

Borate-Catalyzed Reactions of Hydrogen Peroxide: Kinetics and Mechanism of the Oxidation of Organic Sulfides by Peroxoborates

D. Martin Davies,^{*,[a]} Michael E. Deary,^[a] Kieran Quill,^[b] and Robert A. Smith^[c]

Abstract: The kinetics of the oxidation of substituted phenyl methyl sulfides by hydrogen peroxide in borate/boric acid buffers were investigated as a function of pH, total peroxide concentration, and total boron concentration. Second-order rate constants at 25°C for the reaction of methyl 4-nitrophenyl sulfide and H₂O₂, monoperoxoborate, HOOB(OH)₃[−], or diperoxoborate, (HOO)₂B(OH)₂[−], are 8.29 × 10^{−5}, 1.51 × 10^{−2} and 1.06 × 10^{−2} M^{−1} s^{−1}, respectively. Peroxoboric acid, HOOB(OH)₂, is unreactive. The Ham-

mett ρ values for the reactions of a range of substituted phenyl methyl sulfides and hydrogen peroxide, monoperoxoborate or diperoxoborate are -1.50 ± 0.1 , -0.65 ± 0.07 and -0.48 (two points only), respectively. The ρ values for the peroxoborates are of significantly lower magnitude than expected from their reactivity compared

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to other peroxides. Nevertheless the negative ρ values indicate positive charge development on the sulfur atom in the transition state consistent with nucleophilic attack by the organic sulfides on the peroxoborates as with the other peroxides. The kinetic parameters, including the lack of reactivity of peroxoboric acid, are discussed in terms of the differences in the transition state of reactions involving peroxoboron species with respect to those of other peroxides.

Introduction

Hydrogen peroxide is an atom-efficient and environmentally benign oxidant. It is increasingly used in such areas as the manufacture of pharmaceutical and fine chemicals, pulp, paper and textile processing, bleaching and cleaning, waste water treatment and environmental remediation.^[1] Moreover, due to growing concerns about chemical pollutants, and the resulting pressure against nitric acid, chlorine and heavy-metal oxidants, there is a trend to use it even as a bulk chemical oxidant.^[1,2] Although it is a powerful oxidant, the reactions of hydrogen peroxide are generally rather slow, and the challenge is to overcome this kinetic barrier in

more cost-effective and “green chemical” ways. Hydrogen peroxide is activated through the formation of peroxycarboxylic acids, either from a reactive carboxylic acid derivative with a good leaving group (as in the peroxide bleach activators)^[3] or from the parent carboxylic acid and a strong acid catalyst in preparative reactions.^[1] Activation by the formation of peroxycarboxylic acids entails a sharp decrease in atom-efficiency that is avoided in true catalysis. The range of catalysts for any given reaction of hydrogen peroxide is vast.^[4] The properties of simple and effective catalysts such as methyltrioxorhenium, [Re(CH₃)O₃], and tungstate, the latter coupled with a phase-transfer catalyst, have recently been reviewed.^[5,2] The discovery of the hydrogen carbonate catalysed oxidation of organic sulfides and alkenes through peroxymonocarbonate, HOOCO₂[−], is a significant development.^[6–8] Peroxymonocarbonate has been compared with the methyltrioxorhenium system: the latter decomposes above pH 2 in the presence of hydrogen peroxide, whereas the hydrogen carbonate system has the advantage of being stable and functional at neutral pH, although the equilibrium formation of peroxymonocarbonate is rather slow.^[6] Similarly, the functional pH range of tungstate is limited because the bisperoxotungstate anion forms the feebly active dianion above pH 4. The present paper will report that borate is a better catalyst than hydrogen carbonate, with the

[a] Dr. D. M. Davies, Dr. M. E. Deary
Division of Chemical and Forensic Sciences
School of Applied Sciences, Northumbria University
Newcastle upon Tyne NE1 8ST (UK)
Fax: (+44) 191-227-3519
E-mail: martin.davies@unn.ac.uk

[b] Dr. K. Quill
Borax Europe Ltd., 1 A Guildford Business Park
Guildford, Surrey, GU2 8XG (UK)

[c] Dr. R. A. Smith
U.S. Borax Inc., 26877 Tournay Road
Valencia, California 91355 (USA)

rapidly formed peroxoborate (sometimes called peroxyborate or perborate) species being more reactive than peroxy-monocarbonate and extending the functional pH range into the 8–12 region.^[9]

Peroxborates are rapidly formed in solutions of hydrogen peroxide and borate and their salts are selectively crystallised from solution to form perborates, which are available commercially and have synthetic as well as bleaching and cleaning applications.^[10,11] Over fifty years ago Edwards reported that the pH of borate buffer solution drops as hydrogen peroxide is added, due to the rapid equilibrium formation of peroxoborates.^[12] Several years later Wilson suggested the equilibria shown in Equations (1) and (2) for the formation of monoperoxoborate and diperioxoborate, respectively.^[13]



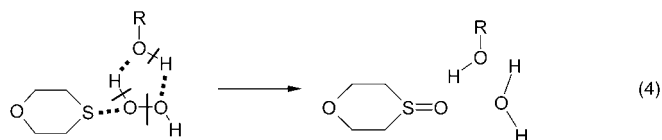
He noted that the formation of peroxoborates has important kinetic consequences in that some reactions in which hydrogen peroxide functions as an electrophile may be substantially accelerated in the presence of a borate buffer, giving as an example the oxidation of the anionic nucleophile, SCN^- . He also stated, without an example, that where hydrogen peroxide itself functions as a nucleophile, peroxoborate appears to be less reactive than HO_2^- (this is certainly the case in the perhydrolysis of *para*-nitrophenyl acetate).^[14] Wilson concludes his paper with the warning “Use of borate buffers in reactions which involve hydrogen peroxide should only be made with care”. This is reiterated in later work by Jones and co-workers who give examples of the “notorious behaviour of borate buffers in complicating the kinetics of peroxide reactions”.^[15] It is, on the one hand, rather surprising, perhaps, that anionic peroxoborates should show a high reactivity towards nucleophiles, particularly anionic ones (and, as the present paper will report, especially since the uncharged, electron-deficient peroxoboric acid, HOOB(OH)_2 is less reactive). This may have led some authors to suggest that HOOB(OH)_3^- can behave as a nucleophile, with B(OH)_3 acting as an uncharged leaving group.^[10,11] On the other hand the bisperoxotungstate monoanion is a well-known anionic electrophile, so the existence of effective negatively charged electrophiles cannot be contested.^[2] In any case, over thirty years after the original observation by Edwards, Pizer and Tihal quantified the effect of hydrogen peroxide on the pH of borate buffer. In addition to the equilibria represented by Equations (1) and (2), they deduced the formation of peroxoboric acid, Equation (3).



The equilibrium constants for the three processes are 2.0×10^{-8} , 2.0 M^{-1} and 0.01 M^{-1} , respectively.^[16] No other peroxoboron species are evident at the fairly low total boron concentrations (less than or equal to 0.1 M) used, although at

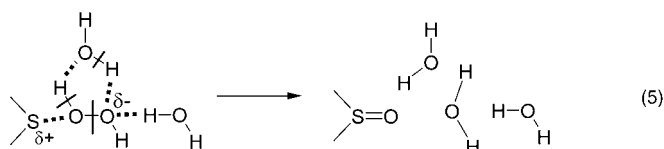
higher boron concentrations there is NMR and Raman spectroscopic evidence for polymeric peroxoborate species.^[17] The work of Pizer and Tihal has opened the way for comprehensive studies of the reactions of peroxoboron species. Despite this, and perhaps because of the earlier warnings in the papers of Wilson, and Jones and co-workers, no rigorous studies of their reactivity toward nucleophiles have been published until now (rigorous studies involve a systematic variation of the ratio of the total concentrations of boron and peroxide; it is not sufficient merely to vary the concentration of a perborate salt added to the reaction mix). The present paper will report on the oxidation of substituted phenyl methyl sulfides by hydrogen peroxide in boric acid/borate buffer.

The oxidation of organic sulfides by hydrogen peroxide and peroxyacids involves nucleophilic attack by the sulfur atom on the (outer, in the case of peroxyacids) peroxidic oxygen atom and is generally well understood.^[18] Recent ab initio calculations provide further insight to the mechanism in aqueous solutions.^[19] Edwards and co-workers found that the rate of reaction of thioxane and hydrogen peroxide in protic solvents, ROH, is overall second-order (first-order in each reactant) and the rate constant shows a positive correlation with the autoprotolysis (i.e., ion product, $[\text{ROH}_2]^+ [\text{RO}]^-$) constant. Edwards concluded that specific solvent interactions provide a mechanistic path that avoids significant charge separation in the activated complex. He proposed that the solvent acted as a proton-transfer agent to stabilise the transition state by minimizing charge separation as shown in Equation (4).



Moreover, in the aprotic solvent dioxane the reaction is overall third-order, (second-order in hydrogen peroxide) showing the participation of a second molecule of the peroxide as the proton-transfer agent, that is, $\text{R}=\text{OH}$ in Equation (4).^[20] Recent ab initio calculations on the oxidation of dimethyl sulfide by hydrogen peroxide in aqueous solution show that the extent of charge development in a transition state involving a single water molecule is $+0.37$ on the sulfur atom and -0.35 on the distal oxygen atom of hydrogen peroxide. It is concluded that the transition state involves O–O bond breaking together with S–O bond formation, and that hydrogen transfer occurs after the system has passed the transition state. The calculated activation energy in this case is much lower than that for direct 1,2-hydrogen transfer of H_2O_2 and shows that solvent molecules can efficiently lower the activation barrier for reaction. The activation barrier is, nevertheless, too high compared with experimental values. It is, however, successfully predicted by using mechanistic pathways involving hydrogen transfer through

one or two water molecules, provided that an additional water molecule stabilises the negative charge on the distal oxygen atom of hydrogen peroxide.^[19] This is shown in Equation (5) for hydrogen transfer involving one water molecule.



Bunton has extensively discussed the effect of substituents on the peroxomonosulfate oxidation of substituted phenyl methyl sulfides in terms of strongly solvated transition states.^[21] The present work uses substituted phenyl methyl sulfides to explore the nature of the reactivity of peroxoborates and peroxoboric acid relative to hydrogen peroxide, and with respect to previous studies of peroxycarboxylic acids, peroxomonsulfate and peroxymonocarbonate.^[22,21,7]

Experimental Section

Materials: The organic sulfides were obtained from Aldrich and aqueous solutions were prepared and standardised as described previously.^[23] Hydrogen peroxide, 30 wt. %, *N-tert*-butyl- α -phenylnitrone (BPN), the disodium salt of ethylenediaminetetraacetate (EDTA), boric acid, sodium nitrate and sodium hydroxide were of the best available grade obtained from Aldrich. Ethylenediaminetetramethylenephosphonic acid (EDTMP) was a gift from Warwick International Limited. All solutions were made up in distilled water. Stock solutions of hydrogen peroxide were standardised by using titanium sulfate, taking the molar absorptivity of the resultant pertitanic complex as $730 \text{ M}^{-1} \text{ cm}^{-1}$ at 410 nm .^[24] Solutions of boric acid and hydrogen peroxide were mixed and brought to the required pH with sodium hydroxide solution and the appropriate amount of sodium nitrate solution added to bring the mix to the required ionic strength.

Kinetics: During kinetic runs well-sealed spectrophotometer cuvettes were used in order to prevent volatilisation of the less polar sulfides, which would give falsely high rate constants. All runs were carried out at 25°C . Total peroxide concentration was at least ten times greater than the sulfide concentration. Pseudo-first-order rate constants, k_{obs} were obtained from nonlinear regression of the monoexponential decrease in absorbance due to the disappearance of the sulfide. The reaction was followed at 352 nm and 310 nm for methyl 4-nitrophenyl sulfide and methyl 4-methylsulfanyphenyl ketone, respectively, and 260 nm for the other sulfides. Hydrogen peroxide absorbs in the UV range and so the variation of peroxide concentration for runs involving the other sulfides was limited in order to keep the measured absorbance within the dynamic range of the spectrophotometer. Unless stated otherwise, runs were carried out at ionic strength 0.1 M , under identical conditions to those used by Pizer and Tihai for the determination of the formation constants of the peroxoboron species.^[16]

Results

Unless stated otherwise, the absorbance dropped exponentially with time showing that the rate of reaction was directly proportional to the concentration of the sulfide as shown in Equation (6).

$$d[S]/dt = k_{\text{obs}}[S] \quad (6)$$

Addition of the metal-ion chelating agents EDTA and EDTMP, and the radical scavenger BPN had no effect on the observed rate constant, k_{obs} ; though, at higher pH, low concentrations ($1 \times 10^{-5} \text{ M}$) of the chelating agents were used to suppress peroxide decomposition. Figure 1 shows the

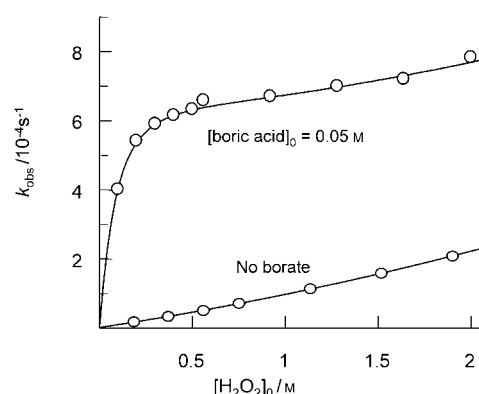


Figure 1. Effect of peroxide concentration on the observed rate constant for reaction with $(11 \text{ or } 2.2) \times 10^{-5} \text{ M}$ methyl 4-nitrophenyl sulfide in the absence (pH 4.5–4.8) or presence (pH 9.6) of borate buffer; ionic strength 0.1 M (NaNO_3). The curves represent Equations (7) or (8), using the rate constants given in Table 1.

effect of hydrogen peroxide concentration on k_{obs} for the oxidation of methyl 4-nitrophenyl sulfide in the presence and absence of borate. The upward curvature in the absence of borate shows that, in addition to a first-order term, there is a second-order component in the hydrogen peroxide concentration dependence, according to Equation (7), which yields the rate constants k_{P1} and k_{P2} , included in Table 1.

$$k_{\text{obs}} = k_{\text{P1}}[\text{H}_2\text{O}_2] + k_{\text{P2}}[\text{H}_2\text{O}_2]^2 \quad (7)$$

Table 1. 4- $\text{XC}_6\text{H}_4\text{SCH}_3$: Hammett σ_p values for the substituents and rate constants $\pm$ standard deviations for the reactions with one and two molecules of hydrogen peroxide and with mono- and diperoxoborate.

X	σ_p	k_{P1} [$10^{-5} \text{ M}^{-1} \text{ s}^{-1}$]	k_{P2} [$10^{-5} \text{ M}^{-2} \text{ s}^{-1}$]	k_{P1BOH} [$10^{-2} \text{ M}^{-1} \text{ s}^{-1}$]	k_{P2BOH} [$10^{-2} \text{ M}^{-1} \text{ s}^{-1}$]
NO_2	0.78	8.29 ± 0.15	1.48 ± 0.09	1.51 ± 0.02	1.06 ± 0.02
$\text{CH}_3\text{C(O)}$	0.50	25.1 ± 0.5	5.08 ± 0.28	2.51 ± 0.02	1.45 ± 0.03
Br	0.23	97.9 ± 7.2	— ^[a]	4.79 ± 0.02	— ^[a]
CO_2^-	−0.16	239 ± 2	— ^[a]	5.77 ± 0.06	— ^[a]
CH_3	−0.17	257 ± 4	— ^[a]	6.66 ± 0.22	— ^[a]
CH_3O	−0.27	378 ± 2	— ^[a]	8.53 ± 0.18	— ^[a]

[a] Not determined under the experimental conditions used.

In the presence of 0.05 M borate there is evident catalysis, which levels off at higher concentrations of hydrogen peroxide at which the borate catalyst becomes saturated with peroxide. The dependence of k_{obs} on peroxide concentration was fitted according to Equation (8), in which the subscripts P1BOH, P2BOH and P1B refer to the reactions of the organic sulfide and monoperoxoborate, diperoxoborate and peroxoboric acid, respectively.

$$k_{\text{obs}} = k_{\text{P1}}[\text{H}_2\text{O}_2] + k_{\text{P2}}[\text{H}_2\text{O}_2]^2 + k_{\text{P1BOH}}[(\text{HO})_3\text{BOOH}^-] + k_{\text{P2BOH}}[(\text{HO})_2\text{B}(\text{OOH})_2^-] + k_{\text{P1B}}[(\text{HO})_2\text{BOOH}] \quad (8)$$

The values of k_{P1} and k_{P2} obtained in the absence of borate were substituted into Equation (8), and the concentrations of the various species were calculated numerically by using the measured pH of the reaction mix, the peroxoboron formation constants of Pizer and Tihai, and their values for the acid ionisation constants of boric acid and hydrogen peroxide, 1.05×10^{-9} and 2.51×10^{-12} M, respectively,^[16] together with the mass balance equations for total boron and total peroxide. Best-fit values of the rate constants and their standard deviations, obtained by nonlinear regression (inserting a routine in the equation editor of Grafit 3.09b to perform the bisection method to determine the concentrations of the various species^[25]), are included in Table 1. The curves in Figure 1 represent the best-fit rate constants with k_{P1B} set to zero.

Figure 2 shows the dependence of k_{obs} on pH. It should be noted at this point that the kinetic runs at low pH showed a small, more rapid phase that comprised about 4% of the total absorbance change independent of the concentration of the peroxide between 0.19 M and 1.91 M (although in the absence of peroxide there was no absorbance change, showing that complex formation between borate and the sulfide was not taking place); the subsequent absorbance change paralleled that in the absence of borate catalyst. This small initial phase was ignored in the calculation of k_{obs} . The de-

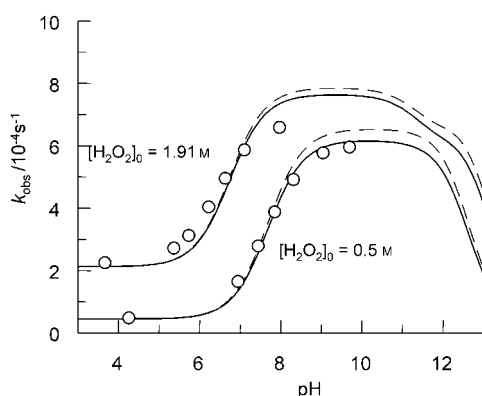


Figure 2. Effect of pH on the observed rate constant for reaction of two different concentrations of hydrogen peroxide with 1×10^{-4} M methyl 4-nitrophenyl sulfide in borate buffer; $[\text{boric acid}]_0$ 0.05 M, ionic strength 0.1 M (NaNO_3). The curves represent Equation (8), using the rate constants given in the text (full lines) and Table 1 (broken lines).

pendence of k_{obs} on pH was fitted by using Equation (8) in exactly the same way as its dependence on peroxide concentration. The best-fit values of k_{P1BOH} and k_{P2BOH} and their standard deviations are $[(1.4 \pm 0.2) \times 10^{-2}$ and $(1.0 \pm 0.2) \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$, respectively] in agreement with, but less precise than, the values from the peroxide concentration dependence shown in Table 1. An upper limit of $k_{\text{P1B}} = 4.1 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ is estimated. This is calculated as $5k_{\text{P1}}$ by assuming a possible 5% error in k_{obs} and by using the formation constant of the predominant low pH peroxoboron species, $\text{HOOB}(\text{OH})_2$, as 0.01 M^{-1} .

Figure 3 shows the dependence of k_{obs} on total boron concentration. The lines show the expected values of k_{obs} calculated according to Equation (8) by using the rate constants

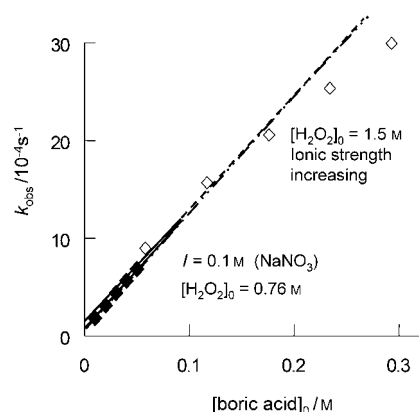


Figure 3. Effect of total boric acid concentration on the observed rate constant for reaction of hydrogen peroxide with 2.2×10^{-5} M methyl 4-nitrophenyl sulfide, pH 9.6. The lines represent Equation (8) using the rate constants in Table 1.

in Table 1. There is excellent agreement between expected and observed values for the runs carried out under identical conditions to those of Pizer and Tihai. In the other runs, the total boron concentration range is extended and the ionic strength is allowed to increase along with the concentration of borate. The small negative deviation from linearity in this case is consistent with the small effect of ionic strength we have observed (results not shown) and does not constitute evidence for the presence of less reactive polymeric peroxoborate species.

The reaction of methyl 4-methylsulfanylphenyl ketone showed an identical pattern of behaviour to that of the methyl 4-nitrophenyl sulfide, and the more precise rate constants obtained from the peroxide concentration dependence runs are shown in Table 1. The estimated upper limit for k_{P1B} is $1.3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. For the other sulfides the maximum peroxide concentration used was between 0.08 and 0.16 M, and the contributions of second-order terms in peroxide concentration to the observed rate constants were negligible. Best-fit rate constants are shown in Table 1. The data are shown in Figure 4 as Hammett plots using *para*-substituent constants.^[26] For hydrogen peroxide the slope (Hammett

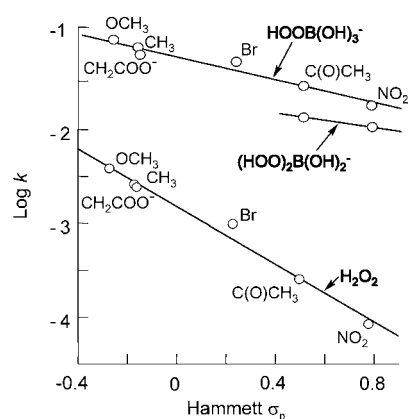


Figure 4. Hammett plots for the reactions of peroxoborates or hydrogen peroxide and substituted phenyl methyl sulfides.

ρ value) is -1.5 ± 0.1 , whereas for monoperoxoborate it is -0.65 ± 0.07 , and for diperoxoborate it is -0.48 (two points only).

Discussion

Oxidation by hydrogen peroxide: For the oxidation of methyl 4-nitrophenyl sulfide and methyl 4-methylsulfanylphenyl ketone, for which the use of a high concentration of peroxide was possible, a second-order term in its concentration appears in the rate equation, [Eq. (7)]. This has been observed previously not only in aprotic solvents, but also in alcohol/water mixtures.^[20,6] The high concentration of hydrogen peroxide competes with the solvent water, either as the proton-transfer agent or the hydrogen-bond donor (or both) in the transition state, see Equations (4) and (5). To compare the stability of the transition state containing one hydrogen peroxide group plus at least one water molecule with that of the transition state containing two molecules of hydrogen peroxide, it is necessary to divide k_{P1} by 55 M, the concentration of bulk water. The third-order rate constants obtained are 1.5×10^{-6} and $4.6 \times 10^{-6} \text{ M}^{-2} \text{ s}^{-1}$ for methyl 4-nitrophenyl sulfide and methyl 4-methylsulfanylphenyl ketone, respectively. These values are about ten times less than the respective values of k_{P2} , in keeping with H_2O being a poorer proton donor/acceptor, and a weaker acid and hydrogen-bond donor than H_2O_2 .

The negative Hammett ρ value for the reaction of substituted phenyl methyl sulfides and hydrogen peroxide is indicative of the development of positive charge on the sulfur in the transition state, with the sulfide behaving, as expected, as a nucleophile.^[18] The actual value of ρ , -1.5 , is commensurate with the difference in charge of the sulfur in the transition state and reactant cluster, $+0.37$, calculated for the oxidation of dimethyl sulfide.^[19]

Oxidation by peroxoborates: To compare the reactivity of peroxides it is usual to construct a Brønsted-type plot of the log of the rate constant for reaction with a particular sub-

strate against the $\text{p}K_a$ of the parent acid of the peroxide. The latter quantity is used as an indicator of the leaving group character of the parent anion formed by heterolytic cleavage of the peroxide bond, and the greater the slope of the plot the greater the significance of peroxide bond cleavage in the transition state.^[18] Figure 5 shows the Brønsted

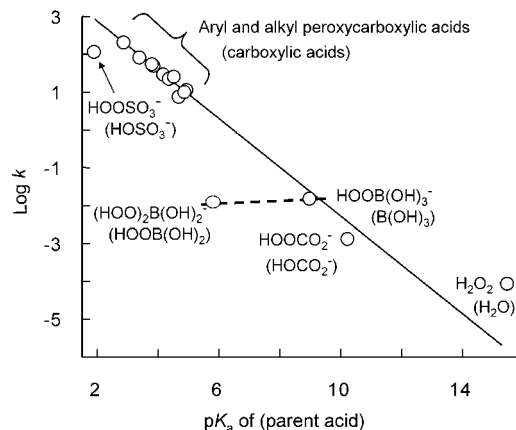


Figure 5. Brønsted-type plot, including parent Lewis acids, for the reactions of peroxides and methyl 4-nitrophenyl sulfide.

plot for methyl 4-nitrophenyl sulfide, including literature data for its reactivity with peroxomonosulfate, peroxycarboxylic acids and peroxymonocarbonate,^[22,21,7] as well as the present results for hydrogen peroxide and monoperoxoborate and diperoxoborate. The $\text{p}K_a$ of HOOB(OH)_2 , the parent acid of diperoxoborate, is 5.7, compared with 8.98 for B(OH)_3 , the parent acid of monoperoxoborate (these values are consistent with HOO^- being less electron donating than HO^-).^[16] Figure 5 shows that the peroxoborates are less reactive than peroxycarboxylic acids, though this disadvantage lessens with increasing pH above their $\text{p}K_a$ values, at which the peroxycarboxylic acids become ionised. The peroxoborates are, however, more reactive than peroxymonocarbonate, and this advantage increases with increasing pH above the $\text{p}K_a$ of hydrogen carbonate.

It should be noted at this point that the parent acids of the peroxoborates are Lewis acids and their $\text{p}K_a$ values denote something different from those of the other (Brønsted) acids in Figure 5. Thus, decreasing $\text{p}K_a$ of a parent Brønsted acid (a measure of the equilibrium between XOH and $\text{XO}^- + \text{H}^+$, in which XOOH is the peroxide) implies easier cleavage of the peroxide oxygen–oxygen bond due to the better leaving group ability of XO^- , whereas decreasing $\text{p}K_a$ of the Lewis acids (a measure of the equilibrium between $\text{X} + \text{H}_2\text{O}$ and $\text{XOH}^- + \text{H}^+$, in which XOOH is the peroxide) implies more difficult cleavage of the boron peroxide bond due to the poorer leaving group ability of X . The line on the plot is drawn through the data points for the peroxycarboxylic acids with Brønsted slope $\beta_{\text{lg}} = -0.65$.^[22] It is evident that peroxomonosulfate, peroxymonocarbonate and hydrogen peroxide lie near to the line, suggesting that their reactions are mechanistically quite similar and oxygen–

oxygen bond breaking is significant in the transition state. Monoperoxoborate also lies close to the line, although this is almost certainly fortuitous since the diperoxoborate does not lie equally close. The rate constants for the peroxoborates are very similar (dashed line on Figure 5) despite their different pK_a values. This shows that boron–oxygen bond breaking is not significant in the transition state, consistent with the peroxoborates not acting as nucleophiles in which the neutral $B(OH)_3$ or $HOOB(OH)_2$ moieties are the respective leaving groups.

A comparison of the Hammett ρ values of the peroxoborates and other peroxides gives further insight into the nature of the transition state. Figure 6 shows a reactivity se-

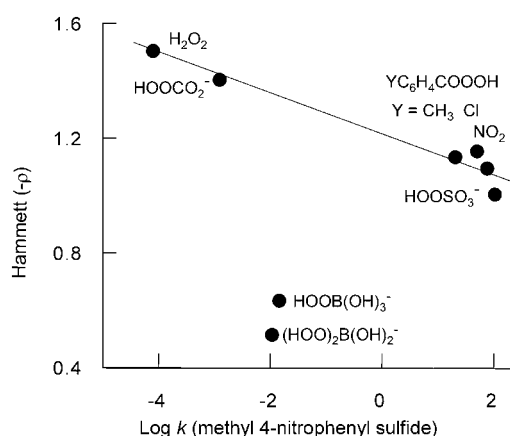
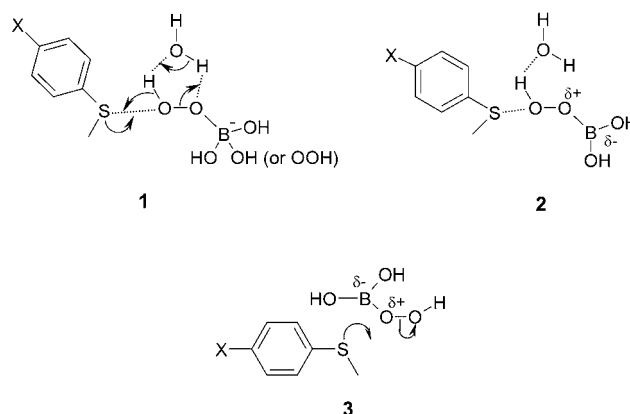


Figure 6. Reactivity-selectivity plot for the reactions of peroxides and substituted phenyl methyl sulfides, with the 4-nitro derivative as the reactivity measure.

lectivity plot including the present data and that reported for peroxydicarbonate, peroxydicarboxylic acids and peroxomonosulfate.^[7,22,21] This plot uses the Hammett ρ values as a measure of the selectivity of the peroxide with respect to the nature of the substituent on the phenyl group, and the logarithm of the rate constant for the reaction with the nitro derivative as a measure of the reactivity of the peroxide. The plot shows that the peroxoborates behave very differently to the other peroxides. The much less negative Hammett ρ values indicates that there is significantly less positive charge development on the sulfur atom in the transition state. The essentially linear reactivity-selectivity relationship including hydrogen peroxide, peroxydicarbonate, the peroxydicarboxylic acids and peroxomonosulfate is consistent with all these peroxides reacting with the sulfides by the same mechanism. This is because, according to the Hammond postulate, the structure of the transition state becomes closer to that of the reactant cluster as the energy difference between the transition state and reactants becomes smaller.^[27] In the present case the more reactive peroxides have a transition state earlier along the reaction coordinate with less positive charge development on the sulfur atom. In the case of the peroxoborates, they are much less selective

than expected from their reactivity compared with the other peroxides. This indicates that the transition states for their reactions lie on a region of the reaction coordinate at which at least some of the relative energy changes involved in sulfur–oxygen bond formation, oxygen–oxygen bond breaking, proton transfer and solvation changes are significantly different due to the presence of the boron atom. It is necessary that any mechanism that is proposed to account for the very different behaviour of the peroxoborates must also accommodate the very low reactivity of peroxoboric acid.

Peroxoboric acid: The upper limits of the rate constants for the reaction of peroxoboric acid and the two sulfides investigated are very small relative to the rate constants for the peroxoborates. At first sight this seems contrary to what is expected, because if the peroxoborates are acting as electrophiles then peroxoboric acid, with its absence of a negative charge and, moreover, the presence of the electron-deficient boron, ought to be a better electrophile. If, however, proton transfer provides a mechanistic path for the reaction of the peroxoborates, as shown in the transition state structure **1** (in which the extent of charge development on the sulfur and respective peroxide oxygen atoms in the transition state, and any additional specific solvent interactions, are not shown) then this path is not available to peroxoboric acid. This is because proton transfer is less favoured due to the positive charge located on the oxygen atom of **2**, associ-



ated with the partial double-bond character of the boron–oxygen bond. Hence, proton transfer as a significant part of the reaction coordinate for the peroxoborates is strongly suggested, because of the lack of reactivity of peroxoboric acid. We propose that the much lower extent of positive charge development on the sulfur atom for the reactions of the peroxoborates, as shown by the lower magnitude of the Hammett ρ values in Figure 6, is due to the greater importance of proton transfer in stabilising the transition state in the case of the peroxoborates.

Finally it is worth noting that the alternative nucleophilic attack of the sulfur atom on the inner peroxide oxygen atom in **3** to form a positively charged intermediate could possibly

be subject to neighbouring group assistance by boron that is well known in organoboron compounds.^[28] Indeed, as described in the results section, the kinetic runs at low pH in the presence of boric acid showed a short rapid initial phase consistent with the formation of an intermediate that breaks down considerably more slowly than the rate of the uncatalysed reaction.

Conclusion

The following conclusions can be drawn.

- 1) The reaction of hydrogen peroxide and substituted phenyl methyl sulfides shows a negative Hammett ρ value consistent with the development of positive charge on the nucleophilic sulfur atom, as predicted by recently published ab initio calculations on a transition state involving S–O bond formation and O–O bond breaking. The calculations also predict that transfer of hydrogen to the distal oxygen atom of hydrogen peroxide through one or more solvent water molecules, although an important part of the reaction coordinate, occurs after the system has passed the transition state, so that the developing negative charge on the distal oxygen atom is stabilised by hydrogen bonding from an additional water molecule.
- 2) At high concentrations of hydrogen peroxide a pathway involving catalysis by a second molecule of the peroxide occurs. This is consistent either with hydrogen peroxide being a better proton donor/acceptor than water, or it being a better hydrogen-bond donor, or both.
- 3) The reaction of hydrogen peroxide and substituted phenyl methyl sulfides is catalysed in aqueous boric acid/borate buffer through the formation of monoperoxoborate and diperoxoborate anions.
- 4) The peroxoborate anions are stable and functional in the pH range 8–12.
- 5) The peroxoborates are less reactive than peroxomonosulfate and peroxycarboxylic acids, but more reactive than peroxymonocarbonate.
- 6) The peroxoborate anions, in common with other peroxides, are subject to nucleophilic attack of the sulfur atom on the outer peroxide oxygen atom, although the development of positive charge on the sulfur atom is much less in the case of the peroxoborates.
- 7) Peroxoboric acid is much less reactive than the peroxoborates. This is strong evidence for the importance of proton transfer through a solvent water molecule in the reaction coordinate for the peroxoborates, since proton

transfer in the reaction involving peroxoboric acid is less favourable due to the positive charge on the acceptor oxygen atom associated with the partial double-bond character of the boron–oxygen bond.

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