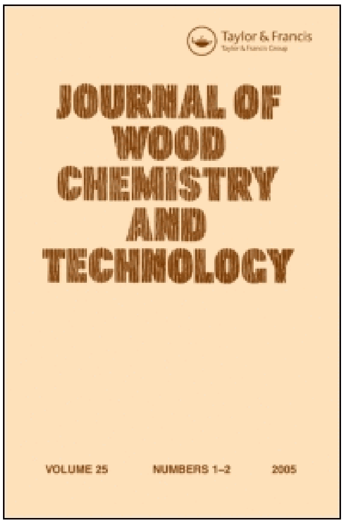

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Stephen D. Kinrade[a]; David G. Holah[a]; Geoffrey S. Hill[a]; Kimberley E. Menuz[a]; Constance R. Smith[a]
[a] Department of Chemistry, Lakehead University, Thunder Bay, Ontario, Canada

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THE PEROXYSILICATE QUESTION. ^{29}SI-NMR EVIDENCE FOR THE ROLE OF SILICATES IN ALKALINE PEROXIDE BRIGHTENING OF MECHANICAL PULP

Stephen D. Kinrade*, David G. Holah, Geoffrey S. Hill,
Kimberley E. Menuz, and Constance R. Smith
Department of Chemistry, Lakehead University,
Thunder Bay, Ontario, Canada P7B 5E1

ABSTRACT

The influence of hydrogen peroxide on the chemistry of aqueous silicates was investigated by high-resolution ^{29}Si-NMR and electrochemical methods. The observations indicate that dissolved silicates form labile complexes with radical H_2O_2-decomposition products, possibly $O_2^{\cdot -}$. An important role of soluble silicates in peroxide bleaching liquors thus might be to affect the activity of free radical species which mediate H_2O_2 bleaching and decomposition reactions. Attempts to prepare the widely reported peroxysilicates from silicate/H_2O_2/NaOH mixtures resulted in the isolation of $Na_2O_2 \cdot 8H_2O$.

INTRODUCTION

Of the hundreds of compounds reported to stabilize hydrogen peroxide, sodium silicate is the material that finds almost universal use as an additive to alkaline peroxide liquors for the bleaching of mechanical pulps, in spite of problems sometimes caused by silicates in other parts of the mill.[1] Not only do silicates reduce peroxide consumption through decomposition, they reportedly yield brighter pulp through more efficient use of the peroxide.[1-4] Roles postulated for aqueous silicates include buffering, deactivation of metal and metal oxide surfaces, sequestering of dissolved metals, quenching of free radicals, and direct interaction with hydrogen peroxide to form compounds generally referred to as "peroxysilicate" anions that may include silicate hydroperoxides $\equiv$Si-OOH, peroxosilicates $\equiv$Si-OO-Si$\equiv$, or silicate peroxohydrates $\equiv$SiOH·nH_2O_2.

In a series of carefully designed experiments, Dence and coworkers[6,7] investigated the various roles proposed and concluded in agreement with others[2,8] that a major, but by no means total,[2] function of silicates is deactivation of the metal cations which catalyze peroxide decomposition. Soon after, Abbot[9] reported evidence for silicate-manganese complexation which he correlated to suppressed catalytic activity of dissolved Mn in the presence of silicates. Yet, metal deactivation does not of itself account for the ability of silicates to enhance pulp brightness. Several studies[10,11] indicate that radicals formed during metal catalyzed H_2O_2 decomposition may play an important role in pulp bleaching (particularly, the hydroxyl radical[11]). Most recently, Gierer *et al.*[11] demonstrated that the primary role of silicates is neither metal complexing nor scavenging of hydroxyl radicals. Existence of peroxysilicates is supported by reports[5,12-14] of solid compounds that are formed from silicate-peroxide mixtures and variously referred to as $Na_2SiO_3 \cdot xH_2O_2$,[12,13] sodium persilicate[14] and sodium peroxysilicate;[5] the latter was shown to bleach pulp. Whiting[15] has obtained UV spectroscopic evidence for an aqueous compound formed between peroxide and silicate and there is a report[16] of the cleavage of benzil by hydrogen peroxide catalyzed by silicates via what is described as a peroxosilicate. It has been suggested that peroxysilicate "increases catalytically the oxidizing effect (bleaching force)" of hydrogen peroxide,[4] although it is not clear if this infers a change in the reduction potential. Another suggestion has been that the peroxysilicates are superior brightening agents that react directly with lignin chromophores.[4,5] Colodette *et al.*[6] on the other hand concluded that, if formed, peroxysilicates neither stabilize peroxide nor enhance its reactivity. Thus, the matter of peroxysilicates is by no means settled. The formation of such species might well be part of complex and highly labile silicate equilibria, the characterization of which is feasible only through high-resolution ^{29}Si-NMR spectroscopy.[17-19] The objective of the present study is therefore to employ NMR spectroscopy to ascertain the nature of silicate-peroxide interactions in solution.

EXPERIMENTAL

Aqueous hydroxide solutions were prepared from NaOH, KOH (both 99.99%), RbOH, CsOH (both 99.9%), tetramethylammonium (TMA) hydroxide and tetra-*n*-propylammonium (TPA) hydroxide (all Aldrich) using deionized (18 Mohm) distilled water. Homogeneous silicate solutions (0.1 to 5.0 mol kg^{-1}) were prepared by dissolving amorphous silica, obtained either by hydrolysis of $SiCl_4$ (Aldrich, 99.999%) or as 67.3% ^{29}Si-enriched SiO_2 (Isotech), in standardized base solutions at *ca.* 90 °C. All samples to be analyzed by NMR were 15% isotopically enriched in deuterium to provide an internal field-frequency lock signal. Hydrogen peroxide (Caledon, 30%; solutions from Aldrich and BDH yielded identical results) was added to silicate solutions at 0 °C. The peroxide content of solutions was periodically determined by titration with $KI/Na_2S_2O_3$.[20] Small quantities of $MgCl_2$ (Caledon), 2,2,6,6-tetramethyl-1-piperidinyloxy ("TEMPO") free radical (Aldrich), and 2,6-dimethoxyphenol were added to selected silicate solutions, with and without peroxide. Solutions were exposed only to surfaces of low-density polyethylene and Teflon FEP/TFE in order to minimize contamination by adventitious metal ions. In most cases, H_2O_2-containing solutions were stable for at least 12 hours at 0 °C, *i.e.*, so long as impurities were carefully eschewed and pH exceeded that required for silicate solubility. Copious evolution of ammonia-smelling gases occurred upon H_2O_2 addition to solutions containing TPA cations but not in the case of solutions containing TMA.

The pH of thermostated solutions was measured at 0 °C (K_w = 14.944) using a low alkali-error glass electrode and a double-junction reference cell with 1 mol kg^{-1} NaOH as the bridging electrolyte. Data were referenced against typical pH standards including saturated $Ca(OH)_2$. Alkali-metal error was overcome by fixing alkali-metal content in those solutions for which pH was to be compared, or eliminated altogether by eschewing cations lighter than Rb^+. In the case of ^2H-enriched solutions, pH measurements were corrected (typically, by −0.3 pH units) based on comparisons of equivalent deuterated and non-deuterated samples. Reduction potential was measured of selected samples.

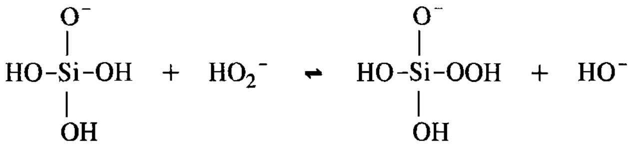
^{29}Si NMR spectra (39.73 MHz) were obtained at −5 to 30 °C on a Bruker AC-E 200 spectrometer using Si-free sample tubes[21] and probe head inserts. 90° pulses were cycled over periods > 3 to 5 times the largest T_1 values. Care was taken to ensure that NMR line shapes were not affected by O_2 bubbles resulting from H_2O_2 decomposition. ESR spectra of selected sodium silicate solutions were obtained on Varian E3 and E104 spectrometers.

RESULTS AND DISCUSSION

Since the ^{29}Si isotope has a natural abundance of only 4.67% and typically undergoes very slow spin-lattice relaxation, it is advantageous to work at high Si concentrations so that NMR spectra can be acquired in reasonable periods of time (*i.e.*, < 24 h). The solubility of silicates increases significantly with increasing pH (*e.g.*, 0.01 and 1 mol kg^{-1} Si at pH 10.5 and 11.5, respectively, at 25 °C) and, therefore, much of this work was done at pH values higher than those typical of alkaline peroxide brightening reactions. Aside from increased solubility, however, an advantage to working at very high pH is that the concentration of HOO^- is also high

$$H_2O_2 + OH^- \rightleftharpoons H_2O + HOO^- \qquad (1)$$

(< 10% of peroxide is present as HOO^- at pH 10.5, > 90% at pH 12.5 [22]) which, as suggested by Colodette *et al.*,[6] may favour formation of peroxysilicates.



$$HO\text{-}\overset{\overset{\textstyle O^-}{|}}{\underset{\underset{\textstyle OH}{|}}{Si}}\text{-}OH + HO_2^- \rightarrow HO\text{-}\overset{\overset{\textstyle O^-}{|}}{\underset{\underset{\textstyle OH}{|}}{Si}}\text{-}OOH + HO^- \qquad (2)$$

To more nearly simulate pulp brightening conditions, *i.e.* lower pH and thus lower silicate concentration (typically 3% on o.d. pulp which is equivalent to ~0.05 mol Si per kg of pulp suspension at 10% consistency), it was necessary to employ ^{29}Si-enriched (67.3%) SiO_2. High peroxide concentrations, ranging up to 2.6 mol kg^{-1}, were used to facilitate detection of peroxysilicates. (A 5% peroxide charge on pulp at 10% consistency would be equivalent to only 0.3 mol kg^{-1} H_2O_2.)

The ^{29}Si-NMR spectra of aqueous silicates, as shown in figure 1, can contain an elaborate pattern of signals arising from a great number of silicate species. ^{29}Si nuclei resonate at progressively lower frequencies as their connectivity to silicate tetrahedra increases. In accordance with established practice, the Q^y symbol is employed to represent a quadrafunctional Si center with *y*-connectivity, *i.e.*, *y*-coordinated $-O-Si\equiv$ linkages. (Often, Q^2 and Q^3 centers are subdivided in accordance with the spectral region, A or B, in which they resonate.) The connectivity of Si can not exceed 3 for true solution species and, therefore, sharp Q^4 resonances are not observed.[18] However, a broad Q^4 band will arise from solid or colloidal silica. Figure 1 also demonstrates the equilibrium shift towards smaller silicate polyanions as dissolved SiO_2 concentration is decreased.[18] All peak assignments are from previous studies.[17,18]

The influence of H_2O_2 content on ^{29}Si-NMR spectra of alkali-metal silicates is demonstrated in figures 2 through 8. Significantly, no new resonances were detected. As the peroxide concentration was raised: **1.** the extent of silicate polymerization, quantified by the relative area under ^{29}Si resonances, increased (figures 3 to 5); **2.** chemical shift δ decreased for all resonances (*i.e.* signals moved down frequency as shown in figure 6); and **3.** peak widths increased,

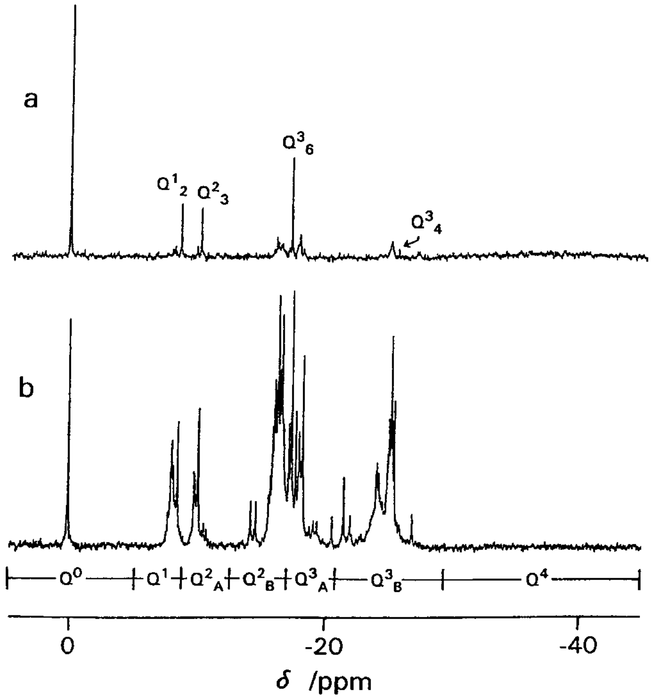


FIGURE 1. ^{29}Si-NMR spectra of solutions (a) with 0.1 mol kg^{-1} SiO_2 (67.3% isotopically enriched in ^{29}Si) and CsOH at -6 °C, and (b) with 3.0 mol kg^{-1} SiO_2 (non-enriched) and NaOH at -3 °C. Solution pH's are (a) 12.6 and (b) 14.3 at 0 °C. The singlet resonances in (a) correspond to symmetrical silicate anions: Q^0, monomer; $Q^1{}_2$, dimer; $Q^2{}_3$, cyclic trimer; $Q^2{}_4$, cyclic tetramer; $Q^3{}_6$, prismatic hexamer; and $Q^3{}_4$, tetrahedral tetramer. (All spectra in this paper have 1 Hz artificial line broadening.)

reached a maximum value, and then decreased (figures 2, 3 and 7), although peaks corresponding to the tetrahedral tetramer $Si_4O_{10}{}^{4-}$ and prismatic hexamer $Si_6O_{15}{}^{6-}$ were less affected. Peroxide similarly influenced spectra of TMA silicates, except for the single resonance corresponding to the octameric $Si_8O_{25}{}^{8-}$ species; this species is shielded from interaction with other solute species by a shell of hydrated TMA cations.[23]

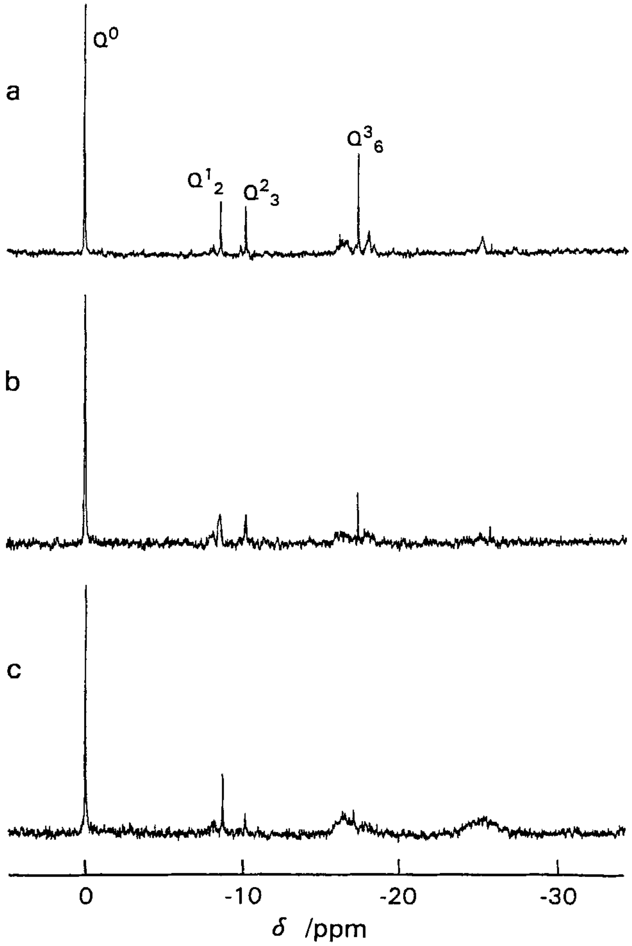


FIGURE 2. ^{29}Si spectra at −6 °C of freshly prepared solutions containing 0.10 mol kg^{-1} SiO_2 (67.3% isotopically enriched) and CsOH. Solution (b) also contains 0.50 mol kg^{-1} H_2O_2 whereas (c) contains 0.50 mol kg^{-1} H_2O_2 plus a further 0.25 mol kg^{-1} CsOH that was added to restore pH. The pH values at 0 °C are (a) 12.6, (b) 11.4 and (c) 12.6. The silicate and peroxide concentrations of solution (b) reasonably approximate that of a pulp brightening liquor.

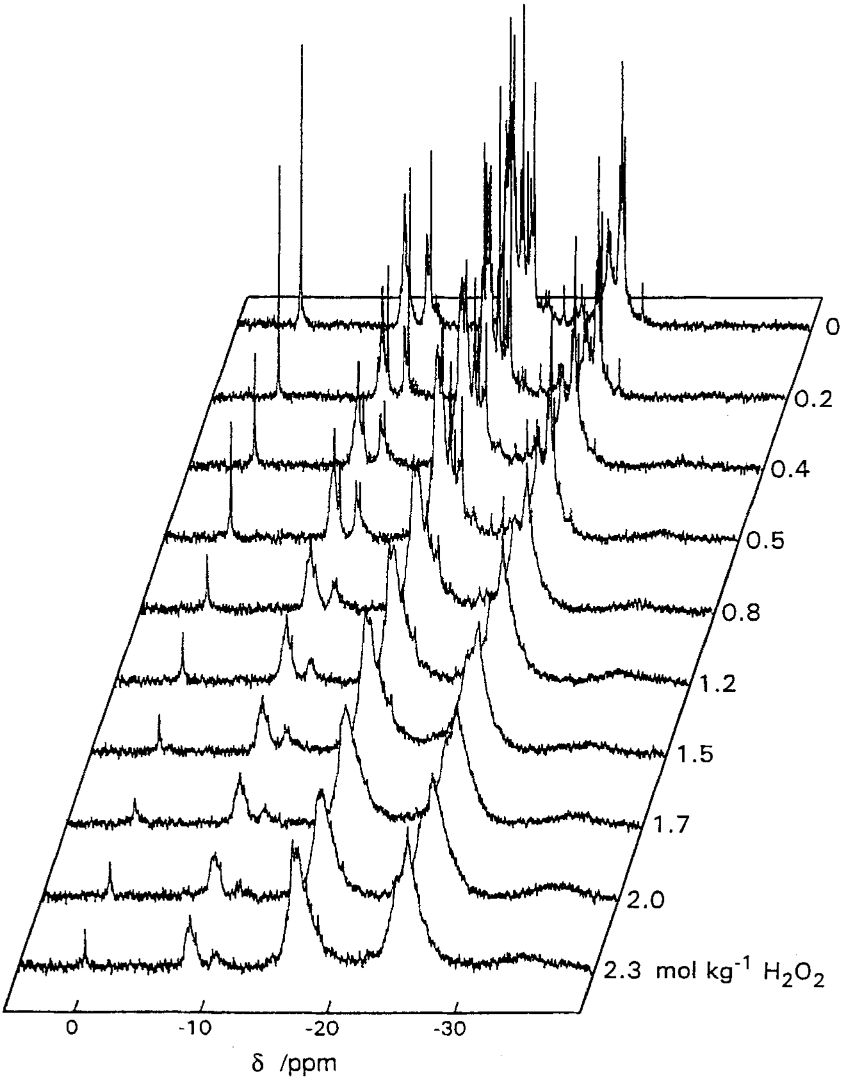


FIGURE 3. ^{29}Si spectra at 3 °C of freshly prepared solutions containing 3.0 mol kg^{-1} SiO_2 and NaOH along with varying amounts of hydrogen peroxide. Solution pH decreased from 14.3 to 11.7 at 0 °C as the H_2O_2 concentration was increased from 0 to 2.6 mol kg^{-1}.

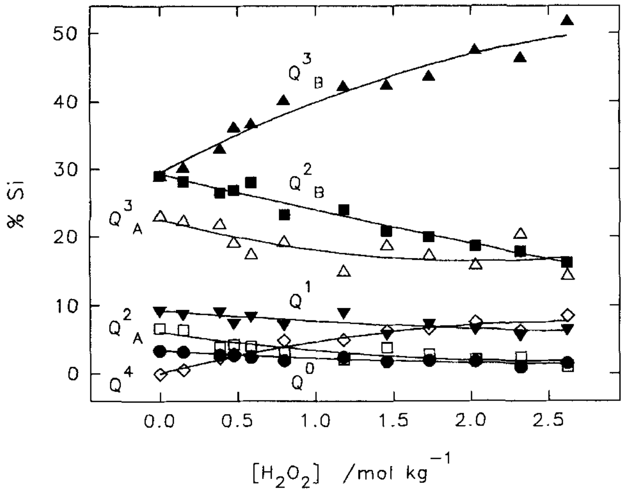


FIGURE 4. Distribution of dissolved silicon among different connectivity states (labelled) as a function of H_2O_2 concentration for the spectra in figure 3.

Commercial H_2O_2 solutions typically contain a stabilizing additive such as sodium pyrophosphate, acetanilide or one of several proprietary formulations. However, ^{29}Si spectra were independent of the source of peroxide and thus of the stabilizer in solution. Nor were they affected by addition to solutions of *ca.* 10^{-2} mol kg^{-1} sodium pyrophosphate or acetanilide. Furthermore, sealed samples in which all peroxide had decomposed over a period of several months – but still containing any contaminants – yielded ^{29}Si spectra identical to those of peroxide-free solutions. Therefore, none of the influences on NMR spectra can be attributed to additives or contaminants introduced with the hydrogen peroxide.

Hydrogen peroxide is a weak acid with $pK_a = 11.8$ at 20 °C. Since pH is well known to affect silicate equilibria and kinetics,[18,19] the next task is to ascertain how much of peroxide's influence on ^{29}Si spectra simply is due to a shift in pH. Experiments were performed using several peroxide silicate solutions

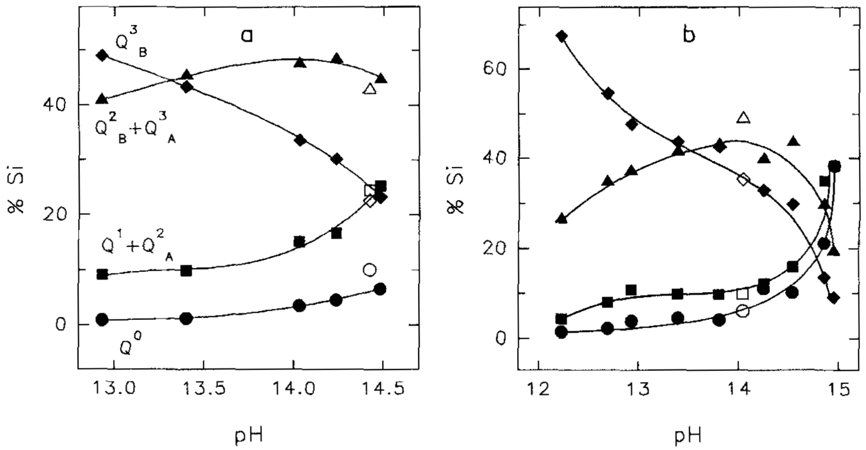


FIGURE 5. Distribution of dissolved silicon among different connectivity states as a function of pH (at 0 °C) in solutions (a) with 3.0 mol kg^{-1} SiO_2, RbOH, and (b) with 1.0 mol kg^{-1} SiO_2, CsOH. Open symbols correspond to solutions without H_2O_2. Addition of 1.35 mol kg^{-1} H_2O_2 caused pH to decrease sharply (to that of the left-most closed symbols). pH was raised by successive additions of the corresponding metal hydroxide. For simplicity, Q^4 connectivity has been excluded.

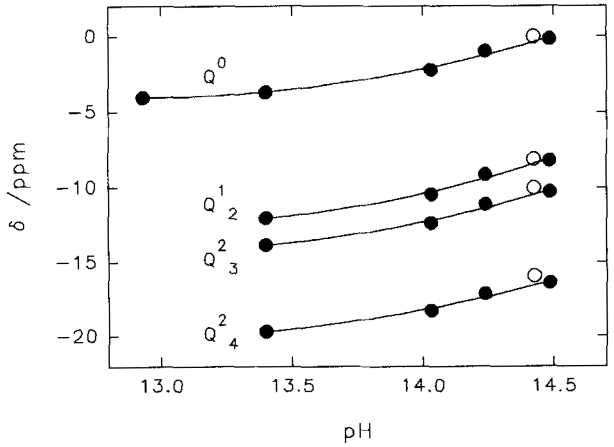


FIGURE 6. pH dependence of selected ^{29}Si resonances for the spectra represented in figure 5a. Chemical shifts δ are relative to the monomer Q^0 signal of the H_2O_2-free solution. Broadening at the lowest pH was so extreme that only the Q^0 resonance could be resolved. Open symbols again correspond to the peroxide-free solution.

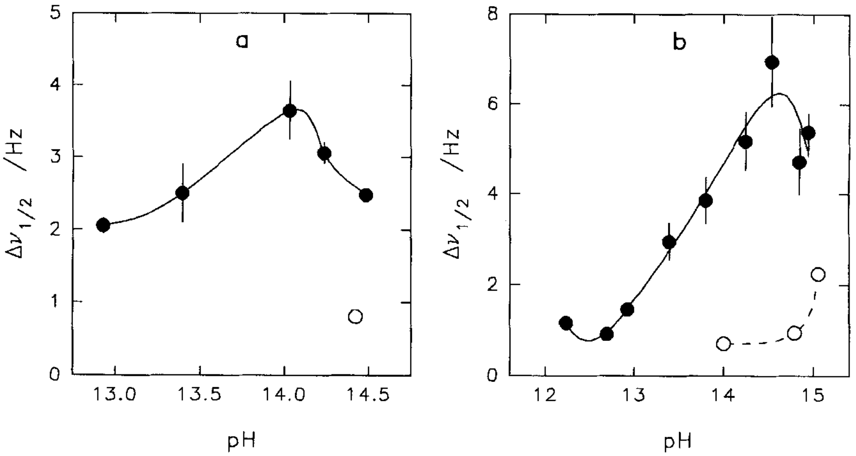


FIGURE 7. Half-height width $\Delta\nu_{1/2}$ of the monomer ^{29}Si signal as a function of pH for the spectra represented in figures (a) 5a and (b) 5b. Symbols are as in figure 5.

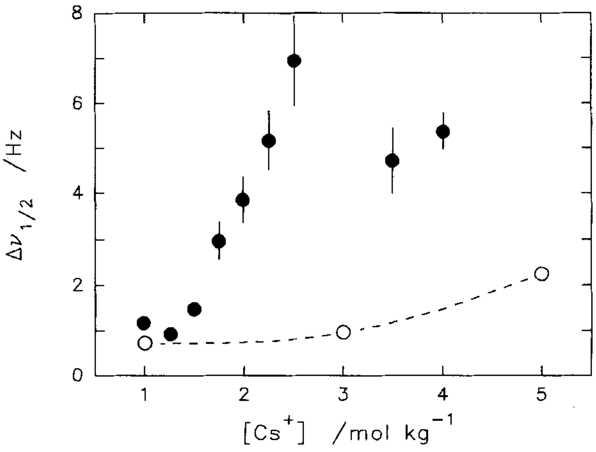


FIGURE 8. Half-height width $\Delta\nu_{1/2}$ of the monomer ^{29}Si signal as a function of Cs$^+$ concentration for the spectra represented in figure 5b. Some line broadening is associated with paramagnetic contaminants in the CsOH, but this is only a fraction of the broadening observed for solutions containing H_2O_2.

in which the hydroxide concentration was raised incrementally so as to restore pH to that of equivalent solutions not containing peroxide. Generally, the extent of polymerization in pH-adjusted peroxide solutions matched levels in the H_2O_2-free solutions (figure 5). Slightly higher levels of polymerization sometimes occurred when proportionately large amounts of base were needed to restore pH (figure 2); this is consistent with the small polymerizing influence exerted by the alkali-metal cations.[24] Chemical shifts also returned to pre-peroxide values following pH adjustment as shown in figure 6. Therefore observations **1.** and **2.** can be attributed almost entirely to the decrease in pH associated with H_2O_2 addition.

Accounting for observation **3.**, *i.e.* the effect of peroxide on ^{29}Si line widths, is not so easy. Even after pH adjustment, silicate solutions containing H_2O_2 consistently yielded broader resonances. (See figure 7 and table 1.) Moreover, line widths initially increased as pH was raised, attained a maximum value, and then decreased. The effect was similar for all alkali-metal and TMA silicate solutions. In the *absence* of peroxide, ^{29}Si line widths generally are unaffected by pH at these temperatures;[19] exchange-broadening occurs at temperatures > 25 °C but *decreases* monotonically as pH is raised.[19] (In the case of cesium silicates, a small fraction of the broadening was associated with paramagnetic contaminants in the added CsOH. See figures 7b and 8.) Broadening due to field inhomogeneity – *e.g.* as caused by O_2 bubbles from H_2O_2 decomposition – was negligible when precautions were taken.

Line widths are proportional to the rate of transverse (T_2) nuclear magnetic relaxation; *i.e.*, $\Delta\nu_{1/2} = \pi^{-1}T_2^{-1}$ where T_2^{-1} is the first-order rate constant for transverse relaxation.[22] Transverse relaxation is induced by the spin transition mechanisms that give rise to longitudinal (T_1) relaxation and also by isoenergetic processes affecting only the phase coherence of spins.[25,26] Yet, ^{29}Si T_1 relaxation rates typically *decreased* upon peroxide addition (table 1) ruling out, for instance, appreciable paramagnetic (outer-sphere) relaxation by H_2O_2-decomposition products O_2, $O_2\cdot^-$ and $HO\cdot$. The dominant T_2 relaxation contribution is therefore a consequence of either **1.** rapid ^{29}Si–^{29}Si spin site

TABLE 1.

Longitudinal (T_1^{-1}) and Translational (T_2^{-1}) Relaxation Rates for ^{29}Si Resonances of Sodium Silicate Solutions.

Solution [a]	$[H_2O_2]$ /mol kg^{-1}	T_2^{-1} /s^{-1} [b]	T_1^{-1} /s^{-1}		
		Q^0	Q^0	Q^1_2	Q^2_3
I	0	1.7	0.15	0.19	0.14
II	1.0	6.2	0.08	0.11	0.13
III	0	17	0.18	0.22	0.15
IV	1.3	≥ 50 [c]	[c]	0.16	[c]

[a] Solutions I and II contain 3.0 mol kg^{-1} SiO_2 and 4.5 mol kg^{-1} NaOH. Solution III has 2.0 mol kg^{-1} SiO_2, 2.0 mol kg^{-1} NaOH, 2.8 mol kg^{-1} NaCl and pH = 13.48. Solution IV has 2.0 mol kg^{-1} SiO_2, 2.7 mol kg^{-1} NaOH and pH = 13.50 (The Na^+ content of solution III was raised to match that of solution IV so that pH readings would have the same Na-error). [b] $T_2^{-1} = \pi \, \Delta\nu_{1/2}$. [c] Resonance is too broad for accurate determination.

exchange between silicates and some form of peroxysilicate(s) or **2.** extended peroxohydrate solvent shells that hinder tumbling of the polysilicate anions. (In peroxide-free silicates, the extreme narrowing condition – *i.e.*, motional correlation time < < reciprocal of Larmour frequency – is valid except at low temperatures and, importantly, there is no evidence of ^{29}Si relaxation caused by the shielding anisotropy mechanism.[26])

Further indication of the mechanism of ^{29}Si T_2 relaxation mechanism was obtained from two additional studies. First, ESR spectra of alkaline peroxide solutions contained no new signals that could be attributed to the presence of sodium silicate. This is consistent with the observations of other investigators.[6,7] Second, addition of small amounts, *ca.* 10^{-3} to 10^{-2} mol kg^{-1}, of Mg^{2+}, TEMPO or 2,6-dimethoxyphenol decreased peroxide-induced line broadening, sometimes eliminating it altogether, and yet had no effect on equilibria (figure 9);[27] none of these additives affected the spectra of peroxide-free solutions. The

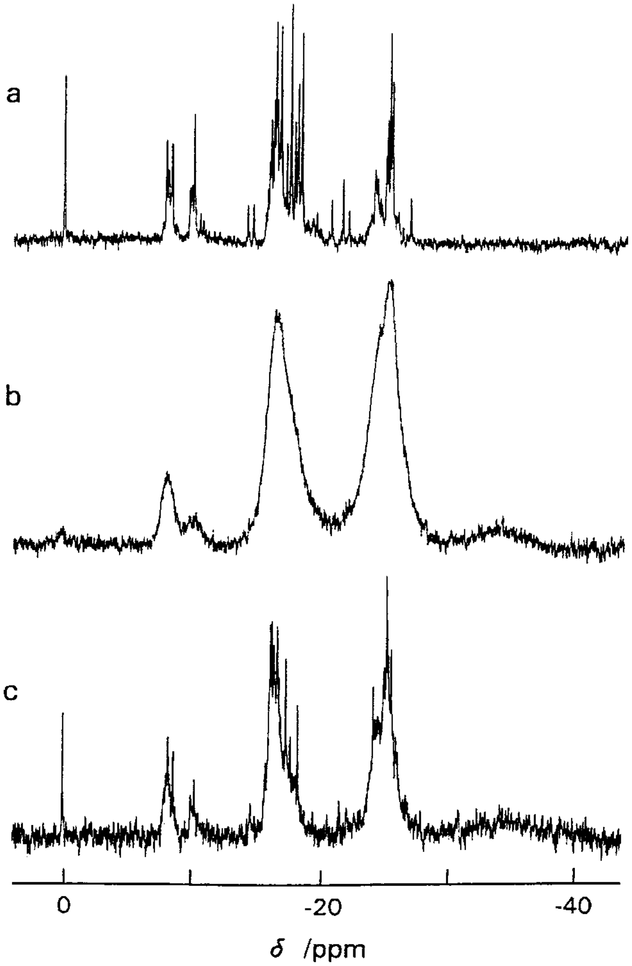


FIGURE 9. ^{29}Si spectra at 0 °C of freshly prepared solutions containing 3.6 mol kg^{-1} SiO_2 and NaOH. Solutions in (b) and (c) contain 1.35 mol kg^{-1} H_2O_2; solution (c) also contains 10^{-3} mol kg^{-1} $MgCl_2$.

radical-scavenging action of Mg^{2+} and 2,6-dimethoxyphenol in peroxide bleaching reactions have been described elsewhere,[7,28] while TEMPO, itself a free radical, is an exceedingly reactive radical quencher. Because these additives mitigate peroxide-induced line broadening and yet do not affect bulk H_2O_2 concentration (over the short term), relaxation can have nothing to do with hydrogen peroxide itself. This leaves, as the probable chief cause of peroxide-induced line broadening, rapid ^{29}Si-^{29}Si exchange associated with radical-mediated formation of labile "peroxysilicate" species. The uniformity of broadening would suggest that virtually all silicate ions participate in the formation of these new species. Indeed, ^{29}Si spectra of silicate-peroxide solutions are very similar to reported spectra of solutions containing labile aluminosilicate[29] or borosilicate[30] anions. The apparent absence of resonances corresponding to the peroxysilicate species themselves is probably due to their low abundance and extremely short life-times, *i.e.*, as in the case of the forementioned metallosilicates. Also, the apparent lack of a corresponding ESR resonance does not preclude the possibility of silicate-radical complexes (*i.e.*, as for the Mg^{2+}-superoxide complex[7]) in which case broadening would also be caused by inner-sphere paramagnetic relaxation.

Given the proposition of rapid and reversible association between silicate anions and H_2O_2 degradation products, the final task is to consider the identity of the latter species. Under alkaline conditions, hydrogen peroxide decomposes into highly reactive hydroxyl radicals and superoxide ions.[31]

$$H_2O_2 + HO_2^- \rightarrow HO\cdot + O_2\cdot^- + H_2O \qquad (3)$$

In strongly alkaline solution, $HO\cdot$ is rapidly converted to its conjugate base $O\cdot^-$ ($pK_a = 11.9$) and is quenched by HO_2^- to form relatively stable $O_2\cdot^-$.[31] The initial broadening of ^{29}Si line widths as pH is increased (figure 7) is consistent with accelerated Si-Si exchange, *i.e.* between silicate anions and "peroxysilicate" species, caused by a rise in concentration of the H_2O_2 decomposition product to which silicates associate. The subsequent decrease in line widths as pH was raised beyond *ca.* 14 indicates that exchange becomes hindered despite the high levels of decomposition radicals. This can be understood by considering that, in the absence of hydrogen peroxide, the rate of intermolecular Si-Si exchange decreases as pH is raised because of the progressive deprotonation of silicate anions and, thus, increased mutual electrostatic repulsion.[19] Similarly, the present data (figure 7) would suggest that direct attack at silicate anions by H_2O_2 decomposition radicals is electrostatically hindered when silicate Q centers become significantly deprotonated. This is further evidenced by the small amount of line broadening observed even at low pH for $Si_4O_{10}^{4-}$ and $Si_6O_{15}^{6-}$ anions which consist only of deprotonated Q^3 centers. Hydrogen bonding, *i.e.* at $\equiv$Si-OH, presumably plays a mechanistic role. All things considered, the superoxide radical $O_2\cdot^-$ is the most likely species to associate with silicates and yield peroxysilicates. Apparently, the TMA-hydration shell about the $Si_8O_{20}^{8-}$ anion in TMA-silicate solutions protects the anion from radical attack. Little else can be discerned about the nature of aqueous peroxysilicates from the NMR evidence alone.

Indirect evidence might be obtained, however, from the solid "peroxysilicates" reported to form at high NaOH and H_2O_2 concentrations.[5,12-14] On numerous occasions throughout this work, colourless, transparent crystals, up to 1 cm in length, occurred in solutions of sodium silicate and hydrogen peroxide above a threshold pH of approximately 14.5 (depending on solution composition and temperature). Similar, well-formed crystals did not form when Na^+ was substituted with Li^+, K^+, Rb^+, Cs^+, TMA^+ or TPA^+. The crystals quickly turned opaque and decomposed when separated from the mother liquor, but could be stabilized under nitrogen in sealed capillaries at liquid nitrogen temperatures. X-ray crystallography revealed that the crystalline solid is hydrated sodium peroxide, $Na_2O_2 \cdot 8H_2O$.[32] In bulk, this product is difficult to obtain free from silicate contaminants and it seems likely that this is the solid "peroxysilicate" product reported by others.[5,12-14] It would also explain why the solid has some brightening activity.[5]

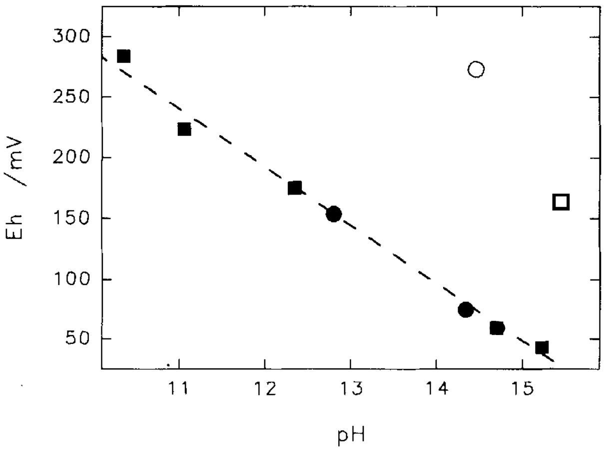


FIGURE 10. Standard reduction potential as a function of pH at 0 °C for solutions containing: □, 3.0 mol kg^{-1} RbOH; ■, 1.35 mol kg^{-1} H_2O_2 and 0.25 to 3.0 mol kg^{-1} RbOH; ○, 3.0 mol kg^{-1} SiO_2 and RbOH; and ●, 1.35 mol kg^{-1} H_2O_2, 3 mol kg^{-1} SiO_2 and 3.0 or 4.0 mol kg^{-1} RbOH. Alkaline peroxide solutions exhibit the same Eh-pH dependence regardless of silicate content.

Thus, while the NMR evidence is consistent with the presence in low concentrations of a labile product formed by peroxide-silicate interaction, we have found no evidence to support the formation of large quantities of "peroxysilicates" and it is therefore unlikely that they play a direct role in the actual brightening process. This is consistent with observations that there is little penetration of silicate into the cell wall during brightening.[33] However, it is possible that one of the roles of silicates is to help stabilize peroxide by scavenging free radical chain carriers involved in H_2O_2 decomposition. It is also possible that silicates enhance the brightening activity of peroxide because they associate primarily with $O_2{\cdot}^-$ ions and thus prevent them from quenching hydroxyl radical which has been proposed[11] as being an important agent in bleaching reactions. The relatively high concentration of silicates (compared with Mg^{2+}) may be required because, although radical trapping may be selective, it is only moderately efficient.

Finally, silicates do not affect the reduction potential of peroxide solutions as shown in figure 10, and therefore silicates do not affect the oxidizing properties of peroxide.

CONCLUSIONS

1. When peroxide is added to silicate solutions, variations in the extent of silicate polymerization and in ^{29}Si chemical shifts occur because of pH and concentration changes.
2. Significant broadening of almost all silicon resonances occurs and is interpreted in terms of the presence of low concentrations of labile "peroxysilicates" undergoing rapid, and reversible, Si-Si exchange with silicates. Resonances corresponding to these new species are not directly observable.
3. Silicates trap free radicals (probably superoxide ions) involved in peroxide decomposition and thus assist in the stabilization of peroxide.
4 The solid formed from aqueous mixtures of silicate, NaOH and H_2O_2 is a hydrated sodium peroxide. No evidence for a solid peroxysilicate was obtained.
5. Silicates do not affect the redox properties of hydrogen peroxide.

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