PAPER

Dioxaborirane: a highly reactive peroxide that is the likely intermediate in borate catalysed electrophilic reactions of hydrogen peroxide in alkaline aqueous solution

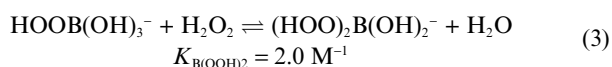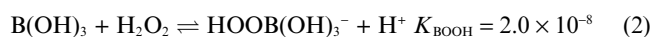**Marcus C. Durrant,**[a] **D. Martin Davies**[a] **and Michael E. Deary***[b]

This paper reports on a kinetic and theoretical study into the borate mediated reaction of dimethyl sulfide with hydrogen peroxide in both acid and alkaline conditions. At high pH, whilst the kinetic data is consistent with the catalytic species being monoperoxoborate, formed from the rapid equilibrium between hydrogen peroxide and boric acid, DFT calculations show that this species is in fact less reactive than hydrogen peroxide, requiring us to seek an alternative catalytic mechanism. DFT provides an important insight for this, showing that although boric acid and peroxoboric acid are primarily Lewis acids, they can exhibit a small degree of Brønsted acidity, allowing, respectively, the $B(O)(OH)_2^-$ and $HOOB(OH)(O)^-$ anions to exist in small concentrations. Whilst the peroxoborate anion, $HOOB(OH)(O)^-$, is predicted to have only marginal catalytic activity, its tautomer, dioxaborirane, $(HO)_2BO_2^-$, a three membered cyclic peroxide, has a very low activation barrier of 2.8 kcal/mol. Hence, even though dioxaborirane is likely to be present in very low concentrations, it is still sufficiently reactive for overall rate enhancements to be observed for this system. This is the first literature report of this species. The observed low selectivity observed for borate catalysed reactions of hydrogen peroxide with a range of substituted phenyl methyl sulfides in our previous study (D. M. Davies, M. E. Deary, K. Quill and R. A. Smith, Chem.–Eur. J. 2005, 11, 3552–3558) is further evidence in favour of a highly reactive catalytic species. At low pH, kinetic data shows that borate catalyses the reaction between hydrogen peroxide and dimethyl sulfide; this is supported by DFT calculations that predict peroxoboric acid to be an effective catalytic intermediate, with an energy barrier of 7.4 kcal mol^{-1} compared to 10.1 kcal mol^{-1} for the uncatalysed system. Nevertheless, the overall contribution of this pathway is small because of the unfavourable equilibrium between hydrogen peroxide and boric acid to form peroxoboric acid.

Introduction

A complex system of peroxoborate species is formed when hydrogen peroxide and boric acid are mixed together in aqueous solution. Boric acid itself exists in equilibrium with the borate anion, which predominates above pH 9, as detailed in eqn (1).[1]

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad K_{BOH} = 1.0 \times 10^{-9} \text{ M} \quad (1)$$
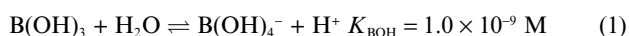
In aqueous hydrogen peroxide, boric acid is in rapid equilibrium with mono- and diperoxoborates, as defined by eqn (2) and (3).[1]

$$B(OH)_3 + H_2O_2 \rightleftharpoons HOOB(OH)_3^- + H^+ \quad K_{BOOH} = 2.0 \times 10^{-8} \quad (2)$$

$$HOOB(OH)_3^- + H_2O_2 \rightleftharpoons (HOO)_2B(OH)_2^- + H_2O$$
$$K_{B(OOH)2} = 2.0 \text{ M}^{-1} \quad (3)$$

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The peroxoborates are the predominant species between about pH 7 and 13, depending on the total concentrations of peroxide and borate. At lower pHs, peroxoboric acid, $HOOB(OH)_2$, is in equilibrium with hydrogen peroxide, according to eqn (4),[1] though the low formation constant ensures that it is only present at about 1% of the total peroxide concentration.

$$B(OH)_3 + H_2O_2 \rightleftharpoons HOOB(OH)_2 + H_2O \quad K_{BO} = 0.01 \text{ M}^{-1} \quad (4)$$
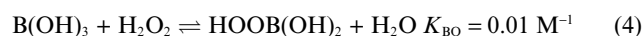
In addition, we have recently shown conclusive evidence for the formation of another significant peroxoborate species at higher pHs, namely monoperoxodiborate, $(HO)_3BOOB(OH)_3^{2-}$, according to eqn (5).[2] It is certainly possible that other peroxoborate species exist in addition to those listed above, though this system has been found to adequately describe the kinetic and absorption data associated with the above studies.

$$B(OH)_4^- + HOOB(OH)_3^- \rightleftharpoons (HO)_3BOOB(OH)_3^{2-} \text{ H}_2O$$
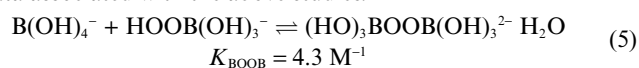$$K_{BOOB} = 4.3 \text{ M}^{-1} \quad (5)$$

Fig. 1 shows a pH distribution diagram of the significant peroxoborate species and hydrogen peroxide, at the high borate to peroxide ratios used in this paper, based on eqn (1) to (5),
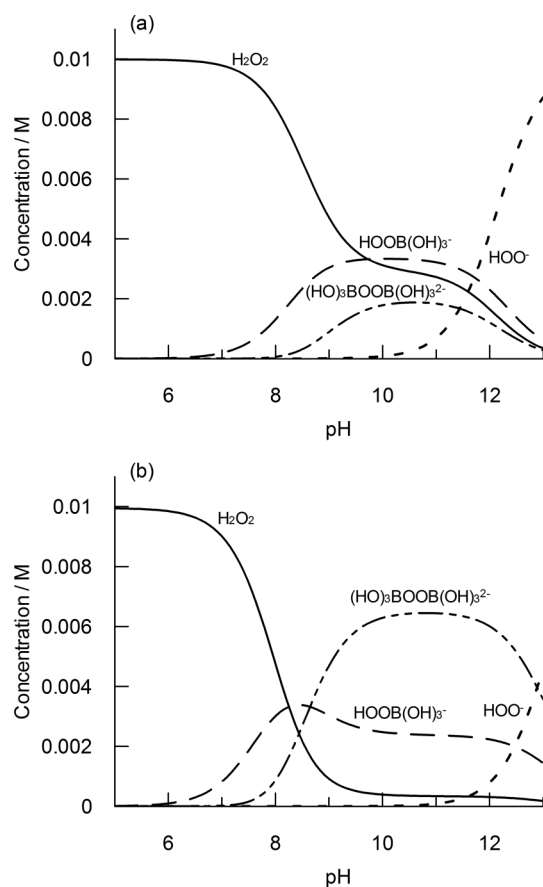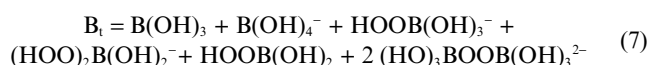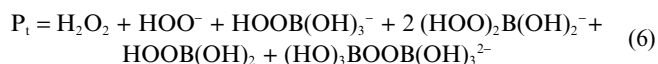
Fig. 1 distribution of the significant peroxoborate species and hydrogen peroxide as a function of pH for a system containing (a) 0.1 M borate and 0.01 M total hydrogen peroxide and (b) 0.5 M borate and 0.01 M total hydrogen peroxide. Concentrations were calculated using Grafit, version 6.0.5 in which the peroxide concentrations were solved numerically, and the borate concentration solved using an analytical equation derived from eqn (1) to (7).

and the mass balance equations for total peroxide, P_t, (6) and borate, B_t, (7). There are only four species present at significant concentrations; the formation of other peroxoborate species are not favoured, either because of a low formation constant (peroxoboric acid) or because there is a low ratio of hydrogen peroxide to borate (diperoxoborate). Above pH 7 significant concentrations of both the monoperoxoborate, $B(OH)_3OOH^-$, and monoperoxodiborate, $(HO)_3BOOB(OH)_3^{2-}$, are formed, with the latter dominating at higher borate concentrations. At higher pHs the nucleophilic hydroperoxy anion, HOO^-, dominates.

$$P_t = H_2O_2 + HOO^- + HOOB(OH)_3^- + 2\,(HOO)_2B(OH)_2^- + HOOB(OH)_2 + (HO)_3BOOB(OH)_3^{2-} \quad (6)$$

$$B_t = B(OH)_3 + B(OH)_4^- + HOOB(OH)_3^- + (HOO)_2B(OH)_2^- + HOOB(OH)_2 + 2\,(HO)_3BOOB(OH)_3^{2-} \quad (7)$$

It has long been known that borate can catalyse electrophilic reactions of hydrogen peroxide, a classic example being Wilson's report of a substantial rate acceleration for the oxidation of the thiocyanate anion in the presence of a borate buffer.[3] More recently we have reported on the hydrogen peroxide oxidation of a range of *p*-substituted phenyl methyl sulfides catalysed by the presence

of borate buffers at different pHs and concentrations. The reactive species at alkaline pHs were presumed to be monoperoxoborate, $HOOB(OH)_3^-$, and diperoxoborate, $(HOO)_2B(OH)_2^-$,[4] though any additional species in equilibrium with these peroxyborates could also act as the catalytic agent, depending on the pre-equilibrium constant. One notable feature of the reaction of peroxoborates with the series of sulfides was the low selectivity (taken as the Hammett ρ value for their reactions with a range of the sulfides) of peroxoborates relative to their reactivity ($\rho = -0.65$[4]), when compared with other hydroperoxides. The catalysis and lack of selectivity were originally explained by us in terms of a transition state, structure **1**, where proton transfer through a solvent water molecule provided a mechanistic path, leading to a lower extent of positive charge development on the sulfur compared with that occurring during reaction with other peroxides.

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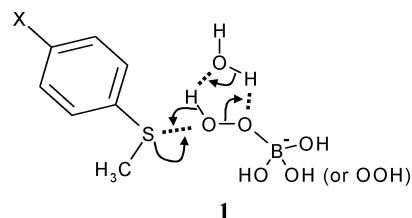
In the present paper we have extended this work[4] to look at the reaction of peroxoborates with the more nucleophilic dimethyl sulfide. In addition, we were particularly interested to know whether the peroxoboric acid species formed at low pH, eqn (4), has any catalytic effect, despite its low formation constant:[1] the lack of reactivity of this species towards *p*-substituted phenyl methyl sulfides observed in our previous study was unexpected because the electron deficiency of the boron and the lack of a negative charge on the acid should make it a better electrophile than the peroxoborate anions.

From a theoretical point of view, using density functional theory (DFT) calculations, we were keen to extend our understanding of the mechanism of peroxoborate catalysis beyond that which might be inferred from linear free energy studies. In this respect, the reaction of dimethyl sulfide with peroxoborate provides an ideal system because the reaction of this substrate has been studied with a wide range of other hydroperoxides[5] and its reaction with hydrogen peroxide has been analysed using high level *ab initio* simulations that include the specific effects of solvent water.[6] This latter study formed the starting point for our theoretical investigation of this reaction system.

Results

Kinetic study

Fig. 2 shows that the observed rate constant, k_{obs}, for the reaction of hydrogen peroxide and dimethyl sulfide under alkaline conditions increases up to a maximum with increasing total boric acid concentration and thereafter decreases. This is consistent with the equilibrium formation of a reactive monoperoxoboron and unreactive monoperoxodiboron species, such as those detailed in eqn (2) and (5).

The dependence of k_{obs} on the total concentration of boric acid can be fitted using the approach described previously,[2,4] according to eqn (8) with the rate constant for the reaction of
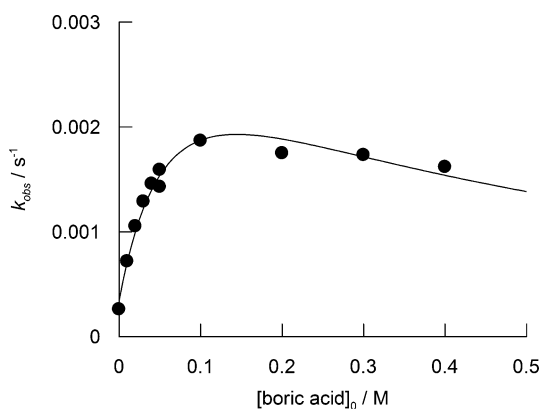
Fig. 2 Effect of total boric acid concentration on the reaction of 5.5×10^{-4} M dimethyl sulfide and 0.01 M hydrogen peroxide, pH 9.72, ionic strength 0.5 M with sodium sulfate. The curve is the best fit to eqn (8) with the rate constants given in the text and with k_{P1BOH2} set to zero.

monoperoxodiborate, k_{P1BOH2} set equal to zero. The concentrations of the peroxide species are calculated using the mass balance equations for total boron (7) and peroxide (6) concentrations and the equations for the various equilibrium constants (1–5) with the measured pH of the solution and the formation constants of monoperoxoborate, K_{BOOH}, and the acid dissociation constant of boric acid, K_{BOH}, as indicated in eqn (4) and (1) respectively. The formation constant of monoperoxodiborate, K_{BOOB}, was a variable in the fitting. This yields best fit values of 0.0346 ($\pm$0.0064) and 0.338 ($\pm$0.016) M^{-1} s^{-1} respectively for the k_{P1} and k_{P1BOH} respectively, and a value of 3.2 ± 0.5 M^{-1} for K_{BOOB}, consistent with it being unreactive, and in good agreement with those previously obtained from a study of the effect of borate/boric acid on the photochemical decomposition of hydrogen peroxide (1.0 ± 0.3 determined from molar absorbtivities or 4.3 ± 0.9 determined from kinetic data).[2]

$$k_{obs} = k_{P1}[H_2O_2] + k_{P1BOH}[(HO)_3BOOH^-] + k_{P1BOH2}[(HO)_3BOOB(OH)_3^{2-}] \qquad (8)$$

Fig. 3 shows the effect of pH on the reaction. At low pH the predominant peroxoboron species is peroxoboric acid, formed according to eqn (4), and the observed rate constant is clearly much less than at higher pH where the monoperoxoborate predominates.
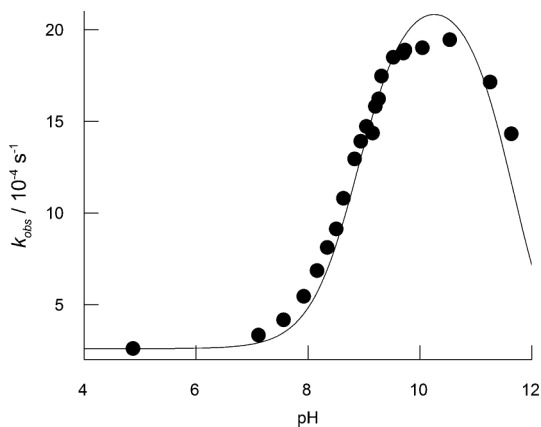

Fig. 3 Effect of pH on the reaction of 5.5×10^{-4} M dimethyl sulfide and 0.01 M hydrogen peroxide in the presence of 0.1 M [boric acid]$_0$. Conditions and curve as Fig. 2.

Notwithstanding the apparent low reactivity for peroxoboric acid indicated at low pH in Fig. 3, the borate dependence under acidic conditions shown in Fig. 4 shows that there is a small rate enhancement with increasing boric acid concentration. Treating the data according to eqn (9), using the value of $K_{BO} = 0.01$ M^{-1},[1] yields a value of 1.2 ± 0.3. M^{-1} s^{-1} for k_{P1B}, the rate constant for the reaction of peroxoboric acid with dimethyl sulfide; this is 35 times greater than that for the reaction with hydrogen peroxide.

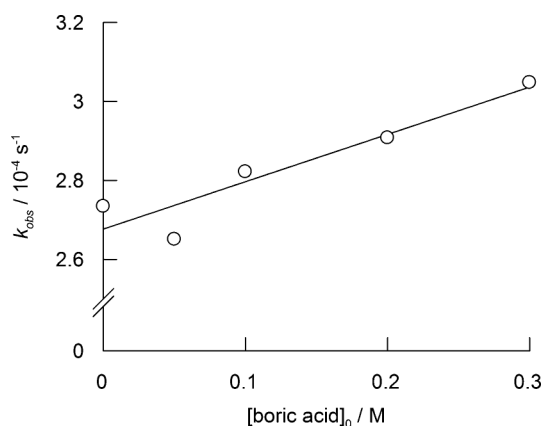$$k_{obs} = k_{P1}[H_2O_2] + k_{P1B}[(HO)_2BOOH] \qquad (9)$$

Fig. 4 Effect of boric acid on the reaction of 5.5×10^{-4} M dimethyl sulfide and 0.01 M hydrogen peroxide at pH 4.6, ionic strength 0.2 M with sodium sulfate.

Theoretical study

In order to better understand our experimental results, we performed DFT calculations on the oxidation of dimethyl sulfide (Me$_2$S) by different peroxoborate species. The uncatalysed reaction between Me$_2$S and H$_2$O$_2$ has been investigated theoretically by Chu and Trout,[6] who found that the inclusion of 1–3 explicit water molecules had a significant effect on the calculated activation energy of the transition state. Thus, the energy barrier for the reaction of Me$_2$S with H$_2$O$_2$ at the MP4//B3LYP/6-31++G(d,p) level was 24.4 kcal mol^{-1} in the presence of a single water molecule, decreasing to 12.7 kcal mol^{-1} when three waters were included. Inclusion of implicit solvent with the polarised continuum model (PCM) made little difference to these results (0.2 kcal mol^{-1}). We started our investigation with a re-examination of the Me$_2$S-H$_2$O$_2$-H$_2$O system, again at the B3LYP/6-31++G(d,p) level of theory but with Solvation Model Based on Solute Electron Density (SMD) solvent corrections.[7] We found very similar results for the gas phase calculations (calculated barrier 25.0 kcal mol^{-1}), but the SMD implicit solvent correction was much more significant than the PCM correction, reducing the barrier to 10.1 kcal mol^{-1} which is similar to the value for the Me$_2$S-H$_2$O$_2$-3H$_2$O system reported by Chu and Trout. We conclude that, as expected, SMD gives more accurate solvation energies than PCM; the inclusion of extra water molecules may help to compensate for the deficiencies of the PCM energies. These results also provide a benchmark, in that any catalytic species should lower the transition state barrier below our calculated value for the Me$_2$S-H$_2$O$_2$-H$_2$O system. We used the SMD solvent correction for all subsequent calculations;
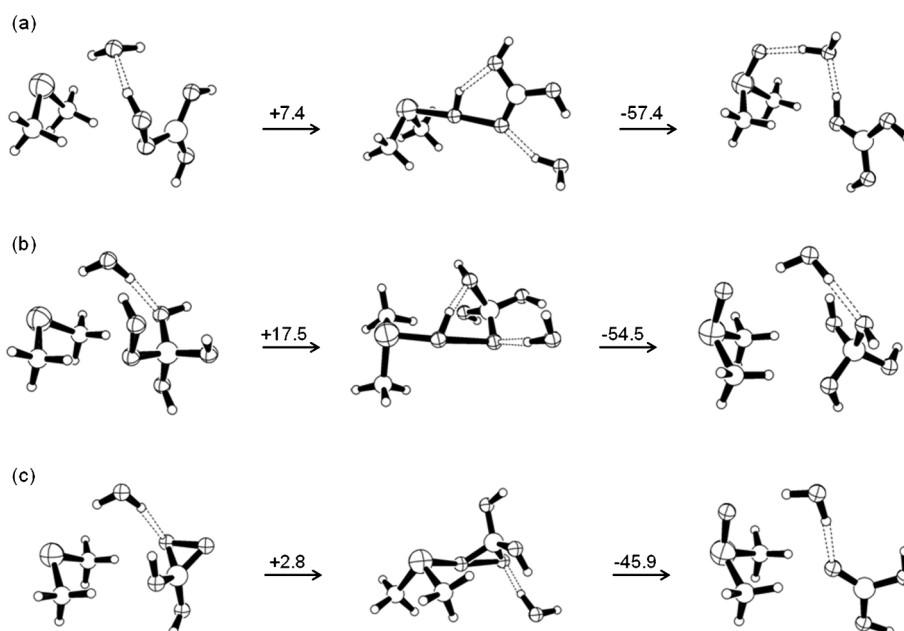
Fig. 5 Calculated initial, transition and final states for potential peroxoborate catalytic systems. Hydrogen bonds are shown as dashes. B, C and H are shown as plain spheres, O and S as octant spheres. Energies for each step (in kcal mol^{-1}, including SMD corrections for implicit solvent water) are given above the arrows. (a) Me_2S-$HOOB(OH)_2$-H_2O; in the transition state, the S–O and O–O distances are 2.046 and 1.926 Å respectively, and the O–H distance for the peroxide oxygen is 0.984 Å. (b) Me_2S-$HOOB(OH)_3^-$-H_2O; in the transition state, the S–O and O–O distances are 1.824 and 2.187 Å respectively, and the O–H distance for the peroxide oxygen is 1.053 Å. (c) Me_2S-$(HO)_2BO_2^-$-H_2O; in the initial dioxaborirane structure, the B–O bond lengths are 1.486 and 1.453 Å, and the O–O distance is 1.544 Å; in the transition state, the S–O and O–O distances are 2.012 and 1.947 Å respectively, and the proximal and distal B–O distances are 1.527 and 1.409 Å respectively.

for consistency, we have also included one water molecule in all our models.

We next considered the catalytic potential of peroxoboric acid by calculations on the Me_2S-$HOOB(OH)_2$-H_2O system. The reactants, transition state and products are shown in Fig. 5(a). The calculated barrier for this system is 14.9 kcal mol^{-1} for the gas phase, decreasing to 7.4 kcal mol^{-1} with implicit solvent correction. Hence, peroxoboric acid is predicted to be an effective catalytic intermediate in this reaction. As with the Me_2S-H_2O_2-H_2O system, the reaction mode is centred on transfer of the oxygen atom from reactant to product, with subsequent hydrogen atom transfer. However, whereas in the former case this was assisted by the water molecule, here the oxygen atom of one of the B-OH groups is involved in hydrogen bonding to the OH group under transfer. This intramolecular hydrogen bonding is evidently more efficient in lowering the barrier than the intermolecular hydrogen bonding found in the uncatalysed system.

The reaction with monoperoxoborate gave unexpected results. The transition state for the Me_2S-$HOOB(OH)_3^-$-H_2O system (Fig. 5(b)) also involved an intramolecular hydrogen bond, but the calculated energy barriers for the gas and aqueous phases were 51.0 and 17.5 kcal mol^{-1} respectively, clearly higher than those for the uncatalysed system. We were unable to find any better transition state for this system. This result argues against the involvement of monoperoxoborate as an active catalyst in this reaction, notwithstanding the experimental observation that the rate increases at high pH. We have identified two possible reasons for the higher barrier for the monoperoxoborate system. As well as the electronic consequences of the negative charge on

the $HOOB(OH)_3^-$ anion, there is also the difference in geometry at the boron, which is tetrahedral in this case. This results in a closer contact between the distal peroxide oxygen and the oxygen of the hydrogen bonding OH group; the O···O distance within the intramolecular hydrogen bond is 2.49 Å in this case, compared to 2.69 Å for peroxoboric acid. Hence, trigonal boron is more suitable than tetrahedral boron for the formation of the intramolecular hydrogen bond required for effective catalysis.

At this point, it is worth reviewing the acid behaviour of boric acid. The pK_a of boric acid is 9.14 but this involves addition of OH$^-$ to give $B(OH)_4^-$, rather than ionisation of $B(OH)_3$. Nevertheless, the balance between these two processes might be quite close. We have recently shown that the pK_a's of hydroxy acids can be estimated empirically from DFT calculations with solvent corrections.[8] We have adapted this approach to the present case. Using a set of 31 hydroxy acids and the B3LYP/6-31++G(d,p) level of theory with SMD corrections, we estimate a pK_a value of 9.6 ± 0.8 for ionisation of $B(OH)_3$ to $B(O)(OH)_2^-$. This value is not much higher than the experimental pK_a. Hence, although boric and peroxyboric acids act primarily as Lewis acids, a small degree of Brønsted acidity is also possible. With this in mind, we investigated the catalytic ability of the peroxoborate $HOOB(OH)(O)^-$. The calculated barrier for catalysis by $HOOB(OH)(O)^-$ is 23.6 kcal mol^{-1} for the gas phase, decreasing to 10.0 kcal mol^{-1} with implicit solvent correction. In the transition state, a proton has migrated such that the reacting species is the $(HO)_2BOO^-$ anion. Within the error limits of the calculations, this suggests that the $HOOB(OH)(O)^-$ anion would have marginal catalytic activity and is probably not responsible for the increased rate under

alkaline conditions. The lower activity of the $HOOB(OH)(O)^-$ anion compared to neutral $HOOB(OH)_2$ can be explained in terms of the electrostatic penalty for electrophilic attack of the anion at the sulfur lone pairs.

Another possible catalytic intermediate is the dioxaborirane, $(HO)_2BO_2^-$. According to our calculations, this species is just 1.0 kcal mol^{-1} higher in energy than the tautomeric peroxyborate. It proved to be a very effective catalyst for the target reaction, giving an energy barrier of 2.8 kcal mol^{-1} with implicit solvent correction (Fig. 5(c); the calculated gas phase barrier was 24.2 kcal mol^{-1}). This low barrier is evidently due to the intrinsic reactivity of the three-membered ring, together with a lack of steric hindrance in the transition state.

Discussion

The results for the reaction of peroxoboric acid with dimethyl sulfide at low pH show that the rate constant, $k_{P1B} = 1.2 \pm 0.3$. M^{-1} s^{-1}, is actually higher than that of peroxoborate, $k_{P1BOH} = 0.338$ (± 0.016) M^{-1} s^{-1}, in contrast to the results obtained previously for substituted phenyl methyl sulfides.[4] Nevertheless, because the formation constant of peroxoboric acid from hydrogen peroxide and boric acid is so small (0.01 M^{-1})[1] the contribution of this pathway is minor compared to that for the direct reaction with hydrogen peroxide, as seen in Fig. 4. Even so, this finding is consistent with the results of our DFT calculations, in which peroxoboric acid emerges as a plausible catalyst for the reaction of hydrogen peroxide with dimethyl sulfide at and below neutral pH.

At higher pHs the situation is more complex: whilst the kinetic data and resultant curve fitting (Fig. 2 and 3) are consistent with the tetrahedral monoperoxoborate anion being the catalytic species, as previously suggested for the *p*-substituted phenyl methyl sulfides, this is not borne out by out DFT calculations, which strongly indicate that this species is likely to be catalytically inactive. This lack of reactivity can be explained in terms of a combination of the electrostatic repulsion between an incoming anion and the sulfur lone pairs, and the steric disadvantage of an internal hydrogen bond involving tetrahedral boron compared to trigonal boron in the transition state. Nevertheless, the considerable increase in rate under basic conditions, as shown in Fig. 2 and 3, requires an explanation. Based on the results of our DFT calculations, we propose that the catalytic intermediate under basic conditions is the dioxaborirane, $(HO)_2BO_2^-$. Although likely to be present at relatively low concentrations, this species has a much lower transition state barrier than the neutral peroxoboric acid. Hence, provided there is rapid exchange between the various peroxoborate species present in alkaline solution, the dioxaborirane should be a very effective catalytic intermediate. The concentration of $(HO)_2BO_2^-$ is likely to be proportional to that of monoperoxoborate. At still higher pH, the hydroperoxide anion, HOO^-, which is a nucleophile and will be unreactive towards dimethyl sulfide, will be present at increasing concentrations (p$K_a = 11.6$) as shown in Fig. 2, consistent with the decrease in rate above pH ~10.5.

Supporting evidence for dioxaborirane, rather than peroxomonoborate itself, being the catalytic intermediate at alkaline pH comes from a reactivity-selectivity plot for the reactions of peroxides and substituted phenyl methyl sulfides considered in
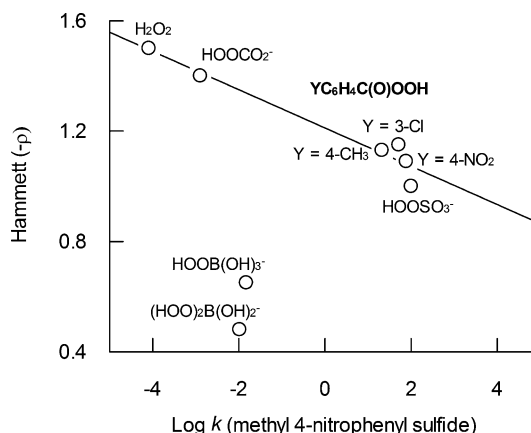

Fig. 6 Reactivity-selectivity plot for the reactions of peroxides and substituted phenyl methyl sulfides, with the 4-nitro derivative as the reactivity measure.

our previous study, and replotted in Fig. 6, in which the rate of reaction of each peroxide with the 4-nitro phenyl methyl sulfide is taken as the reactivity measure. The linear reactivity-selectivity relationship observed for the series including hydrogen peroxide,[4] peroxomonocarbonate,[9] peroxomonosulfate,[10] and peroxycarboxylic acids[11] indicates that these peroxides react *via* the same mechanism: the more reactive peroxides, such as monoperoxosulfate, are less selective, consistent with the Hammond Postulate that the transition state occurs earlier along the reaction coordinate, with, in this case, minimal charge development on the sulfur and oxygen atoms. However, the mono- and diperoxoborate species deviate substantially from the main trend shown by other peroxides, being far less selective than would be expected for their reactivity. In our previous study this was taken as evidence supporting a transition state, Structure **1**, whereby charge development was circumvented by the involvement of a water molecule. Clearly in the light of our DFT calculations where, even with the involvement of a water molecule in the transition state, the monoperoxoborate anion is shown to be catalytically inactive, this argument no longer holds. However, this low selectivity is consistent with a highly reactive dioxaborirane intermediate, as predicted from our DFT calculations, that is present at a low concentration relative to the monoperoxoborate.

We have not carried out any DFT calculations on the analogous mono-cyclic peroxide form of diperoxoborate, but similar arguments would apply; the Hammett ρ value for the reaction of this species with a series of phenyl methyl sulfides is more uncertain because it is based only on two points.[4]

The enhanced reactivity of three-membered cyclic peroxides is well known from work on dioxiranes which are produced by the reaction of ketones with peroxyacids, most commonly peroxomonosulfate.[12] Dimethyl dioxirane, formed from acetone, is the most widely researched dioxirane; it is noted to participate in a wide variety of oxygen atom transfer reactions, including aryl methyl sulfides[13,14] under mild conditions without need of acid or base catalysis.[12] The peroxide bond length for dimethyldioxirane, 1.52 Å, is very similar to that calculated by us for dioxaborirane (1.54 Å); such long bond lengths implying instability consistent with their reactivity.

Conclusions

The most significant outcome of this work has been the identification through DFT calculations of a highly reactive peroxide, dioxaborirane, that is the likely catalytic intermediate in borate mediated electrophilic reactions of hydrogen peroxide in alkaline aqueous solution. The dioxaborirane exists in equilibrium with the monoperoxoborate, though from its predicted pK_a and energy barrier for formation, is likely to be present in only tiny concentrations. It is, nevertheless, sufficiently reactive to result in significant rate enhancements for reactions of hydrogen peroxide with alkyl and aryl alkyl sulfides in alkaline conditions. Selectivity-reactivity correlations support the DFT conclusions. This species has not previously been reported in the literature. In future work we will extend the range of substrates under study.

In acidic conditions, we have shown that even though the formation constant for peroxoboric acid is low, it does catalyse the reaction of hydrogen peroxide with dimethyl sulfide, and we have confirmed through DFT calculations that it is a plausible catalytic intermediate.

Finally, we can reflect that the hydrogen peroxide – borate system provides us with two highly reactive peroxide species, peroxoboric acid and dioxaborirane, covering both acidic and alkaline conditions, but that the low formation constants for both conspire to limit their applicability.

Experimental section

Kinetics

The general procedure has been described previously.[4] Dimethyl sulfide was obtained from Adrich. Reactions with dimethyl sulfide were carried out with a large excess of hydrogen peroxide, monitoring the loss of the substrate absorbance spectrophotometrically at a suitable wavelength. Observed pseudo-first-order rate constants, k_{obs}, were obtained using nonlinear regression of the (in most cases) monoexponential loss of absorbance with time. Values of k_{obs} were obtained from linear plots of $\ln(A - A_\infty)$ *versus* time. All reactions were carried out at 25 °C, and in the pH ranges indicated on the figures.

DFT Calculations

All DFT calculations were carried out within Gaussian09W[15] using the B3LYP functional and 6-31++G(d,p) basis set for all atoms. Output geometries were verified as true minima or first order saddle points by the appropriate frequency calculations. SMD implicit solvent corrections were then obtained for single point jobs using the optimized geometries and water as solvent.

Acknowledgements

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