On the mechanism of alkaline hydrogen peroxide oxidation of the lignin model *p*-hydroxyacetophenone

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The oxidation of *p*-hydroxyacetophenone by a small excess of alkaline hydrogen peroxide has been found to be an autocatalysed process in which hydroquinone monoacetate and the peracetate ion are generated and consumed at similar rates. The reaction proceeds at a maximum rate when the base concentration is about 0.3 M. A chain-type mechanism that involves peracetate as the oxidizing agent is proposed for the reaction that explains the observed dependence of rate on base concentration. At high pH *o*-hydroxyacetophenone reacts by the same mechanism, whereas *m*-hydroxyacetophenone does not react with hydrogen peroxide under these conditions.

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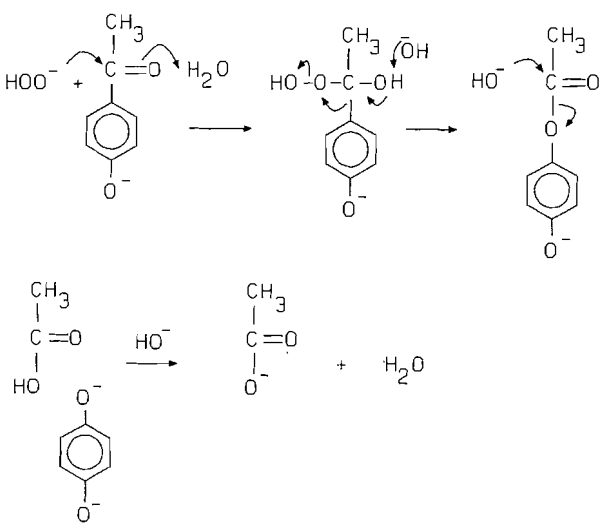
On a trouvé que l'oxydation de la *p*-hydroxyacétophénone par un léger excès de peroxyde d'hydrogène alcalin est un processus autocatalysé dans lequel le monoacétate de l'hydroquinone et l'ion peracétate sont générés et consommés à des vitesses relativement semblables. La réaction se produit avec une vitesse maximale lorsque la concentration de la base est d'environ 0,3 M. On suggère que le mécanisme est de type «en chaîne» et qu'il implique le peracétate comme agent oxydant; ce mécanisme explique la relation entre la vitesse de la réaction et la concentration de la base. À des pH plus élevés, l'*o*-hydroxyacétophénone réagit par le même mécanisme alors que, dans ces conditions, la *m*-hydroxyacétophénone ne réagit pas avec le peroxyde d'hydrogène.

[Traduit par la Rédaction]

Introduction

Aromatic hydroxyketones and other compounds with oxygen atoms *para* to unsaturated groups are of interest relevant to the bleaching of wood pulp, because they contain chromophores similar to those found in lignin (1, 2). Investigation of the oxidation reactions of compounds of this type gives information on the processes that are likely to occur during the bleaching of wood pulp. It has long been accepted that the initial step in the hydrogen peroxide oxidation of an aromatic *o*- or *p*-hydroxyketone under alkaline conditions is the nucleophilic attack of the carbonyl carbon atom of the ketone by the hydroperoxide anion (3, 4). This is followed by a Baeyer–Villiger type rearrangement to give an ester that may react further, depending on conditions (Scheme 1).



SCHEME 1

Hocking (5) showed earlier that the rate of reaction of the lignin model *p*-hydroxyacetophenone (*p*HAP) with a 100-fold excess of aqueous alkaline hydrogen peroxide depended on the concentration of hydrogen peroxide to the power 1.4. Under different conditions they detected and isolated hydroquinone monoacetate (HMA) as an intermediate in the reaction. Normally this ester is hydrolysed during the reaction to the final products hydroquinone and the acetate ion (6). They also noted that concentrations of reactant *p*HAP and product acetate could be monitored by NMR from their methyl resonances since these were sharp, upfield from water and separated by about 0.6 ppm. To try to clarify the role of the intermediate HMA in the mechanism, we have now extended the study of the alkaline peroxide oxidation of hydroxyketones in aqueous solution to situations in which the hydrogen peroxide is in 2–10 times excess, conditions that more closely resemble the stoichiometric to 6 times excess, peroxide to carbonyl content, typically used in the bleaching of wood pulp (7).

Results and discussion

The fractions of the original amount of a 0.29 mmol sample of *p*HAP left during its reaction with 1.44 mmol of hydrogen peroxide in the presence of sodium hydroxide or sodium carbonate in 1.2 mL of aqueous solution at 30°C was determined from the relative peak heights of the proton methyl resonances of the *p*HAP reactant and the acetate product (Scheme 1). Hydroquinone, the aromatic product, did not rapidly undergo significant further reaction under the conditions used. The reaction was predictable and the results were surprisingly consistent from one kinetic run to the next. No evidence of oxygen formation, which could indicate the presence of free radicals, was seen, probably because phenols are effective free radical scavengers.

Figure 1 shows the rate curve for this reaction in the presence of 0.30 mmol of base. Examples of the raw concentration data used to draw the graphs in Figs. 1 and 3 are given in Table 1. In both sodium carbonate and sodium hydroxide solutions the reaction has an induction period, which was very helpful for the monitoring method used, followed by a period when the reac-

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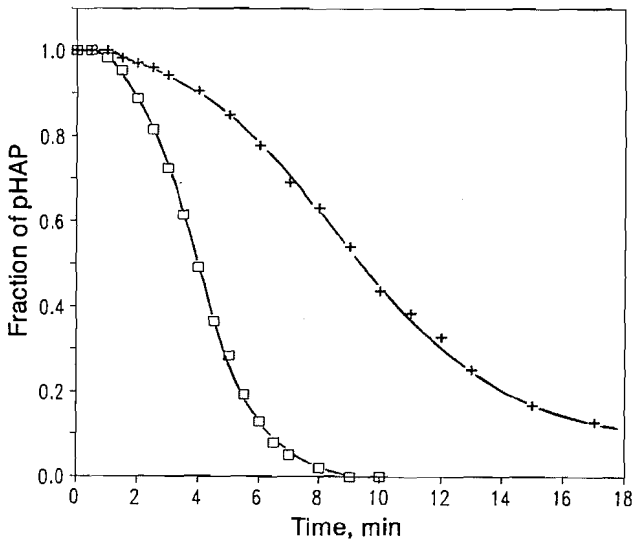


FIG. 1. Fraction of initial amount of *p*HAP remaining vs. time on oxidation of 0.29 mmol of *p*HAP with 1.44 mmol H_2O_2 in 1.2 mL of aqueous 0.25 M base at 30°C. +, for sodium hydroxide, run 3; □, for sodium carbonate, run 12.

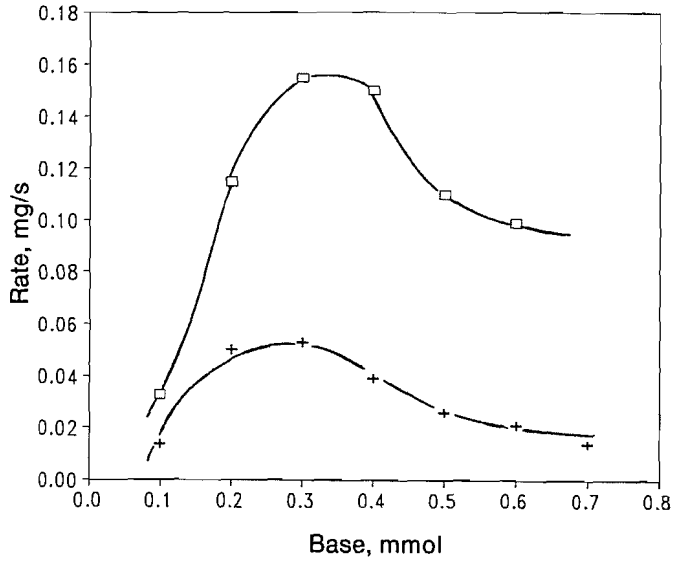


FIG. 2. Rate of oxidation of 0.29 mmol of *p*HAP with 1.44 mmol of hydrogen peroxide in 1.2 mL of aqueous base at 30°C. +, for sodium hydroxide runs 1–8; □, for sodium carbonate, runs 9–15.

TABLE 1. Effect of additives on the fraction of initial *p*HAP left for the reaction of 40 mg of *p*HAP (0.29 mmol) with 1.44 mmol of H_2O_2 and 0.30 mmol of NaOH, in a total volume of 1.2 mL at 30°C

	Fraction[a] of *p*HAP left with the following additives			
Time (min)	None, run 3	Hydroquinone (9.1 μmol), run 21	HMA (9.1 μmol), run 22	Sodium peracetate (9.1 μmol), run 24
0	1.000	1.000	1.000	1.000
1	1.000	1.000	0.919	0.882
2	0.962	0.984	0.818	0.750
3	0.943	0.967	0.727	0.603
4	0.907	0.935	0.615	0.485
5	0.850	0.865	0.477	0.338
6	0.778	0.818	0.383	0.228
7	0.692	0.730	0.304	0.161
8	0.632	0.666	0.216	0.128
9	0.540	0.581	0.174	
10	0.436	0.484	0.132	
11	0.385	0.421	0.101	
12	0.326	0.341		
13	0.250	0.274		
15	0.166	0.241		
17	0.127	0.143		

[a]Values of (*p*HAP methyl peak height)/(sum of *p*HAP methyl and acetate methyl peak heights) were calculated to three significant figures and are accurate to two figures. Estimated error in fraction data is ±4%.

tion occurs at a relatively constant rate. The rate of reaction was taken to be the slope of the linear portion of the rate curve in milligrams of *p*HAP per second. A series of kinetic runs with various initial concentrations of reactants gave similarly shaped rate curves, although the induction period varied from 1 to 7 min. The rate, which was reproducible to within ±5% for the same set of conditions, depended on the nature of the base used and the initial concentration of reactants. Values of rates obtained are given in Table 2.

The curves plotted in Fig. 2, for the reaction of 0.29 mmol of *p*HAP with 1.44 mmol of hydrogen peroxide in various molar concentrations of aqueous base, show that the rate is invariably greater in sodium carbonate than sodium hydroxide solution, and that there is an optimum base concentration for each base to obtain the maximum rate. Interestingly this parallels the observed behaviour of alkaline hydrogen peroxide in the bleaching of wood pulp, which also shows an optimum base concentration for maximum effectiveness (7, 8).

Sigmoidal-shaped rate curves similar to the ones in Fig. 1 are characteristic of reactions that are autocatalysed and depend on the presence of an intermediate generated during the induction period by the reaction. To determine the nature of the intermediate, the oxidation reactions were repeated in the presence of various additives. Addition of magnesium sulphate, which is commonly used as a stabilizer in pulp bleaching (7), or the reaction products acetate and hydroquinone had little effect on the rate. However, addition to the reaction mixture of either hydroquinone monoacetate or sodium peracetate in amounts of about 0.5 mol% of the hydrogen peroxide concentration eliminated the induction period and increased the rate somewhat.

Figure 3 shows the reactant remaining during the same reactions (0.29 mmol *p*HAP, 1.44 mmol peroxide, and 0.30 mmol NaOH in 1.2 mL solution at 30°C) with and without the presence of 0.0054 mmol of sodium peracetate added at the start of the reaction at the same time as the hydrogen peroxide.

An extension of earlier NMR studies confirmed that HMA and other phenyl esters, such as hydroquinone diacetate and acetyl salicylate, in the presence of alkaline hydrogen peroxide are hydrolysed to phenols and peracetate rather than acetate (6). That peracetate was produced was confirmed by both ^1H and ^{13}C NMR (Table 3). However, peracetate possesses limited stability in the alkaline solutions used. Its slow decay to acetate could be followed by ^1H NMR scans at 5-min intervals; under the conditions used for the kinetic runs, half of a sample of peracetate had decomposed to acetate within 10 min. Hofman et al. have studied the hydrolysis by alkaline hydrogen peroxide of various *N*- and *O*-acetyl esters and found that peracetate, rather than acetate, is the major hydrolysis product (10). Clearly the

TABLE 2. Summary of measured data for the oxidation of *o*HAP and *p*HAP in 1.2 mL of aqueous solution at 30°C using proportions of reactants given

Run	Hydroxyketone[a]	Base[b]	Hydrogen peroxide[a]	Additives[a,c]	Rate[d] (mg/s)	Induction period[e]	Initial pH[f]
1	0.29 *p*	0.10 H	1.44		0.014		
2	0.29 *p*	0.20 H	1.44		0.050		8.5
3	0.29 *p*	0.30 H	1.44		0.052		9.4
4	0.29 *p*	0.30 H	1.44		0.052		
5	0.29 *p*	0.40 H	1.44		0.039		10.7
6	0.29 *p*	0.50 H	1.44		0.026		11.5
7	0.29 *p*	0.60 H	1.44		0.021		11.9
8	0.29 *p*	0.70 H	1.44		0.014		
9	0.29 *p*	0.10 C	1.44		0.033		7.9
10	0.29 *p*	0.20 C	1.44		0.12		8.7
11	0.29 *p*	0.30 C	1.44		0.16		9.3
12	0.29 *p*	0.30 C	1.44		0.15		
13	0.29 *p*	0.40 C	1.44		0.14		9.7
14	0.29 *p*	0.50 C	1.44		0.11		9.8
15	0.29 *p*	0.60 C	1.44		0.099		
16	0.29 *p*	0.40 C	2.16		0.17		
17	0.29 *p*	0.40 C	2.88		0.18		
18	0.15 *p*	0.40 C	1.44		0.033		
19	0.44 *p*	0.40 C	1.44		0.23		
20	0.29 *p*	0.30 C	1.44	0.050 Mg	0.057		
21	0.29 *p*	0.30 H	1.44	0.0091 Hq	0.051		
22	0.29 *p*	0.30 H	1.44	0.0066 HMA	0.071	No	
23	0.29 *p*	0.30 H	1.44	0.0132 HMA	0.12	No	
24	0.29 *p*	0.30 H	1.44	0.0054 Pa	0.087	No	
25	0.29 *p*	0.40 H	1.44	0.0091 Hq	0.033		
26	0.29 *p*	0.40 H	1.44	0.0074 Ac	0.036		
27	0.29 *p*	0.40 H	1.44	0.0132 HMA	0.041	No	
28	0.29 *p*	0.60 C	1.44	0.0066 HMA	0.10	No	
29	0.29 *p*	0.60 C	1.44	0.0054 Pa	0.089	No	
30	0.29 *o*	0.60 H	0.72		0.5 (est)	No	
31	0.29 *p*	0.60 H	0.72		0.011		
32	0.29 *o*	0.90 H	0.72		0.042		
33	0.29 *o*	0.90 H	0.72	0.0054 Pa	0.076	No	
34	0.25 *p*	0.40 H	0.0	0.27 Pa	2.8* (est)	No	

[a]Reactant and additive quantities are given in millimoles. *p* = *p*HAP, *o* = *o*HAP.
[b]H = sodium hydroxide, C = sodium carbonate. Quantities are given in millimoles.
[c]Additives: Mg = magnesium sulphate; Hq = hydroquinone; Ac = sodium acetate; HMA = hydroquinone monoacetate; Pa = sodium peracetate; none where none specified.
[d]Rate is the slope of the linear portion of the rate curve, except for the asterisk where the rate is calculated from the slope of 1/(fraction of *p*HAP left) vs. time. est reactions were too fast to allow accurate determination of the rate.
[e]All runs had an induction period, except where noted.
[f]The pH was measured at the start of the reaction for the runs given.

peracetate ion, generated from hydroquinone monoacetate and hydrogen peroxide, is the active oxidizing agent in this autocatalysed reaction. A probable mechanism for the reaction that fits the observed requirements is shown in Scheme 2.

The key sequence of reactions in the mechanism proposed is the nucleophilic attack of peracetate on the carbonyl carbon of *p*HAP, followed by rearrangement of the peroxy adduct to hydroquinone monoacetate. This is hydrolysed by the hydroperoxide anion to hydroquinone and another peracetate ion that continues the oxidation cycle. The peracetate concentration rapidly builds up to a steady state, resulting in the constant rate observed in these reactions.

The reaction went only slightly faster, 0.17 vs. 0.14 mg *p*HAP per second, when the initial amount of hydrogen peroxide was increased to 2.16 mmol in run 16 from 1.44 mmol in run 13. When the initial amount of *p*HAP was increased from 0.29 mmol in run 13 to 0.44 mmol in run 19, the reaction rate increased markedly from 0.14 to 0.23 mg/s. These observations would indicate that step 4 in the mechanism, attack of peracetate on the hydroxyketone, is slower than step 3, hydrolysis of HMA by hydroperoxide anion to peracetate.

The mechanism presented is also supported by the results of the reaction of *p*HAP with an equivalent amount of peracetate in slightly basic solution (run 34 in Table 2). This reaction has no induction period and, with a rate of 2.8 mg/s, was 70 times faster than the rate observed for the oxidation of *p*HAP with hydrogen peroxide. These characteristics meant that the reaction of *p*HAP with peracetate was particularly difficult to follow by the NMR method used and reliable numerical data were hard to obtain, hence information on the rate of the reaction was of doubtful value.

Ogata and Sawaki (11) reported that the oxidation of hydroxyketones by peroxybenzoic acid is a second-order process, so it is likely that the oxidation of *p*HAP by peracetate, a similar process, also follows second-order kinetics. When the reaction between *p*HAP and peracetate in sodium hydroxide

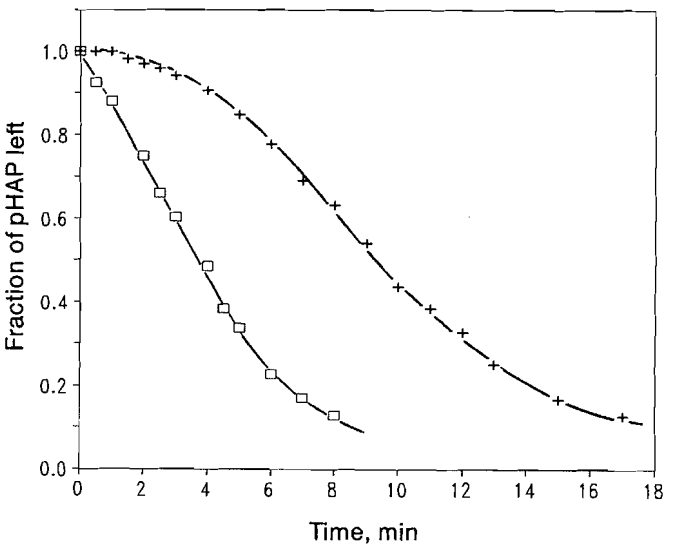
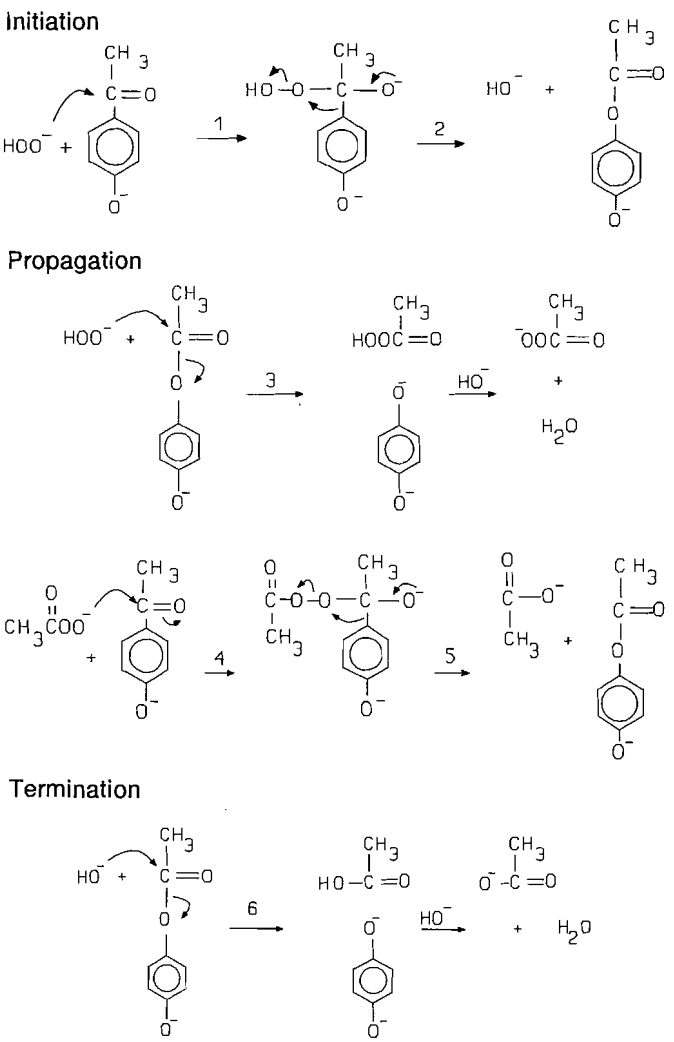


FIG. 3. Fraction of 0.29 mmol of *p*HAP remaining during oxidation by 1.44 mmol hydrogen peroxide in 1.2 mL of solution containing 0.3 mmol of sodium hydroxide at 30°C. +, without other additives, run 3; □, with 5.4 μmol of added peracetate, run 24.



SCHEME 2. Proposed mechanism for the hydrogen peroxide oxidation of *p*HAP which produces and uses peracetate.

solution at pH 8 was scaled up and subsequently extracted with ether, it was possible to obtain crystals of HMA in 10% yield. NMR scans of this reaction mixture prior to extraction showed much larger concentrations of HMA present (by far the largest peak) in addition to hydroquinone and acetate ions, but rapid hydrolysis of the rather labile HMA under the basic conditions used decreased the actual recovery of solid product. High-amplification NMR scans of the reaction mixture of *p*HAP and hydrogen peroxide used earlier in the kinetic runs showed small methyl resonances at the shifts expected for peracetate and HMA, in addition to those of reactant and product. The elimination of the induction period by initial addition of peracetate, the known formation of peracetate from hydrogen peroxide and HMA, and the fast reaction of peracetate and *p*HAP strongly support the proposed mechanism.

Previous studies of the reaction of *o*HAP with alkaline hydrogen peroxide showed that the reaction is fast at low pH, but much slower at pHs over 12 (11, 12). The reaction between 0.3 mmol of *o*HAP and 0.72 mmol of hydrogen peroxide in the presence of 0.9 mmol (0.75 M) of sodium hydroxide in a total volume of 1.2 mL was quite slow and found to have an induction period that was removed when peracetate was added at the start of the reaction. It seems probable that under these conditions the *ortho* isomer also reacts by a mechanism similar to that proposed earlier for the *para* isomer. When the concentration of sodium hydroxide was decreased to 0.5 M (0.6 mmol of NaOH added), this reaction was much faster; it was essentially complete in 90 s (e.g., runs 32 and 30 in Table 2). This was too fast to quantitatively measure by the NMR method used, nor could an induction period be detected under these conditions. Therefore, it is likely that the fast oxidation of *o*HAP proceeds via a different mechanism, one that does not require generation of peracetate, when the base concentration is lower.

*m*HAP, which is much less reactive than the *ortho* and *para* isomers for electronic reasons, did not react with either hydrogen peroxide or peracetate in dilute aqueous sodium hydroxide.

The mechanism proposed for the reaction of *p*HAP with alkaline hydrogen peroxide explains the observed dependence of the rate on base type and concentration. Base is required to ensure significant dissociation of hydrogen peroxide to the hydroperoxide anion required for the cleavage of hydroquinone monoacetate to peracetate and hydroquinone. Hydroxide ions, when present in excess of the amount required to produce the hydroperoxide anion, can hydrolyse HMA to hydroquinone and acetate and so will compete with the hydroperoxide anion for the available HMA, causing a lower steady-state concentration of both HMA and peracetate and hence a slower reaction. Thus, we would expect the rate of ketone oxidation to be greater in aqueous sodium carbonate, which provides sufficient alkalinity without a high concentration of hydroxide ions, than in aqueous sodium hydroxide solution. This explanation would also predict that there should be an optimum base concentration for maximum rate as is observed, rather than a progressive increase of rate with base concentration.

Interpretation of the relevance of these results to the brightening reactions of softwood mechanical pulps is complex (13, 14). As seen with the model compound here, there is an optimum ratio of sodium hydroxide to pulp for any given peroxide:pulp ratio to achieve maximum brightness. However, this is not so much rate related as a factor of residual hydroxide ion concentration (or pH) at the time that the peroxide component of the brightening system used is exhausted. Too high a pH at this stage promotes pulp-darkening reactions.

TABLE 3. Summary of experimentally observed NMR shift data

Substances	^{1}H NMR (ppm)[a]	^{13}C NMR (ppm)[b]
Sodium acetate	1.9	20.2 (CH_3), 176.5 (CO)
Sodium peracetate	2.1	16.7 (CH_3), 172.6 (CO)
Hydroquinone	6.9	(115.6, 149.7)[c]
Hydroquinone monoacetate	2.3, 7.0d (J = 1 Hz)	
HMA + H_2O_2[d]	2.1, 2.3, 6.9, 7.0d (J = 1 Hz)	
HMA + H_2O_2 + Na_2CO_3[e]	2.1, 6.9	16.7, 20.2, 116.2 148.8, 172.6, 176.6
*p*HAP	2.5, 6.7d, 7.7d (J = 10 Hz)	
Runs 3 (high amplitude)	1.9, 2.1, 2.3, 2.5 (CH_3 only)	

[a]All ^{1}H NMR spectra were measured on 10-ppm sweep widths at 30°C on a Perkin Elmer R-32 continuous wave spectrometer at 90 MHz in 2% aqueous solution relative to an external TMS standard in $CDCl_3$. d, doublet.

[b]^{13}C NMR shifts were referenced to TMS, were measured on 188-ppm sweep width in aqueous solution at ambient temperature on a Bruker AMX 360 FT spectrometer at 90.568 MHz locked to an internal D_2O reference, and are nonquantitative. Collection parameters for the sodium acetate and sodium peracetate spectra: acquisition time, 0.623 s; relaxation delay, 0.100 s; recycle time, 0.723 s; from 700 transients. Collection conditions for the oxidation mixture spectrum (footnote *e*) were as follows: acquisition time, 0.819 s; relaxation delay, 0.100 s; recycle time, 0.919 s, for a total of 3300 transients.

[c]From ref. 9; in dimethyl sulphoxide.

[d]21.5 mg HMA in 1 mL of D_2O and 0.2 mL of 7.2 M H_2O_2.

[e]21.5 mg HMA in 1 mL of D_2O and 0.2 mL of 7.2 M H_2O_2, and 0.2 mL of 1 M Na_2CO_3.

It is also difficult to directly translate the promising rate measurements of *p*HAP oxidation in aqueous sodium carbonate to the brightening reactions of mechanical pulps. Decreased brightness gains of 1–1.5 points, but with improved brightness stability, has been reported from tests of partial replacement of sodium hydroxide by sodium carbonate in the peroxide brightening of spruce chemithermomechanical pulp (CTMP) (15). Full replacement of sodium carbonate has also been reported to yield equivalent final brightness with aspen CTMP, while also providing superior peroxide stabilization and consequent higher peroxide residuals (16). Our model compound rate findings confirm the need evident from these results to further explore the benefits to be achieved by optimized conditions for sodium carbonate replacement in the peroxide-based bleaching of wood pulps.

Experimental

Commercial *p*HAP and *m*HAP were purified by recrystallization from toluene and then water before use. Hydroquinone monoacetate was obtained as previously described (5). Commercial peracetic acid (32%) was analyzed for acid equivalence by titration with sodium hydroxide solution, for peroxide concentration by titration with permanganate solution (17), and for total oxidizing ability by addition of potassium iodide and subsequent titration with thiosulphate (18). The concentration of commercial 30% hydrogen peroxide was checked by addition of iodide and then titration with aqueous thiosulphate solution (18). It was diluted with distilled and deionized water to make its concentration 7.2 M before use.

^{1}H NMR spectra and the quantitative work for the kinetic runs were carried out on aqueous solutions at 30°C on a Perkin Elmer R-32 continuous wave spectrometer at 90 MHz. ^{13}C spectra were run at ambient temperature at 90.568 MHz on a Bruker AMX 360 FT NMR spectrometer. Values of pH were measured on a Metrohm 632 pH meter standardized at pH 9.18. Mass spectra were run on a Finnigan 3300 quadrupole GC–MS system spectrometer.

Kinetic experiments

The starting amount of hydroxyketone (usually 40 mg, 0.29 mmol) was dissolved in the required volume of 1.0 M base. The required amount of distilled, deionized water was added so that the final volume after all additions would be 1.2 mL for all kinetic runs. The solution was placed in the spectrometer in a 5-mm NMR tube and allowed to reach 30°C. The required amount (usually 0.2 mL) of 7.2 M hydrogen peroxide solution (1.44 mmol) was added to the sample, timing was started, and the mixture was shaken for 5 s. NMR scans of the methyl peaks in the region of 2.6–1.8 ppm were made every 30 or 60 s as the HAP methyl resonance decreased in size, while that of the acetate increased. In most cases the sum of the two peak heights stayed remarkably constant (about 80 mm) during the run. The fraction of reactant remaining was calculated from the relative peak heights. Previous studies had indicated that the peak height was a reliable measure of the relative amount of substance in solution (5, 12). Occasionally impurities caused decomposition of the peroxide to oxygen, which resulted in a rapid loss of resolution and collapse of the methyl resonances. Additives, when used, were dissolved in the appropriate amount of water and added to the mixture immediately after the hydrogen peroxide solution. To prevent premature decomposition of the peracetic acid, it was diluted and neutralized immediately before use by adding 0.1 mL of it to 10 mL of 0.122 M NaOH solution. One tenth of a millilitre of this diluted solution contained 0.0054 mmol of neutralized peracetate ion.

Preparation of HMA from peracetate and pHAP

*p*HAP (500 mg) was dissolved in 6 mL of 1 M NaOH. To this was added 6 mL of 1 M NaOH containing 1 mL of peracetic acid. The pH was adjusted to 8 by addition of a few more drops of NaOH solution. The mixture was stirred for 15 min at room temperature and then extracted with three 10-mL portions of diethyl ether. The combined extracts were dried with anhydrous sodium sulphate and the ether was evaporated under reduced pressure. The residual oil was pumped on a vacuum line for 1 h. The residue was extracted with two 60-mL portions of hot hexane, which were allowed to cool very slowly (24 h) to −10°C. The yield was very variable, during several repetitions; 45–100 mg of crystalline HMA was obtained, mp 55–58°C (lit. (19) mp 61–63°C). The ^{1}H NMR spectrum was identical to that of authentic material. The chemical ionization mass spectrum showed peaks at 154 (M + 1), 181 (M + 29), and 193 (M + 41).

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