by mixed peroxomolybdate complexes in organic solvents that have very low activation energies,[16] as is typical of direct oxygen transfers to sulfides from inorganic oxidants.[20]

Oxidation by $MoO(O_2)_3^{2-}$ is also shown as a direct oxygen transfer, but our data do not exclude the possibility of a contribution of reaction involving $^1O_2$. Nardello *et al.*[12] conclude that generation of $^1O_2$ from peroxomolybdates is largely through decomposition of $MoO(O_2)_3^{2-}$. Oxidations by $Mo(O_2)_4^{2-} + H_2O_2$ in water-in-oil microemulsions are believed to involve generation of $^1O_2$ and its escape into the bulk organic solvent and reaction with organic substrates that are excluded from the aqueous interior of the reversed micelle.[18] This intervention of reaction with $^1O_2$ is more probable in this than in a strictly homogeneous medium, where $MoO(O_2)_3^{2-}$ and the sulfide can come into direct contact.

Very little sulfone is formed (Experimental), consistent with attack of a nucleophilic sulfide on an oxygen center.[16] However, sulfones are formed in oxidations of sulfides by $^1O_2$ by reaction of a first-formed intermediate with the sulfide.[17c]

CONCLUSIONS

Peroxomolybdates rapidly oxidize thioanisole to sulfoxide, with little formation of sulfone, in mildy alkaline H_2O:*t*-BuOH. The tetraperoxomolybdate is much more reactive than the triperoxomolybdate, and in dilute H_2O_2 a rapid reaction with $Mo(O_2)_4^{2-}$ is followed by the kinetically significant conversion of it from $Mo(O_2)_3^{2-}$. The decomposition of $MoO(O_2)_3^{2-}$ is considerably faster than that of $Mo(O_2)_4^{2-}$,[12] and, from a practical point of view, it is useful to use high $[H_2O_2]$,[19] where oxidation is fast and the low concentration of $MoO(O_2)_3^{2-}$ limits spontaneous decomposition. The utility of this approach has been demonstrated in the destruction of chloroalkylsulfides on a significantly larger scale than that used in the present work.[19]

These oxidations occur at a pH such that reactions of nucleophilic anions with phosphonofluoridates will be rapid.[1–3] The fluoridates are more reactive than **VX** towards nucleophilic anions, but in water at 25 °C and 0.1 M HO_2^- the half-life for reaction of **VX** is *ca* 45 s.[3b] The pK_a of H_2O_2 is 11.0–11.5, depending on conditions,[13] and $Mo(O_2)_4^{2-}$ is formed up to pH 10,[11] which should allow a significant reaction with HO_2^- in moderately concentrated H_2O_2. Phosphonothioates and related thio esters are oxidized by peroxy acids.[2] These reactions are slower than those of alkyl sulfides,[20b,21] and $Mo(O_2)_4^{2-}$ may react oxidatively with **VX**, although at present we have no evidence on this question. We used H_2O_2 in our work, but peroxy-borates and carbonates and the urea–H_2O_2 adduct are convenient solid precursors.

EXPERIMENTAL

Materials

We generally used 30% H_2O_2 (Fisher), but unstabilized 30% H_2O_2 (ACROS) was used in some experiments (Table 2). Concentrations were regularly monitored, but changed little with time provided that solutions were stored in a refrigerator. Sodium molybdate dihydrate (Reagent Plus) was from Aldrich and PhSMe was from ACROS. We used HSO_5^- as Oxone to oxidize PhSMe partially or completely to PhSO·Me and $PhSO_2$·Me and measured the following chemical shifts (ppm). PhSMe: *o*-H, 7.30 (d); *m*-H, 7.35 (t); *p*-H, 7.21 (t), CH_3, 2.56. PhSO·Me: 7.70 (3H); 7.79 (2H); CH_3, 2.94. $PhSO_2$·Me: *o*-H, 8.03 (d); *m*-H, 7.77 (t); *p*-H, 7.88 (t); CH_3, 3.32. All measurements were made in H_2O:*t*-BuOH 7:3 v/v referred to external sodium 3-(trimethylsilyl)propionate (TSP) in D_2O with suppression of the H_2O signal. Solutions were freshly made up in deionized, redistilled, H_2O. They were made up by weight to correspond to H_2O:*t*-BuOH 7:3 v/v.

Equilibria

The equilibrium between $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ was monitored from the absorbance at 452 nm following the general procedure of Cszanyi *et al.*,[11] who examined this equilibrium in H_2O_2–H_2O. We observed a clean isosbestic point between $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$ at 372 nm with $[H_2O_2] > 0.1$ M and, therefore, consider only these complexes in fitting the data. We allowed sufficient time for complex equilibration before monitoring the spectra; $[Na_2MoO_4] \approx 10^{-3}$ M, but we corrected the absorbances to 0.001 M Na_2MoO_4. We used glass cuvettes in most experiments to reduce the possibility of light-induced reactions.

Kinetics

The quenching of the absorbance of $Mo(O_2)_4^{2-}$ at 452 nm by excess PhSMe was followed at 25.0 °C on an HP-8451A diode-array spectrophotometer, but there are limitations on the conditions of the experiment. It is desirable to choose [PhSMe] such that its reaction is much faster than interconversion of $MoO(O_2)_3^{2-}$ and $Mo(O_2)_4^{2-}$, but then the reaction tends to be too fast for convenient measurement, because we could not use a stopped-flow spectrophotometer. Reactions were started by adding PhSMe in *t*-BuOH from a Hamilton spring-loaded syringe to a stirred solution of $H_2O_2 + Na_2MoO_4$. Solutions were freshly prepared and a mild vacuum was used to disperse bubbles. Bubbling gave intermittent spikes in the plots of absorbance against time, but first-order plots were linear over 2.5 half-lives with correlation coefficients >0.99.

The subsequent slower oxidation of PhSMe was followed by using ^1H NMR spectroscopy (Varian Unity 500 MHz for ^1H), and monitoring signals of PhSMe and PhSO·Me in the aromatic and aliphatic regions, and concentrations were averaged from peak areas in both regions. So little $PhSO_2$·Me was formed (<2%), even towards the end of reaction, that we neglected its signals. Solutions were made up with H_2O, *t*-BuOH and H_2O_2, and we used solvent suppression of the O^1H signal. The aliphatic signals of PhSMe and PhSO·Me are separated from that of *t*-BuOH.

The solution of $H_2O_2 + Na_2MoO_4$ was made up and, after sufficient time for equilibration of the peroxomolybdates, PhSMe was added. The color of $Mo(O_2)_4^{2-}$ disappeared rapidly and the NMR tube was placed in the spectrometer. Time was required for shimming (*ca* 5 min) and spectra were then taken over a period of time. Times were taken as the midpoint of each acquisition, which took *ca* 1 min, with 16 scans and delay of 3 s.

It is desirable to take a large number of data points, but there are several limiting factors. With $H_2O_2 \approx 2$ M the half-life is approximately 3 min and we could follow only the last part of the reaction. There are different limitations for reactions in dilute H_2O_2, where the reaction does not have a simple integral kinetic order. For these reactions it is desirable to estimate the apparent first-order rate constant k_{obs} with respect to [PhSMe], from data obtained over a short time, which limits accuracy because we follow relative peak areas of PhSMe and PhSO·Me. These relative areas are least reliable when one compound is in large excess. Our rate data from plots of ln[PhSMe] against time are, therefore, less reliable than those obtained by conventional methods, e.g. spectrophotometry or conductivity. However, the rate constants are self-consistent, except for reaction with 0.423 M H_2O_2 and 3.03×10^{-4} [Na_2MoO_4], where the value is significantly higher than predicted (Table 2), and we see no reason for the discrepancy.

Most reactions were followed at 25.0 °C; initially, some experiments were at 21.4 °C, but oxygen transfers have very low activation energies[16,20] and the temperature effect appears to be relatively unimportant.

There is an uncatalyzed oxidation of PhSMe in H_2O_2 and a correction was applied to values of k_{obs}:

$$k_c = k_{obs} - k_{H_2O_2}$$

where $10^4 k_{H_2O_2} = 0.2$, 0.3, 1.0, 1.6, 3.0, 4.5, 6.0 and 7.1 s^{-1} in 0.08, 0.176, 0.40, 0.66, 1.11, 1.56, 1.89 and 2.14 M H_2O_2 respectively.

In fitting the kinetic data from NMR spectroscopy in terms of Eqns (6), (7) and (12) we use concentrations of PhSMe and H_2O_2, calculated from peak areas at the time of acquisition of the first spectrum.

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