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Photochemistry of Peroxoborates: Borate Inhibition of the Photodecomposition of Hydrogen Peroxide

Sébastien Rey and D. Martin Davies*[a]

Abstract: The UV absorbance and photochemical decomposition kinetics of hydrogen peroxide in borate/boric acid buffers were investigated as a function of pH, total peroxide concentration, and total boron concentration. At higher pH borate/boric acid inhibits the photodecomposition of hydrogen peroxide (molar absorptivity and quantum yield of H_2O_2 and HO_2^-, (19.0±0.3) $\text{M}^{-1}\,\text{cm}^{-1}$ and 1, and (237±7) $\text{M}^{-1}\,\text{cm}^{-1}$ and 0.8±0.1, respectively). The results are consistent with the equilibrium formation of the anions monoperoxoborate, $K_{BOOH} = [H^+][HOOB(OH)_3^-]/([B(OH)_3][H_2O_2])$, 2.0×10^{-8}, R. Pizer, C. Tihal, *Inorg. Chem.* **1987**, *26*, 3639–3642, and monoperoxodiborate, $K_{BOOB} = [BOOB^{2-}]/([B(OH)_4^-][HOOB(OH)_3^-])$, 1.0±0.3 or 4.3±0.9, depending upon the conditions, with molar absorptivity, (19±1) $\text{M}^{-1}\,\text{cm}^{-1}$ and (86±15) $\text{M}^{-1}\,\text{cm}^{-1}$, respectively, and respective quantum yields, 1.1±0.1 and 0.04±0.04. The low quantum yield of monoperoxodiborate is discussed in terms of the slower diffusion apart of incipient $^{\bullet}OB(OH)_3^-$ radicals than may be possible for $^{\bullet}OH$ radicals, or a possible oxygen-bridged cyclic structure of the monoperoxodiborate.

Keywords: atmospheric chemistry · boron · green chemistry · hydroxyl radical · photolysis

Introduction

Hydrogen peroxide is an atom-efficient and environmentally benign oxidant. Although it is powerful, its reactions are rather slow and require some form of catalysis or activation. In this respect, we have recently shown that the electrophilic oxidation of organic sulfides by hydrogen peroxide is catalyzed in borate/boric acid buffers by the formation of peroxoborates.[1] Relevant equilibria are given in Equations (1) and (2), where K_{BOOH} is the formation constant of monoperoxoborate,[2] and K_{BOH} is the formation constant of borate (i.e. the acid dissociation constant of boric acid).

$$B(OH)_3 + H_2O_2 \rightleftharpoons HOOB(OH)_3^- + H^+ \quad K_{BOOH} \tag{1}$$

$$B(OH)_3 + H_2O \rightleftharpoons B(OH)_4^- + H^+ \quad K_{BOH} \tag{2}$$

Hydrogen peroxide is also used as a source of hydroxyl radicals in the treatment of contaminated waters or industrial wastewaters in processes known as “advanced oxidation techniques”. One such process involves the photolysis of hydrogen peroxide,[3] which, in a different context, is a source of hydroxyl radicals in atmospheric liquid water. This water often contains minerals from sea foam (boron is a major inorganic chemical constituent of sea water)[4] that contribute to atmospheric chemistry.[5] The present work explores the photochemistry of peroxoborate species formed from hydrogen peroxide in borate/boric acid buffers.

The photolysis of hydrogen peroxide results in its decomposition to oxygen and water, and is well understood.[6] The primary process is the cleavage of the peroxide bond to form hydroxyl ($^{\bullet}OH$) radicals. These abstract a hydrogen atom from hydrogen peroxide to form water and hydroperoxyl ($^{\bullet}OOH$) radical. Two hydroperoxyl radicals (or at higher pH a hydroperoxyl radical and its conjugate base, the superoxide radical anion, $^{\bullet}OO^-$) disproportionate into hydrogen peroxide (or its conjugate base, the hydroperoxide anion, HOO^-) and oxygen. The rate depends on the amount of light absorbed, and on the quantum yield of the primary process, which is close to unity.[7–10] Boric acid has no effect on the quantum yield at low pH.[11] The effect of boric acid/borate on the photolysis of hydrogen peroxide at higher pH has not been studied previously.

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[a] S. Rey, Dr. D. M. Davies
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

Experimental Section

Boric acid, sodium hydrogen carbonate, sodium hydroxide and unstabilised 30% w/v hydrogen peroxide were BDH AnalaR grade. All solutions were prepared in distilled water. Measurements of pH were carried out using a Jenway 3010 pH-meter calibrated with standard BDH buffers at pHs 4.00, 7.00 and 9.20, and with saturated $Ca(OH)_2$ solution at pH 12.45.[12] Stock hydrogen peroxide, boric acid and sodium hydroxide solutions were mixed (taking precautions to exclude carbon dioxide when necessary) to give the required pH and total borate concentration. The total peroxide concentration, [P], about 2.2×10^{-3} M, unless stated otherwise, was determined as the titanium IV complex.[1]

Absorbance at 254 nm, A_{254}, was measured by using a Nicolet Evolution 300 spectrophotometer with a silica cell of optical path length, l, 1 cm. Equation (3) was used to calculate the apparent molar absorptivity, ε_{254}, due to the various peroxide species present.

$$A_{254} = \varepsilon_{254}[\mathrm{P}]l \tag{3}$$

Photolysis was carried out at 25 °C using a Hamamatsu pen type low-pressure, 254 nm, mercury lamp (type L937–01, with a San Gabriel Pen-Ray model PS-1 power supply) fitted with a quartz thermostatic jacket in a Pyrex reaction vessel holding 75 cm^3 of stirred solution. The rate of decomposition of total peroxide is given by Equation (4), where Φ_{obs} is the observed quantum yield due to the various peroxide species present and I_a is the amount of light absorbed. Equation (5) is the relationship between the absorbance and the incident, I_0, and transmitted light intensities at 254 nm. From Equations (3)–(5), the integrated rate equation, Equation (6), is obtained, with the observed rate constant, k_{obs}, defined in Equation (7). For weakly absorbing solutions Equation (6) reduces to Equation (8),[7] which can be written as Equation (9) in terms of the absorbance, A, of the reaction solution at any convenient wavelength.

$$-\mathrm{d}[\mathrm{P}]/\mathrm{d}t = \Phi_{\mathrm{obs}} I_a \tag{4}$$

$$A_{254} = \log_{10}(I_0/(I_0 - I_a)) \tag{5}$$

$$\ln((10^{\varepsilon_{254}[\mathrm{P}]l} - 1)/(10^{\varepsilon_{254}[\mathrm{P}]_0 l} - 1)) = -k_{\mathrm{obs}}t \tag{6}$$

$$k_{\mathrm{obs}} = 2.303\varepsilon_{254} l \Phi_{\mathrm{obs}} I_0 \tag{7}$$

$$\ln([\mathrm{P}]/[\mathrm{P}]_0) = -k_{\mathrm{obs}}t \tag{8}$$

$$\ln((A - A_\infty)/(A_0 - A_\infty)) = -k_{\mathrm{obs}}t \tag{9}$$

Photolysis reactions and dark control reactions were carried out simultaneously under identical conditions of composition and temperature. In all cases the dark reactions were very slow compared to the corresponding photolysis reaction. For runs above pH 9.5, small aliquots were removed from the reaction vessel at measured time intervals and analysed for total peroxide using the titanium IV method.[1] Values of k_{obs} were determined using Equation (6) with the value of l for the reaction vessel that was determined as described in the next paragraph. For runs below pH 9.5, where the peroxide absorbs weakly at 254 nm, the absorbance of the reaction solution at 220 nm was measured directly, and k_{obs} values determined using Equation (9).

Hydrogen peroxide, 5.5×10^{-2} M, was used as a chemical actinometer exhibiting complete absorption at 254 nm. The rate of decomposition of hydrogen peroxide is given by Equation (4), with I_a set equal to I_0 (because of the complete absorption), and the quantum yield was set equal to unity.[7] A linear decrease in hydrogen peroxide concentration with time was observed that yielded I_0, 4.31×10^{-6} Einstein L^{-1} s^{-1}. We used Equation (7) with k_{obs} measured under weakly absorbing ($[H_2O_2]_0$, 2.2×10^{-3} M) conditions, together with the value of ε_{254} equal to 19.6 M^{-1} cm^{-1},[7] to obtain the optical path length of the reaction vessel, l, 1.9 cm.

Results

Figure 1 shows that increasing the total boric acid concentration causes an increase in the apparent molar absorptivity of the peroxide, ε_{254}, in the pH range between about 8 and 11, whereas at higher pH it causes a decrease. This is clearly due to the formation of one or more peroxoborate species having a greater molar absorptivity than that of hydrogen peroxide, $\varepsilon_{\mathrm{HOOH}}$, but less than that of the hydroperoxide anion, $\varepsilon_{\mathrm{HOO}}$, formed according to Equation (10), where K_{HOO} is the formation constant (i.e. the acid dissociation constant of hydrogen peroxide). Equation (11) is used to fit the data, with $\varepsilon_{\mathrm{BOOH}}$, the molar absorptivity of monoperoxoborate, and $\varepsilon_{\mathrm{BOOB}}$, that of a linear or cyclic monoperoxodiborate, BOOB^{2-}, formed according to Equations (12a) or (12b), respectively, with formation constant, K_{BOOB}. The concentrations of the peroxide species were calculated using the mass balance equations for the total boron and peroxide concentrations and the equations for the various equilibrium constants, with the measured pH value of the solution and $K_{\mathrm{BOOH}} = 2.0\times10^{-8}$,[2] $K_{\mathrm{BOH}} = 1.05\times10^{-9}$,[2,13] and K_{BOOB} and K_{HOO} variable.

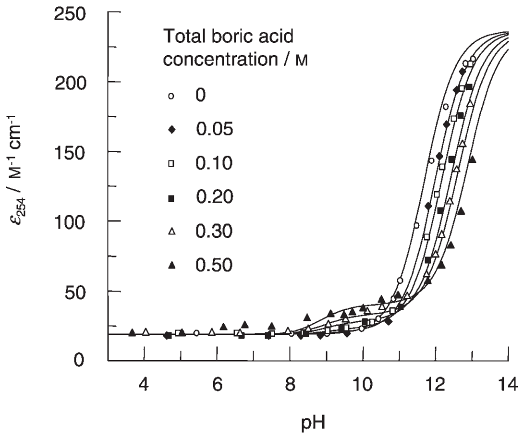

Figure 1. Effect of pH on the apparent molar absorptivity at 254 nm of peroxide at different boric acid concentrations. The curves represent Equation (11), using the parameters given in Table 1.

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \quad K_{\mathrm{HOO}} \tag{10}$$

$$\varepsilon_{254} = (\varepsilon_{\mathrm{HOOH}}[H_2O_2] + \varepsilon_{\mathrm{HOO}}[HO_2^-] + \varepsilon_{\mathrm{BOOH}}[HOOB(OH)_3^-] + \varepsilon_{\mathrm{BOOB}}[BOOB^{2-}])/[\mathrm{P}] \tag{11}$$

$$B(OH)_4^- + HOOB(OH)_3^- \rightleftharpoons (HO)_3BOOB(OH)_3^{2-} + H_2O \quad K_{\mathrm{BOOB}} \tag{12a}$$

$$B(OH)_4^- + HOOB(OH)_3^- \rightleftharpoons (HO)_2B(OO)(O)B(OH)_2^{2-} + 2H_2O \quad K_{\mathrm{BOOB}} \tag{12b}$$

Best-fit values of K_{BOOB}, K_{HOO} and the molar absorptivity of each of the peroxide species, together with 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)[14] are included in Table 1. The curves in Figure 1 are calculated from the values in the Table using Equation (11). Setting the formation constant of the monoperoxodiborate species to zero resulted in a considerably worse fit to the data.

Table 1. Peroxide molar absorptivity at 254 nm, photolysis kinetics, and equilibrium constants.

XOOY	ε_{XOOY} [M^{-1} cm^{-1}]	k_{XOOY} [10^{-4} s^{-1}]	Φ_{XOOY}
H_2O_2	19.0±0.3	3.5±0.1	1
HO_2^-	237±7	36±2	0.8±0.1
$HOOB(OH)_3^-$	19±1	3.8±0.5	1.1±0.1
$BOOB^{2-}$	86±15	0.6±0.6	0.04±0.04
K_{HOO} [M]	(2.0±0.2)×10^{-12}[a]	(2.7±0.4)×10^{-12}[b]	
K_{BOOB} [M^{-1}]	1.0±0.3[a]	4.3±0.9[b]	

[a] From molar absorptivity data. [b] From kinetic data.

Figure 2 shows kinetic data for the photolysis, treated according to Equation (6). The slopes of the plots give k_{obs} values that are essentially independent of total peroxide concentration over a wide range of borate concentrations. This means that the photochemical processes are first-order in peroxide and hence diperoxo species such as $(HO)_2B(OOH)_2^-$ or $(HO)_2B(OO)_2B(OH)_2^{2-}$ are not significantly involved.

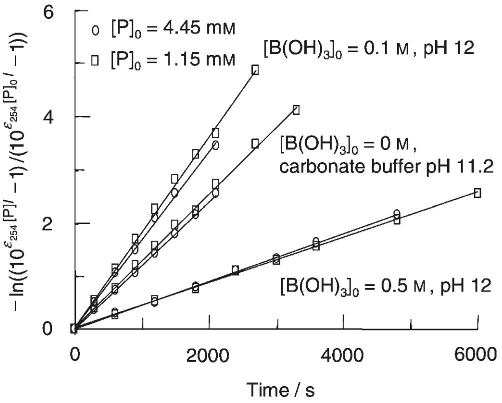

Figure 2. Typical kinetic plots for the determination of k_{obs}, which is independent of peroxide concentration.

Figure 3 shows the effect of pH on k_{obs} under various conditions. At low pH the rate constant in the presence of boric acid is the same as it is in water and carbonate buffer. At higher pH the photolysis increases due to the higher molar absorptivity of the hydroperoxide anion. The onset of this increase occurs at higher pH in the presence of borate. In the pH range from about 8 to 11, k_{obs} actually decreases slightly with boric acid/borate present. Figure 3 also shows that lowering the carbonate buffer concentration has very little effect on the observed rate constant, neither does adding carbonate to the borate. The data in Figure 3 obtained in water, 0.1 M carbonate buffer and 0.1 M and 0.3 M borate buffer were treated according to Equation (13), where the rate constants are for the peroxide species indicated, and the concentrations of the species are calculated in the same way as for Equation (11).

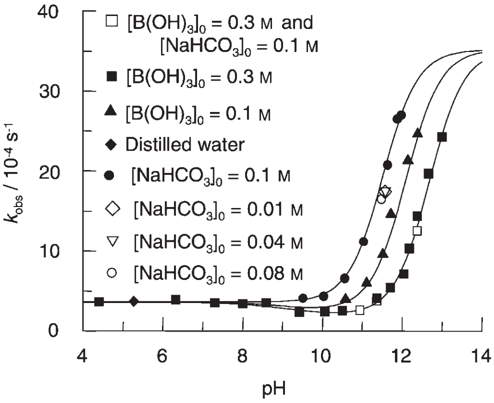

Figure 3. Effect of pH on the photolysis of peroxide in water, borate and carbonate buffers. The curves represent Equation (13), using the parameters given in Table 1.

$$k_{obs} = (k_{HOOH}[H_2O_2] + k_{HOO}[HO_2^-] + k_{BOOH}[HOOB(OH)_3^-] + k_{BOOB}[BOOB^{2-}])/[P] \qquad (13)$$

Best-fit values of K_{BOOB}, K_{HOO} and the rate constants for the peroxide species, together with their standard deviations are included in Table 1. The curves in Figure 3 are calculated from the values in the Table using Equation (13). Setting the formation constant of the monoperoxodiborate species to zero resulted in a considerably worse fit to the data. Quantum yields, calculated using equations corresponding to Equation (7) for the individual peroxide species, are also shown in Table 1.

Figure 4 shows independent measurements of k_{obs} carried out at pH 12 at different total boric acid concentrations. The full curve shows the expected values of k_{obs}, calculated according to Equation (13) by using the parameters in Table 1. This is in good agreement with the data points. The dashed line shows values of k_{obs} calculated from the best fit values of the parameters (not given) obtained from the data in Figure 3 after setting the formation constant of the monoperoxodiborate species to zero in Equation (13). There is a clear systematic deviation of this line from the data points. This confirms the importance of monoperoxodiborate in the data analysis.

Discussion

The influence of borate concentration on the pH dependence of the apparent molar absorptivity of peroxide and its observed first-order photolysis rate constant (Figure 1 and Figure 3, respectively) cannot be explained simply by the

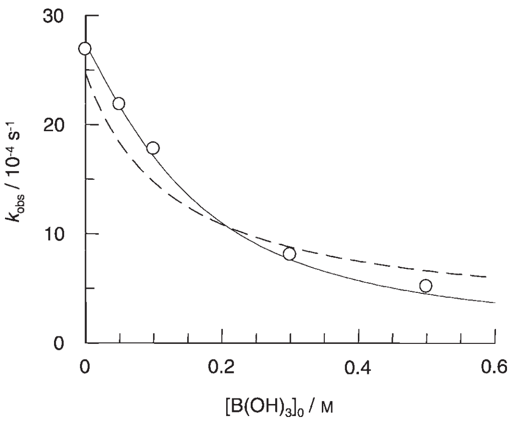

Figure 4. Effect of total boric acid concentration on the photolysis of peroxide at pH 12. The point at zero boric acid concentration is for a run in 0.1 M carbonate. The full curve represents Equation (13), using the parameters given in Table 1. The dashed curve represents Equation (13) using the best-fit parameters obtained with the formation constant of monoperoxodiborate, K_{BOOB}, set to zero.

formation of a monoperoxoborate species [Eq. (1)]. A peroxodiborate species is also implicated. The first-order dependence of the photolysis kinetics on peroxide concentration (Figure 2) rules out the involvement of diperoxo species such as $(HO)_2B(OO)_2B(OH)_2^{2-}$. Therefore we conclude that a monoperoxodiborate species is involved [Eq. (12a) or (12b)]. There is ^{11}B NMR chemical shift evidence for the existence of a monoperoxodiborate species, which was formulated $(HO)_3B(OO)B(OH)_3^{2-}$.[15] There is also ^{11}B NMR evidence of dimeric di-μ-peroxoborates such as $(HO)_2B(OO)_2B(OH)_2^{2-}$ existing at high concentrations of both peroxide and borate,[15,16] The present work was carried out at low ratios of peroxide to borate, conditions that favour monoperoxodiborate formation.

The present work is the first to estimate the formation constant, K_{BOOB}, of the monoperoxodiborate species. Table 1 shows that the best-fit value is somewhat dependent on the conditions under which it was measured. The absorbance measurements were carried out with sodium borate as the only electrolyte, whereas the kinetics were obtained in the presence of sodium salts of borate, hydrogen carbonate and carbonate. The effect of the different conditions is clearly apparent in the different acid dissociation constants of hydrogen peroxide, K_{HOO}, shown in Table 1. These lie above the value, 1.78×10^{-12}, reported by Evans and Uri at zero ionic strength.[17] The increased value of K_{HOO} (see [Eq. (10)]) in stronger electrolyte solution is due to the lowered attraction between H^+ and HOO^-. Similarly, the increased value of K_{BOOB} (see [Eq. (12a) and (12b)]) in stronger electrolyte is expected because of the lowered repulsion between $B(OH)_4^-$ and $HOOB(OH)_3^-$.

Polyborates are known to form in solution at pH values around the pK_a of boric acid (pK_{BOH}, see [Eq. (2)]) and the published values of their formation constants are very dependent upon the conditions under which they are measured.[13,18,19,20] We have carried out a full analysis of our data taking the highest estimates of these formation constants into account,[18] and the results (not shown) are essentially the same as those in Table 1. The analysis shows that the concentration of the polyborates is so low compared with the total borate/boric acid concentration that it does not significantly perturb the equilibrium concentrations of the peroxoborates formed under the conditions of our experiments.

The molar absorptivity values of hydrogen peroxide and the hydroperoxide anion, ε_{HOOH} and ε_{HOO} in Table 1, are in good agreement with the values in the literature.[7] The molar absorptivity of monoperoxoborate, ε_{BOOH}, is similar to that of hydrogen peroxide. This is also the case for the values of the molar absorptivity of other inorganic peroxoacids, such as peroxomonosulfate, peroxomonophosphoric acid, and the peroxomonophosphates.[21] The molar absorptivity of the monoperoxodiborate species is about four times that of monoperoxoborate. It is interesting, in this respect, that the molar absorptivity of acetyl peroxide is about six times higher than that of peracetic acid.[22,23] It seems that the replacement of a hydrogen by a second $COCH_3$ or $B(OH)_3$ has a similar influence on the electronic transitions taking place. This differs from the effect of a second *tert*-butyl group on *tert*-butyl hydroperoxide where the second substituent lowers the molar absorptivity.[21]

At acid or neutral pH the quantum yield of hydrogen peroxide has been variously reported as 1.0 (25 °C), 0.98 (25 °C), and 0.94 (27 °C).[7–9] Since we used hydrogen peroxide as the chemical actinometer, taking the quantum yield as unity,[7] the quantum yields shown in Table 1 are relative to this. It clearly does not involve much of a change in conditions for the quantum yield to drop because of significant radical recombination, since it is about 0.76 at 0 °C.[7,8,10] In alkaline solution the quantum yield remains close to unity, as reported previously,[7] although the decomposition is faster due to the higher molar absorptivity of HOO^-. Carbonate and hydrogen carbonate anions react rapidly with $^{\bullet}OH$ to form $^{\bullet}CO_3^-$, which reacts further to produce oxygen.[24,25] This does not affect the primary rate-limiting formation of $^{\bullet}OH$ radicals and, as seen in this work, carbonate and hydrogen carbonate have no effect on the overall photolysis of hydrogen peroxide. Hydrogen carbonate interacts with hydrogen peroxide to form peroxymonocarbonate,[26] but under the experimental conditions used in this work the amount formed is negligible.

Compared with hydrogen peroxide, borate and boric acid have negligible rates of reaction with $^{\bullet}OH$,[24,27] and so they cannot influence the decomposition of hydrogen peroxide via a radical scavenging mechanism. A major effect at higher pH is the formation of the monoperoxoborate anion at the expense of the hydroperoxide anion. Although the quantum yields of the two anions are similar (Table 1), this causes less photodecomposition because ε_{BOOH} is an order of magnitude lower than ε_{HOO}.

A second effect, important at high borate concentrations, is the formation of a monoperoxodiborate species that has a much lower quantum yield than the other peroxides, causing the decrease in k_{obs} in the pH range 8–12 seen in Figure 3. The monoperoxodiborate species could be either linear or have a cyclic oxygen bridged structure, shown in Equations (12a) and (12b), respectively. The linear structure $(HO)_3BOOB(OH)_3^{2-}$ might have a lower quantum yield than $HOOB(OH)_3^-$ because the incipient pair of $^{\bullet}OB(OH)_3^-$ anion radicals, despite their like charges, are unable to diffuse apart as rapidly as a radical pair involving $^{\bullet}OH$. This radical is believed to diffuse rapidly through water by the widely accepted hydrogen exchange mechanism. Recent ab initio density functional theory molecular dynamics simulations of solvated $^{\bullet}OH$ radicals suggest, however, that the hydrogen exchange mechanism of diffusion may need to be reconsidered.[28] If this really is the case,[29,30] then the cyclic oxygen bridged structure, $(HO)_2B(OO)(O)B(OH)_2^{2-}$, would favour intramolecular radical recombination after the primary peroxide bond photolysis, resulting in the lower quantum yield.

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