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# Equilibria, Kinetics, and Mechanism in the Bicarbonate Activation of Hydrogen Peroxide: Oxidation of Sulfides by Peroxymonocarbonate

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**Abstract:** Bicarbonate ion is an effective activator for hydrogen peroxide in the oxidation of sulfides. Kinetic and spectroscopic results support the formation of peroxymonocarbonate ion ($HCO_4^-$) as the oxidant in the catalytic reactions. The reaction of hydrogen peroxide and bicarbonate to form $HCO_4^-$ occurs rapidly at 25 °C ($t_{1/2} \approx 300$ s) near neutral pH in aqueous solution and alcohol/water mixtures, and an equilibrium analysis of the reaction by $^{13}C$ NMR leads to an estimate of the electrode potential for the $HCO_4^-/HCO_3^-$ couple (1.8 V vs NHE). Solubility of the bicarbonate catalyst is enhanced by the use of $NH_4HCO_3$ rather than by the use of group 1 salts, which tend to have lower solubility in the mixed solvents and can lead to phase separation. Rate laws and mechanistic analyses are presented for the oxidation of ethylphenylsulfide and related sulfides. The second-order rate constants for sulfide oxidations by $HCO_4^-$ are ~300-fold greater than those for $H_2O_2$, and this increase is consistent with expectations based on a Brønsted analysis of the kinetics for other heterolytic peroxide oxidations. At high concentrations of $H_2O_2$, a pathway that is second order in $H_2O_2$ is significant, and this path is interpreted as a general acid catalysis by $H_2O_2$ of carbonate displacement accompanying substrate attack at the electrophilic oxygen of $HCO_4^-$. Increasing water content up to 80% in the solvent increases the rate of oxidation. The BAP (bicarbonate-activated peroxide) oxidation system is a simple, inexpensive, and relatively nontoxic alternative to other oxidants and peroxyacids, and it can be used in a variety of oxidations where a mild, neutral pH oxidant is required. Variation of bicarbonate source and the cosolvent can allow optimization of substrate solubility and oxidation rates for applications such as organic synthesis and chemical warfare agent decontamination.

## Introduction

Hydrogen peroxide is a widely used oxidant with high active oxygen content,[1] but it is a rather slow oxidizing agent in the absence of activators. In large-scale bleaching applications[2] and many synthetic oxidations, activation via formation of peroxycarboxylic acids is a favored method (i.e., $RC(O)X + H_2O_2 \rightleftharpoons RC(O)OOH + HX$).[1,3,4] The activation is often accomplished in situ by using a reactive carboxylic acid derivative with a good leaving group that leads to rapid conversion to the peroxyacid. Alternatively, a peroxyacid can be formed from the parent acid (X = OH) by strong acid catalysis and high concentrations of $H_2O_2$.

A novel method for activating $H_2O_2$ by using bicarbonate ion was described by Drago and co-workers in their study of the oxidation of chemical warfare agents and simulant sulfides in mixed *tert*-butyl alcohol/water solvent.[5] They concluded on the basis of NMR evidence that the active oxidant in the catalytic pathway is peroxymonocarbonate ion ($HCO_4^-$)[6] formed by a labile preequilibrium reaction between bicarbonate ion and $H_2O_2$ (eq 1).

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O \qquad (1)$$

The use of an alcohol cosolvent provides for organic substrate solubility and shifted the equilibrium of eq 1 to the right, favoring increased formation of peroxymonocarbonate ion. Recent experiments reported by Richardson et al,[7] and Xu[8]

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(6) The nomenclature for $HCO_4^-$ and associated species is not universally accepted. The parent acid $H_2CO_4$ (RN 593-69-9) is indexed by CAS as *carbonoperoxoic acid* and is named by IUPAC as *hydrogen dioxoperoxocarbonate(2-)*. Common names for the acid include *monoperoxycarbonic acid* and *percarbonic acid*. By analogy to $H_2SO_5$ (CAS name *peroxymonosulfuric* acid), *peroxymonocarbonic acid* could also be used as a common name. Salts of $HCO_4^-$ are indexed by CAS as carbonoperoxoic acid derivatives (e.g., *carbonoperoxoic acid, monopotassium salt*), while IUPAC would name the same salt *potassium hydrogendioxoperoxocarbonate(1-)*. Common names for the same salt are *potassium percarbonate*, *potassium peroxycarbonate,* and *monopotassium peroxymonocarbonate*. In this paper, we have chosen to use the common name *peroxymonocarbonate* for the ion $HCO_4^-$. The commonly employed prefix "mono" readily distinguishes various monomeric oxyanions from their dimeric and polymeric counterparts, and the choice parallels the common use of *peroxymonosulfate* for the analogous $HSO_5^-$ ion. A difficulty with this choice is that the name could also apply to $CO_4^{2-}$, but it assumed in this work that at pH values less than ~9 the predominant ionization state is $HCO_4^-$. The more cumbersome *hydrogenperoxymonocarbonate* can be used when confusion is likely.

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showed that increases in catalytic efficiency of the BAP system (bicarbonate activated peroxide) could be achieved by using a more soluble source of bicarbonate ($NH_4HCO_3$) and primary alcohols in place of $NaHCO_3$ and *tert*-butyl alcohol, respectively.

The goal of the present study was to investigate the mechanism of bicarbonate-catalyzed oxidation of sulfides by $H_2O_2$ in alcohol/water media via a detailed investigation of rate laws. Bicarbonate catalysis of hydrogen peroxide oxidations has many potential advantages over other peroxyacids and oxidants for applications such as organic synthesis, bleaching, and chemical warfare agent decontamination.[9−11] Hydrogen peroxide has a high active oxygen content compared to other stoichiometric oxidants, e.g., peroxycarboxylic acids, periodate, and peroxymonosulfate.[12] The conditions of the BAP system are mild with pH around neutral or weakly alkaline rather than the strongly alkaline conditions often employed for peroxide bleaching.[13] The components of the system are inexpensive and environmentally friendly. Experiments with chemical warfare agents such as HD (mustard), GB, and VX show that the system can be used as a broad-spectrum decontamination solution ("Decon Green").[14] In other work to be published separately,[15] we have shown that the BAP system is active in the epoxidation of alkenes near neutral pH, so that a wide range of functional groups that are normally oxidized using reactive peroxyacids are likely to be substrates for the BAP system.

The peroxymonocarbonate ion has been isolated in various salts and characterized by vibrational spectroscopy[16,17] and X-ray crystallography ($KHCO_4{\cdot}H_2O_2$).[18] Peroxymonocarbonate is a true peroxide with structure $HOOCO_2^-$. Metal complexes of $CO_4^{2-}$ have been prepared and are heterolytic oxidants.[19,20] The solution properties of the ion have also been studied by NMR,[16,21] and salts have been shown to rapidly hydrolyze to form $HCO_3^-$ and $H_2O_2$ in water (reverse reaction of eq 1). Given the relative difficulty of isolating and storing the unstable peroxycarbonate salts, formation of $HCO_4^-$ in situ is likely to be the preferable method in most applications.

The equilibrium reaction in eq 1 and subsequent oxidations by $HCO_4^-$ are also of interest in view of the possible but rarely mentioned[22] role of $HCO_4^-$ as a nonradical reactive oxygen species (ROS)[23,24] in biological systems. The ubiquity of $CO_2$/$HCO_3^-$ buffers in biology and the well-known production of $H_2O_2$ in both normal metabolism[25] and the immune response[26] argue for careful analysis of the formation and reactivity of $HCO_4^-$ in water. The present report confirms the catalysis of sulfide oxidation by bicarbonate ion, and we have also demonstrated the bicarbonate ion catalysis of methionine oxidation to methionine sulfoxide by $H_2O_2$ in water.[27] Oxidation of methionine is a marker for oxidative stress in biological systems.[28,29] Methionine residues may serve as intrinsic protein antioxidants,[30] and methionine is the only amino acid that is known to have a specific reductase enzyme system to reverse its oxidation in vivo.[31] Some types of protein oxidation are not readily explained by radical chemistry,[32] suggesting that heterolytic oxidative pathways should be considered.

Rate laws for $HCO_4^-$ oxidations have not appeared in the literature. On the basis of the $pK_a$ of the leaving group conjugate acid (i.e., $CO_3^{2-}$ leaving group, $pK_a(HCO_3^-) = 10.3$), it is expected that $HCO_4^-$ will be intermediate in reactivity compared to $H_2O_2$ itself ($OH^-$ leaving group, $pK_a(H_2O) = 15.7$) and typical organic peroxyacids ($RC(O)O^-$ leaving group, $pK_a(RC(O)OH) \approx 4-5$). The mechanism of equilibration via eq 1 is also of interest because formation of $HCO_4^-$ occurs rapidly in the absence of strong acid catalysts or highly reactive carboxylation agents; however, detailed mechanistic information on the reaction of eq 1 is not available in the literature.

In the present work, rate constants for the primary oxidation reactions of $HCO_4^-$ have been obtained for various alcohol cosolvents. In addition, the equilibration of eq 1 in alcohol/water mixtures has been studied quantitatively with respect to equilibrium constants and the rate of equilibration. The results support the previously assumed mechanism and the role of $HCO_4^-$ or its kinetic equivalent as the direct oxidant in the catalysis. In addition, we have investigated the details of the peroxide concentration dependence in the reactions and provide evidence for a catalytic role for $H_2O_2$ in reactions with high hydrogen peroxide concentration. Implications of the results for applications such as chemical warfare agent decontamination and organic synthesis are described.

## Results

**Equilibrium Formation of Peroxymonocarbonate.** We used 99% $^{13}C$-enriched $NaHCO_3$ to examine bicarbonate-peroxide equilibria in water and mixed alcohol/water solvents by $^{13}C$ NMR at 25 °C. Concentrations of hydrogen peroxide in the range 0.2−4.0 M were employed, and $[H^{13}CO_3^-] = 0.10$ M for all studies.

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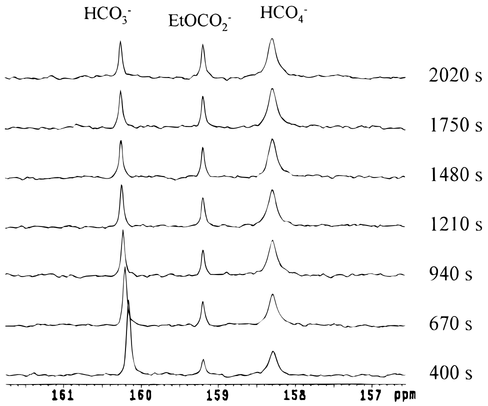

**Figure 1.** $^{13}$C NMR spectra for a solution at 25 °C of $\mathrm{NaH^{13}CO_3}$ in 1.76:1 (v/v) ethanol/water with $[\mathrm{H_2O_2}] = 2.0$ M. The half-life for formation of $\mathrm{HCO_4^-}$ is ~300 s and that for ester formation is ~500 s. Times shown are for the completion of acquisition from the time of mixing.

In water, besides the peak for bicarbonate at 163.6 ppm, a single additional peak at 161.7 ppm assigned[16] as $\mathrm{HCO_4^-}$ was observed (chemical shifts relative to $d_4$-TMSP). From relative peak intensities and the concentration of $\mathrm{H_2O_2}$, $K_2 = 0.32 \pm 0.02\ \mathrm{M^{-1}}$ was obtained for eq 2.

$$\mathrm{HCO_3^-\ (aq) + H_2O_2\ (aq) \rightleftharpoons HCO_4^-(aq) + H_2O}\quad K_2 = \frac{[\mathrm{HCO_4^-}]}{[\mathrm{H_2O_2}][\mathrm{HCO_3^-}]} \quad (2)$$

The observed rate constant at pH = 7.4 for equilibration of eq 2 at $[\mathrm{H_2O_2}] = 2.0$ M and 25 °C is $(1.96 \pm 0.04) \times 10^{-3}\ \mathrm{s^{-1}}$. From the value of $K_2$, the forward rate constant for the reaction of eq 2, $k_\mathrm{f}$, is $3.8 \times 10^{-4}\ \mathrm{M^{-1}\ s^{-1}}$, and for the reverse reaction $k_\mathrm{r} = 1.2 \times 10^{-3}\ \mathrm{s^{-1}}$. Noting that $E°(\mathrm{H_2O_2/H_2O}) = 1.77$ V (vs NHE), $E°(\mathrm{HCO_4^-/HCO_3^-}) = 1.8 \pm 0.1$ V.

In alcohol/water mixtures (1.76:1 alcohol:water, v/v), eq 3 applies.

$$\mathrm{HCO_3^-\ (solv) + H_2O_2\ (solv) \rightleftharpoons HCO_4^-(solv) + H_2O\ (solv)}\quad K_3 = \frac{[\mathrm{HCO_4^-}][\mathrm{H_2O}]}{[\mathrm{H_2O_2}][\mathrm{HCO_3^-}]} \quad (3)$$

By decreasing $[\mathrm{H_2O}]$ in the solution, the equilibrium amount of $\mathrm{HCO_4^-}$ is increased. In *tert*-butyl alcohol/water, the effective equilibrium constant $K_3 = 23 \pm 1$ and was found to be independent of temperature in the range of 15−35 °C. Thus, in 1 M $\mathrm{H_2O_2}$, 54% of the bicarbonate is converted to $\mathrm{HCO_4^-}$ in *tert*-butyl alcohol with $[\mathrm{H_2O}] = 19.6$ M. In ethanol, $K_3 = 27 \pm 1$ at 25 °C, and the observed equilibration rate constant is $(2.4 \pm 0.1) \times 10^{-3}\ \mathrm{s^{-1}}$. After correcting $K_2$ for the experimental concentration of water to obtain $K_3 \approx 17 \pm 1$ for water as the only solvent, we note that the magnitude of the effective equilibrium constant for eq 2 is increased slightly as alcohol is added.

Primary alcohols react with bicarbonate to form alkyl carbonate esters, $\mathrm{RCO_3^-}$, and a third peak is observed in the NMR spectrum (the spectrum for R = Et is shown in Figure 1). For eq 4,

$$\mathrm{HCO_3^-\ (solv) + C_2H_5OH\ (solv) \rightleftharpoons C_2H_5CO_3^-(solv) + H_2O\ (solv)}\quad K_4 = \frac{[\mathrm{RCO_3^-}][\mathrm{H_2O}]}{[\mathrm{ROH}][\mathrm{HCO_3^-}]} \quad (4)$$

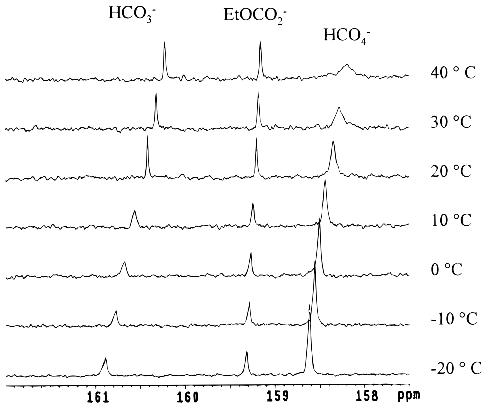

**Figure 2.** Variable temperature $^{13}$C NMR spectra for a solution of $\mathrm{NaH^{13}CO_3}$ in 1.76:1 (v/v) ethanol/water with $[\mathrm{H_2O_2}] = 2.0$ M. Significant lifetime broadening of the $\mathrm{HCO_4^-}$ peak occurs above ~0 °C. At lower temperatures the line widths for all major species are comparable.

$K_4 = 1.8 \pm 0.2$, and the rate constant for equilibration at 25 °C is $(1.4 \pm 0.2) \times 10^{-3}\ \mathrm{s^{-1}}$. Ester formation is not observed for *tert*-butyl alcohol/water solutions.

At room temperature, it is typically observed that the $\mathrm{HCO_4^-}$ peak is somewhat broadened, and we carried out a variable temperature $^{13}$C NMR study to investigate the temperature dependence of the peak width in ethanol/water (Figure 2). Below 0 °C, the line widths of all resonances are comparable, but the $\mathrm{HCO_4^-}$ peak broadens substantially at higher temperatures. The broadening is pH dependent, and with $\mathrm{K_2{}^{13}CO_3}$ (pH of peroxide/water solution = 9.4) as the bicarbonate source the $\mathrm{HCO_4^-}$ peak sharpens significantly, while the $\mathrm{HCO_3^-/CO_3^{2-}}$ peak shifts (to 163 ppm referenced to ethanol at 57.0 ppm) as expected due to increased $\mathrm{CO_3^{2-}}$ at equilibrium. This observation is consistent with a proton-dependent chemical exchange reaction as the origin of the line-broadening, but a second $^{13}$C species participating in the exchange was not observed and is evidently at low concentration.

**Oxidation of Ethylphenylsulfide by Hydrogen Peroxide**. The oxidation of ethylphenylsulfide (EPS) was followed by monitoring the loss of absorbance in the 290−300 nm range. The sulfoxide and sulfone products do not absorb significantly in this region, presumably due to the shift or elimination of the n(S)-$\pi$* band. To ensure equilibration of eq 3, the peroxide−bicarbonate solutions were prepared and were allowed to stand for at least 20 min as required before addition of the substrate. The oxidation was usually followed for at least one half-life, and linear first-order plots were obtained. The contribution of the noncatalytic background oxidation was subtracted to obtain the phenomenological rate law for the catalytic path (discussed for different solvents below).

In accord with studies[33] on sulfide oxidation by periodate ion, ionic strength effects are small. We extensively investigated possible buffer effects by comparing the rates of EPS oxidation in $\mathrm{H_2O_2}$ solutions with no added salts and with added $\mathrm{(NH_4)_2HPO_4}$, which yields a pH close to that of $\mathrm{NH_4HCO_3}$ solutions (7.9 in water). No significant differences were detected in the oxidation rates, but we controlled ionic strength in some studies described below using $\mathrm{(NH_4)_2HPO_4}$.

Although the contribution of background oxidation by $\mathrm{H_2O_2}$ is normally small compared to the catalytic pathway at low $[\mathrm{H_2O_2}]$ values, a kinetic analysis shows that apparent higher

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**Table 1.** Rate Constants and Equilibrium Constants for the Bicarbonate-Catalyzed Oxidation of Sulfides by Hydrogen Peroxide[a]

| substrate | solvent | $10^5\ k_{01}$/ $M^{-1}\ s^{-1}$ | $10^5\ k_{02}$/ $M^{-2}\ s^{-1}$ | $10^5\ k_{03}$/ $M^{-3}\ s^{-1}$ | $10^3\ k_1$/ $M^{-1}\ s^{-1}$ | $10^3\ k_2$/ $M^{-2}\ s^{-1}$ | $K_{14}$[b] | $K_{15}$[b] | $k_1/k_{01}$ |
|---|---|---|---|---|---|---|---|---|---|
| ethylphenylsulfide | EtOH/$H_2O$ | 8.0 ± 0.5 | 0.7 ± 0.3 | 1.8 ± 0.1 | 19 ± 1 | 8.9 ± 0.3 | 27 ± 1 | 1.8 ± 0.2 | 240 |
|  | *t*-BuOH/$H_2O$ | 2.5 ± 0.7 | 0.7 ± 0.4 | 0.72 ± 0.06 | 11 ± 1 | 2.8 ± 0.1 | 23 ± 1 | n/a | 440 |
| 2-chloroethylphenylsulfide | EtOH/$H_2O$ | 1.3 ± 0.7 | 0.7 ± 0.4 | 0.09 ± 0.06 | 3.0 ± 0.5[c] | 1.6 ± 0.2 | 27 ± 1 | 1.8 ± 0.2 | 230 |
| 2-hydroxyethylphenylsulfide[d] | EtOH/$H_2O$ | 4.3 ± 0.7 |  |  | 12 ± 1 |  | 27 ± 1 | 1.8 ± 0.2 | 280 |

[a] Rate constants obtained from nonlinear regression analyses of kinetic data (25 °C). Solvent is 1.76:1 v:v alcohol/water. Rate constants for the background oxidation in the absence of bicarbonate ($k_{01}$, $k_{02}$, $k_{03}$) were obtained from eq 5. Constants for the catalytic pathways ($k_1$ and $k_2$) were derived from nonlinear fits to eq 20. Error limits are ± standard errors from the fits. [b] Equilibrium constants for eqs 14 and 15 as determined from replicate NMR measurements described in the text. These values used in fits via eq 20. [c] Determined from fits to data at low [$H_2O_2$]. [d] Kinetic data only obtained at low [$H_2O_2$] (<1 M); only $k_{01}$ and $k_1$ could be determined.

order pathways become important when [$H_2O_2$] > 1 M. The data were fit by eq 5.

$$\frac{-d[RSR']}{dt} = \{k_{01}[H_2O_2] + k_{02}[H_2O_2]^2 + k_{03}[H_2O_2]^3\}[RSR'] \quad (5)$$

Resulting rate constants are given in Table 1, and a fit for data in *tert*-butyl alcohol/water is shown in Figure 3. An attempted fit up to second order only is also shown for comparison in Figure 3.

**Bicarbonate-Activated Oxidation of Ethylphenylsulfide in *tert*-Butyl Alcohol/Water.** In *tert*-butyl alcohol/water (1.76:1, v/v), bicarbonate ion accelerates the $H_2O_2$ oxidation significantly. Variation of [$HCO_3^-$] shows the catalytic reactions are first order in bicarbonate ion. The concentration of $NH_4HCO_3$ was sufficiently low in the kinetic experiments (≤0.1 M) such that solubility saturation effects were not observed (at high concentrations of bicarbonate salts, especially group 1 salts, phase separation or insolubility of the salt makes kinetic studies impossible). The use of $NH_4HCO_3$ as the source of $HCO_3^-$ allows higher catalyst concentration than the use of alkali metal salts before solubility saturation effects become apparent.

Dependence of the reaction rates on [$H_2O_2$] shows the reaction to be first order in peroxide at [$H_2O_2$] < 0.3 M, and saturation kinetics are observed at higher concentrations. However, the curve is not fit well by a simple saturation rate law, and a more complex empirical rate law is required that includes a second-order pathway in [$H_2O_2$] (eq 6).

$$\frac{-d[RSR']}{dt} = \frac{\{a[H_2O_2] + b[H_2O_2]^2\}d[HCO_3^-][RSR']}{c + d[H_2O_2]} = k_{obs}[RSR'] \quad (6)$$

Equation 6 yields excellent fits to the observed pseudo-first-order rate constants, $k_{obs}$. Values of the constants *a* and *b* are obtained when *c* and *d* are equated to known quantities (see Discussion).

$^1$H NMR studies of the oxidation reaction were done to assess product distributions. Subsequent oxidation of the initially formed sulfoxide to the sulfone was not observed under conditions (~5 M $H_2O_2$, *tert*-butyl alcohol/water, 0.03 M bicarbonate, 25 °C) and reaction times similar to those used here. Slow conversion to the sulfone was observed for longer reaction times since excess oxidant was present. Oxidation of sulfide with equimolar hydrogen peroxide and sulfide at ~0.3 M or less gave sulfoxide as the only major product (by GC analysis).

**Bicarbonate-Activated Oxidation of Ethylphenylsulfide in Ethanol/Water.** Bicarbonate-catalyzed EPS oxidations in ethanol/water (1.76:1, v/v) are generally faster than those in *tert*-butyl alcohol/water by a factor of ~2. The kinetics in ethanol/water were done by controlling the ionic strength via addition of $(NH_4)_2HPO_4$, which has an insignificant effect on the observed background reaction rates compared to reactions done with no added salts or buffers. The kinetic behavior of the catalytic reaction conforms to the rate law of eq 6.

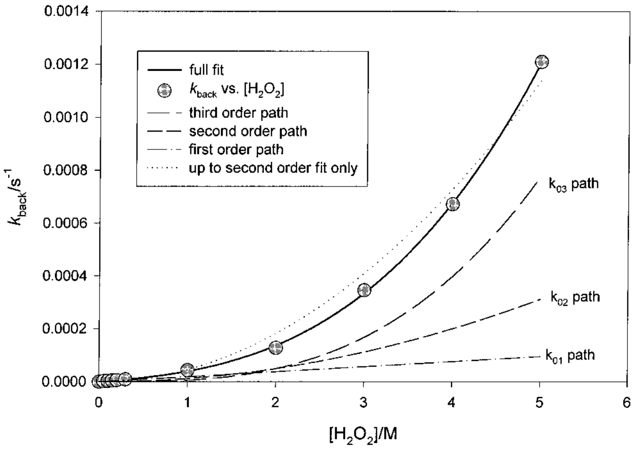

**Figure 3.** Plot of observed rate constants for $H_2O_2$ oxidation of EPS in 1.76:1 (v/v) *tert*-butyl alcohol/water as a function of [$H_2O_2$] at 25 °C. The solid line is a fit to eq 5 (i.e., a cubic polynomial) with the rate constants given in Table 1. The contributions of the first-, second-, and third-order terms are illustrated. An attempt at fitting the data with a version of eq 5 truncated at second order (i.e., a quadratic polynomial) is shown as the dotted line.

Studies on the pH dependence of rate constants by using phosphate buffers showed that changes in the kinetic constants are negligible within the experimental error in the pH range of 7−8.4 (pH of peroxide/water before alcohol addition). Above pH 9, the catalytic rate does decline significantly.

The polydentate ligand diethylenetriaminepentaacetic acid (DTPA) was used in several experiments (up to 5 mM) and was found to have no effect on the observed rate constants. Thus, the oxidation of EPS does not appear to have any radical component due to Fenton chemistry involving adventitious iron, which would be deactivated by DTPA.

Catalysis by sodium bicarbonate, potassium bicarbonate, and ammonium bicarbonate were carefully studied in ethanol/water to establish that any counterion effect is negligible, and the source of bicarbonate has no significant effect on the rates of oxidation.

**Bicarbonate-Activated Oxidation of Ethylphenylsulfide in Other Solvents.** Other alcohol cosolvents and water contents were surveyed to determine kinetic trends as a function of solvent polarity (Figure 4 and Table 2). The data in Figure 4 show that lighter alcohol cosolvents lead to higher overall rates, and the leveling off in the plots shows that the point of saturation of bicarbonate salt solubility is much higher in ethanol/water than in *tert*-butyl alcohol/water. In addition, a solvent deuterium

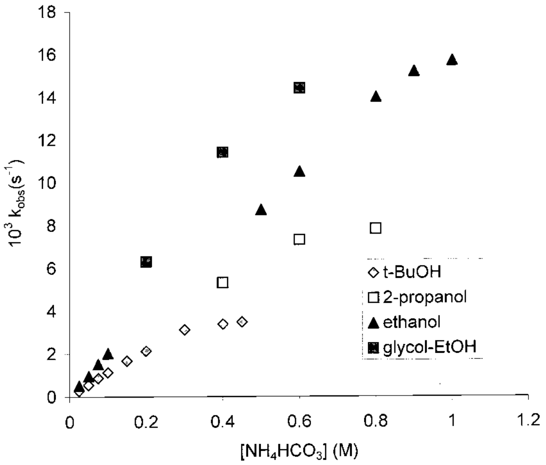

**Figure 4.** Variation of observed first-order rate constants for EPS oxidation for different alcohol cosolvents (1.76:1 alcohol:water, v/v). Reaction conditions: 25 °C, 2.0 M $H_2O_2$. For the glycol−ethanol cosolvent, the alcohol was 1:1 ethanol:propylene glycol (v/v).

**Table 2.** Dependence of EPS BAP Oxidation Rates on Solvent Composition[a]

| solvent composition (v/v) | $10^5\ k_{01}$/ $M^{-1}s^{-1}$ | $10^5\ k_{so}$/ $M^{-1}s^{-1}$ | $10^3\ k_1$/ $M^{-1}s^{-1}$ |
|---|---|---|---|
| 80:20 $H_2O$:*t*-BuOH | 41 | 690 | 140 |
| 70:30 $H_2O$:*t*-BuOH | 19 | 320 | 57 |
| 50:50 $H_2O$:*t*-BuOH | 5.9 | 140 | 33 |
| 40:60 $H_2O$:*t*-BuOH | 4.6 | 120 | 12 |
| 70:30 $H_2O$:EtOH | 58 | 720 | 145 |
| 60:40 $H_2O$:EtOH | 22 | 344 | 66 |
| 50:50 $H_2O$:EtOH | 14 | 264 | 48 |
| 40:60 $H_2O$:EtOH | 7.1 ± 0.3 | 153 ± 8 | 26 ± 1 |
| 40:60 $D_2O$:EtOD | 4.2 ± 0.2 | 102 ± 9 | 17 ± 2 |

[a] Estimated standard errors on rate constants ±20% except where noted. Errors shown in last two entries are 95% confidence levels. The $k_1$ values are derived from $k_{so}$ values from eq 23 assuming that $k_2[H_2O_2]$ is negligible. Conditions: 25 °C, $[H_2O_2] = 0.1$ M, $[HCO_3^-] = 0-0.05$ M.

isotope effect for the catalytic pathway (1.50 ± 0.15 at the 95% confidence level) was measured for $C_2H_5OD/D_2O$ solvent. Kinetic data are listed in Table 2 for various alcohol/water ratios and the isotope effects. The solvent isotope effect was determined in $C_2H_5OD/D_2O$ to be 1.69 ± 0.14 for the background reaction, that is, direct oxidation of EPS by $H_2O_2$ (Table 2).

**Activation Parameters for Ethylphenylsulfide Oxidation.** The temperature dependence of the catalytic EPS oxidation from 15 to 35 °C was studied in *tert*-butyl alcohol/water (1.76:1, v/v) with 0.1 M $H_2O_2$ and up to 0.05 M bicarbonate. The second-order rate constant (after correction for background oxidation) was used to construct an Eyring plot of $\ln(k_1/T)$ vs $1/T$, and activation parameters were derived (thermodynamics of pre-equilibria are not included in the parameters; $k_1$ is defined in the Discussion). From a regression analysis, $\Delta H^{\ddagger} = 38 \pm 1$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -154 \pm 4$ J mol$^{-1}$ K$^{-1}$ (errors are standard errors, $N = 6$). An Eyring analysis of the background data for direct $H_2O_2$ oxidation led to $\Delta H^{\ddagger} = 55 \pm 5$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -145 \pm 17$ J mol$^{-1}$ K$^{-1}$.

**Oxidation of Other Sulfides**. Kinetic parameters for two other sulfides, 2-chloroethylphenylsulfide (CEPS) and 2-hydroxyethylphenylsulfide, are given in Table 1. The latter compound forms slowly from CEPS in aqueous solution ($t_{1/2} \approx 96$ h under our conditions). The oxidation of CEPS was studied under conditions in which the hydrolysis was negligible during data collection.

### Scheme 1

$$HCO_3^- + H^+ \rightleftharpoons H_2CO_3 \tag{7}$$

$$H_2CO_3 \rightleftharpoons CO_2 + H_2O \tag{8}$$

$$CO_2 + H_2O_2 \rightleftharpoons H_2CO_4 \tag{9}$$

$$H_2CO_4 \rightleftharpoons HCO_4^- + H^+ \tag{10}$$

## Discussion

**Kinetics and Thermodynamics of Peroxymonocarbonate Formation.** The equilibrium constant for eq 2 is near unity and shows that $HCO_4^-$ is a potent oxidant in aqueous solution with an electrode potential (1.8 ± 0.1 V vs NHE) close to that of $H_2O_2$. The acceleration of oxidation reactions upon formation of $HCO_4^-$ from $H_2O_2$ and $HCO_3^-$ arises from a kinetic advantage for the oxidation by $HCO_4^-$ that is not derived from an increase in thermodynamic driving force.

The activation of $H_2O_2$ for synthetic transformations proceeding via heterolytic oxidation is typically achieved through the formation of peroxyacids, which are generally several orders of magnitude more reactive toward nucleophilic substrates than $H_2O_2$ itself.[3] Generation of peroxyacids from acids and $H_2O_2$ in situ is usually catalyzed by added strong acids for practical reasons. For example, the equilibration of acetic acid and $H_2O_2$ to form peracetic acid has a forward rate constant of $\sim 10^{-7}$ M$^{-1}$ s$^{-1}$ in the absence of catalyst,[34] and the peroxyacid is often prepared by addition of sulfuric acid as catalyst. In view of such slow peroxyacid equilibration in the absence of catalyst, it is perhaps unexpected that the bicarbonate ion accelerates oxidations of sulfides via the equilibrium of eq 1, where peroxymonocarbonate is formed in a few minutes at pH ≈ 7−9 with no acid catalyst added.

The reaction of eq 1 was studied by Griffith and co-workers by NMR,[16] and they also noted that the equilibration of $HCO_4^-$ is complete within several minutes in water. Drago and co-workers[5,35] report comparable studies in mixed alcohol/water solvents in which the equilibration is completed in minutes. Our kinetic results confirm the previous observations and provide rate constants for the forward and reverse reactions of the equilibria at pH = 7.4.

The kinetic study was done to provide more details that might lead to a mechanism for the relatively rapid equilibration of eq 1. On the basis of the known chemistry of bicarbonate ion and hydrogen peroxide, it is likely that $CO_2$ and/or $HO_2^-$ are involved. A role for $CO_2$ seems probable in view of the dehydration/hydration chemistry[36] of $HCO_3^-$ solutions. The mechanism of Scheme 1 can be constructed to account for the observations. The kinetic and equilibrium parameters for eqs 7 and 8 are well-known.[36] Equation 7 and presumably eq 10 can be treated as rapid proton-transfer equilibria. The reaction of eq 9 is the perhydration analogue of the hydration reaction (reverse of eq 8). At sufficiently low pH (≤8), the rate of formation of $CO_2$ via eqs 7 and 8 ($k_8 \approx 20$ s$^{-1}$) is sufficiently rapid to explain the observed equilibration rate of eq 1 (i.e, the sum of eqs 7−10). The assumptions of this analysis are that peroxycarbonic acid decomposition (reverse of eq 9) has kinetic parameters comparable to the analogous reaction for carbonic acid and the p$K_a$ for percarbonic acid (eq 10) is estimated by that for carbonic acid (p$K_a$ = 3.8).

It is notable that the rate constant for equilibration of the carbonate ethyl ester $EtCO_3^-$ ($1.4 \times 10^{-3}$ s$^{-1}$) is similar to that

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(34) Schneider, H.-J.; Becker, N.; Philippi, K. *Chem. Ber.* **1981**, *114*, 1562−1566.
(35) Frank, K. M.; Drago, R. S., unpublished work.
(36) Palmer, D. A.; Van Eldik, R. *Chem. Rev.* **1983**, *83*, 651−731.

for the formation of $HCO_4^-$ ($3.0 \times 10^{-3}$ $s^{-1}$) under the conditions of the NMR study. This result is consistent with a common reactive intermediate, and ester formation probably proceeds via eqs 7 and 8 followed by the reaction $CO_2 + EtOH \rightarrow HEtCO_3$ by analogy to the dehydration/hydration mechanism for carbonic acid. Thus, it is likely that eq 9 accounts for the initial formation of peroxycarbonic acid.

The effect of added $CO_2$ on the reaction of eq 1 was investigated. The pH of the solution is reduced to ~6 by addition of $CO_2$ because of the formation of a carbonic acid/bicarbonate buffer. We observed that the equilibration rate for $H^{13}CO_3^-$/$H^{13}CO_4^-$ is increased in solutions that are partially saturated by $CO_2$, and this result supports the role of the acid-dependent reaction of eq 7 in the overall equilibration mechanism.

The explanation for the rapid, pH-dependent exchange detected in the variable temperature NMR studies is not obvious. It may be associated with the exchange of eq 11 (i.e., sum of the reverse reactions of eqs 9 and 10).

$$HCO_4^- + H^+ \rightleftharpoons CO_2 + H_2O_2 \tag{11}$$

However, if the exchange reaction of eq 11 is responsible for the line-broadening, the forward and reverse reactions for deperhydration/perhydration (eq 9) must be substantially faster than dehydration/hydration (eq 8), and such a large rate difference seems unlikely. In more basic media (pH ≈ 9), the line width for the $H^{13}CO_4^-$ resonance is comparable to that of $H^{13}CO_3^-$, consistent with a proton-dependent exchange.

At higher pH values (>8), the rate of carbonic acid formed via eqs 7 and 8 is probably too low to explain the equilibration rate for eq 1. However, the highly nucleophilic hydroperoxide ion becomes more available at higher pH values via eq 12 of Scheme 2 and may account for the formation of $HCO_4^-$ by either net displacement at bicarbonate (eq 13a) or carbonic acid (eq 13b).

**General Mechanism for Heterolytic Oxidations by Peroxides.** The generally accepted mechanism of heterolytic peroxide oxidation reactions is considered here to guide our mechanistic analysis of $HCO_4^-$ oxidations (Scheme 3).[37]

The mechanism involves nucleophilic attack of substrate at the electrophilic oxygen of YOOH with displacement of the leaving group $OY^-$. In the case of protic solvents ("AH") such as water and alcohols, proton transfers can lead to displacement of YOH and immediate formation of NuO. As a consequence, peroxide oxidations tend to accelerate as the acidity of the solvent increases (as measured by the p$K_a$ or autodissociation constant).[38] In aprotic solvents, the catalytic role can be played by hydrogen peroxide itself, and the oxidations become second order in $H_2O_2$ under such conditions.[38]

Many oxidants can be used to convert sulfides into sulfoxides and sulfones.[12] The oxidations of sulfides by two other anionic, main group peroxides, peroxymonosulfate ($HSO_5^-$)[39] and periodate ($IO_4^-$),[33] are particularly useful for comparison to $HCO_4^-$ reactions. Both are believed to react via a nucleophilic attack of the substrate at oxygen, but the role of proton transfer from solvent in the transition state is apparently small in view of modest solvent deuterium isotope effects. Reactions of both oxidants with sulfides are accelerated by increasing solvent polarity, and this has been interpreted to be a consequence of significant charge separation in the $S_N2$ transition states ("normal" anion−neutral $S_N2$ displacements are slower in more polar solvents as a result of charge delocalization in the transition state compared to the reactants).

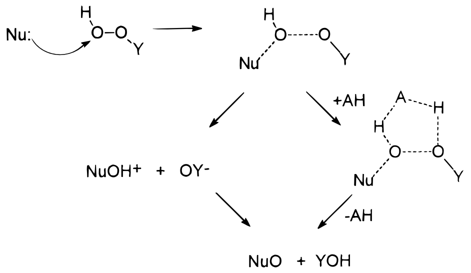
**Scheme 2**

$$H_2O_2 \rightleftharpoons HO_2^- + H^+ \tag{12}$$

$$HO_2^- + HCO_3^- \rightleftharpoons HCO_4^- + OH^- \tag{13a}$$

$$HO_2^- + H_2CO_3 \rightleftharpoons HCO_4^- + H_2O \tag{13b}$$

**Scheme 3**



**Mechanism for Oxidation of Sulfides by Hydrogen Peroxide.** At low $H_2O_2$ concentrations, the background reactions (where $H_2O_2$ is the only oxidant) are first order in $H_2O_2$, but at the higher concentrations used in this study, the data are better fit by the empirical rate law of eq 5. We interpret the second-order term as the result of an autocatalyzed oxidation, wherein a second peroxide assists the displacement reaction by general acid catalysis. This explanation parallels that given by Edwards and co-workers for the appearance of a second-order term in $H_2O_2$ for sulfide oxidations in the aprotic solvent dioxane.[38] In our case, the high [$H_2O_2$] coupled with the higher acidity of $H_2O_2$ (p$K_a$ = 11.7) vs $H_2O$ (p$K_a$ = 15.7) and alcohols (p$K_a$ >15) makes hydrogen peroxide the most potent acid catalyst in the system, and the second-order term appears even in mixed water/alcohol at high peroxide concentrations.

The appearance of a third-order term for $H_2O_2$ in eq 5 is required to achieve an acceptable empirical fit for the direct reaction with sulfides (Figure 3), but the origin of the term is not easily rationalized and the deviation from a fit to first and second order only is small. It could represent a transition state that involves two hydrogen peroxides acting in general acid−base catalysis proton transfer, but the apparent increase in order at high concentrations could also result from medium effects as the $H_2O_2$ concentration displaces solvent alcohol and increases the polarity of the solvent. Experiments maintaining a constant concentration of alcohol while holding the sum of water and peroxide concentrations constant show small decreases in rate (<10%) at the highest peroxide concentrations. The similarity of water and hydrogen peroxide/water mixtures in their macroscopic physical properties[40] should be noted in this regard.

We also determined the activation parameters for $H_2O_2$ oxidation ($k_{01}$) of EPS in *tert*-butyl alcohol/water in the range 15−35 °C ($\Delta H^\ddagger = 55 \pm 5$ kJ mol$^{-1}$ and $\Delta S^\ddagger = -145 \pm 17$ J mol$^{-1}$ K$^{-1}$), and these values can be compared with those in the literature for thioxane as a substrate in dioxane ($\Delta H^\ddagger = 78$ kJ mol$^{-1}$ and $\Delta S^\ddagger = -92$ J mol$^{-1}$ K$^{-1}$).[38]

**Mechanism for Bicarbonate-Catalyzed Oxidation of Sulfides.** The empirical rate law of eq 6 is consistent with the

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[37] Edwards, J. O. In *Peroxide Reaction Mechanisms*; Edwards, J. O., Ed.; Interscience: New York, 1962; pp 67−106.

[38] Dankleff, M. A. P.; Curci, R.; Edwards, J. O.; Pyun, H. Y. *J. Am. Chem. Soc.* **1968**, *90*, 3209−3218.

[39] Bunton, C. A.; Foroudian H, J.; Kumar, A. *J. Chem. Soc., Perkin Trans. 2* **1995**, 33−39.

[40] Kolczynski, J. R.; Roth, E. M.; Shanley, E. S. *J. Am. Chem. Soc.* **1957**, *79*, 531−533.

mechanism of eqs 14−18. Equations 14 and 15

$$HCO_3^- + H_2O_2 \rightleftharpoons HCO_4^- + H_2O \quad K_{14} \tag{14}$$

$$HCO_3^- + R''OH \rightleftharpoons R''CO_3^- + H_2O \quad K_{15} \tag{15}$$

$$HCO_4^- + RSR' \rightarrow RS(O)R' + HCO_3^- \quad k_1 \tag{16}$$

$$HCO_4^- + RSR' + H_2O_2 \rightarrow RS(O)R' + HCO_3^- + H_2O_2 \quad k_2 \tag{17}$$

$$RS(O)R' + [O] \rightarrow RS(O)_2R' \tag{18}$$

are preequilibria that are assumed here to be rapid on the time scale of the subsequent reactions, and the values of $K_{14}$ and $K_{15}$ are obtained from the $^{13}$C NMR data. The rate of disappearance of substrate is given by eq 19, where $[HCO_4^-]$ is the concentration of peroxymonocarbonate at equilibrium.

$$\frac{-d[RSR']}{dt} = (k_1 + k_2[H_2O_2])[HCO_4^-][RSR'] \tag{19}$$

The initial concentration of bicarbonate is related to its equilibrium forms by $[HCO_3^-]_0 = [HCO_3^-] + [HCO_4^-] + [R''CO_3^-]$. Assuming that the initial concentrations $[R''OH]_0$, $[H_2O]_0$, $[H_2O_2]_0 \gg [HCO_3^-]_0$ and $[H_2O_2]_0 \gg [RSR']$, the rate law in eq 20 is obtained from eqs 14−17 and eq 19.

$$\frac{-d[RSR']}{dt} = \frac{(k_1 + k_2[H_2O_2]_0)K_{14}[H_2O_2]_0[HCO_3^-]_0[RSR']}{[H_2O]_0 + K_{14}[H_2O_2]_0 + K_{15}[R''OH]_0} = k_{obs}[RSR'] \tag{20}$$

The observed pseudo-first-order rate constants correspond to $k_{obs}$. At low peroxide concentration such that $K_{14}\,[H_2O_2]_0 \ll [H_2O]_0 + K_{15}[R''OH]_0$ and $k_2[H_2O_2]_0 \ll k_1$, eq 21 applies and the reaction is first order in hydrogen peroxide.

$$\frac{-d[RSR']}{dt} = \frac{k_1K_{14}[H_2O_2]_0[HCO_3^-]_0[RSR']}{[H_2O]_0 + K_{15}[R''OH]_0} \tag{21}$$

It is apparent that the kinetic complexity can be reduced by going to low peroxide concentrations, but we also chose to study high concentrations of $H_2O_2$ in view of the potential applications of the BAP system in rapid oxidation of organic substrates for synthetic and decontamination applications. At high peroxide concentration such that $K_{14}\,[H_2O_2] \gg [H_2O]_0 + K_{15}[R''OH]$, eq 22 applies, and the reaction depends on hydrogen peroxide

$$\frac{-d[RSR']}{dt} = (k_1 + k_2[H_2O_2]_0)[HCO_3^-]_0[RSR'] \tag{22}$$

only via the $k_2$ pathway. This latter limit is not generally attained even with $[H_2O_2] = 5$ M, however, and the full rate law of eq 20 was used to fit the data.

Comparison of the empirical rate law, eq 6, to eq 20 requires that $k_1 = a$, $k_2 = b$, $[H_2O]_0 + K_{15}[ROH]_0 = c$, and $K_{14} = d$. Values for $k_1$ and $k_2$ were obtained from nonlinear regression analysis of the parameters in eq 20 (with $K_{14}$ and $K_{15}$ fixed by the NMR results above) and are given in Table 1 for various solvents and substrates. The term $K_{15}[R''OH]$ in eq 20 arises from ester formation (eq 15) and therefore is not included in the fits for *tert*-butyl alcohol/water solvent where ester formation is not observed by NMR. Data for low $[H_2O_2]$ were used to establish the value of $k_1$ in all cases (via eq 21), and the resulting values compare favorably with the tabulated $k_1$ values from the full fits. (CEPS is an exception, and the tabulated $k_1$ is derived from low $[H_2O_2]$ data.) A graphical display of the complete fit is not possible since $[H_2O]$ varies along with $[HCO_3^-]$, $[R''OH]$ and $[H_2O_2]$ in our experimental design. However, the variations of $[H_2O]$ and $[R''OH]$ are relatively small (±10%), and good fits can be obtained by using the average value for the concentration of water and ethanol (Figure 5 shows such a fit for *tert*-butyl alcohol/water).

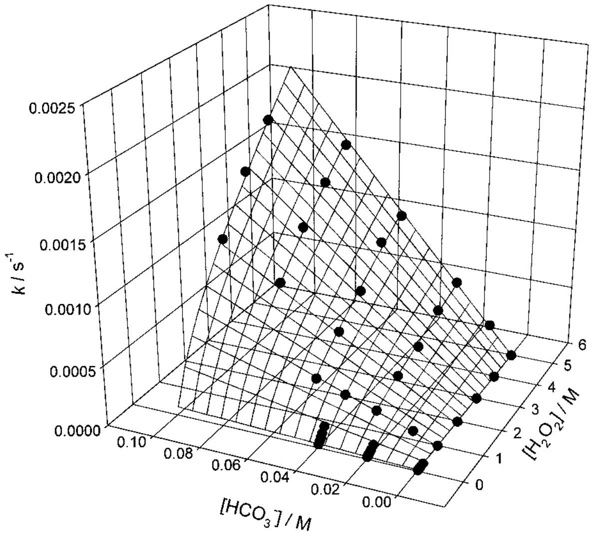

**Figure 5.** A 3D plot of the fit of eq 20 (mesh plot) to the observed catalytic first-order rate constants $k_{obs}$ (●) as a function of $[H_2O_2]$ and $[HCO_3^-]$ ($[H_2O]$ =19 M, [*t*-BuOH] = 10.3 M for this fit). The data are for the oxidation of EPS in *tert*-butyl alcohol/water (1.76:1, v/v) at 25 °C.

From plots of $k_{obs}$ vs $[HCO_3^-]$ at fixed $[H_2O_2]$, second-order rate constants, $k_{so}$, can be determined, and from eq 20 they are interpreted by eq 23.

$$k_{so} = \frac{(k_1 + k_2[H_2O_2]_0)K_{14}[H_2O_2]_0}{[H_2O]_0 + K_{14}[H_2O_2]_0 + K_{15}[R''OH]_0} \tag{23}$$

A plot of experimental $k_{so}$ values vs $[H_2O_2]$ can be produced (Figure 6). Assuming that water is constant at an average value, a fit to eq 23 can be done, and, as expected, the resulting rate constants are essentially unchanged from those in Table 1. The contributions of the $k_1$ and $k_2$ steps can be obtained by separating eq 23 into two terms and are illustrated in Figure 6. The two paths make roughly equal contributions at $[H_2O_2] = 3.5$ M for the example shown. At low $H_2O_2$ concentrations the $k_1$ path dominates.

In *tert*-butyl alcohol/water at low $[H_2O_2]$ a reciprocal plot equation can be obtained from eq 24, which is derived from eq 23 assuming $k_2[H_2O_2] \ll k_1$ and noting that the $K_{15}$ term is not applicable.

$$\frac{1}{k_{so}} = \frac{[H_2O]_0}{k_1K_{14}[H_2O_2]_0} + \frac{1}{k_1} \tag{24}$$

From the slope and intercept of a plot of $1/k_{so}$ vs $[H_2O]/[H_2O_2]$, the value of $k_1$ ($0.010 \pm 0.003$ M$^{-1}$ s$^{-1}$) and a kinetic value for the equilibrium constant $K_{14}$ ($25 \pm 7$) are obtained. The

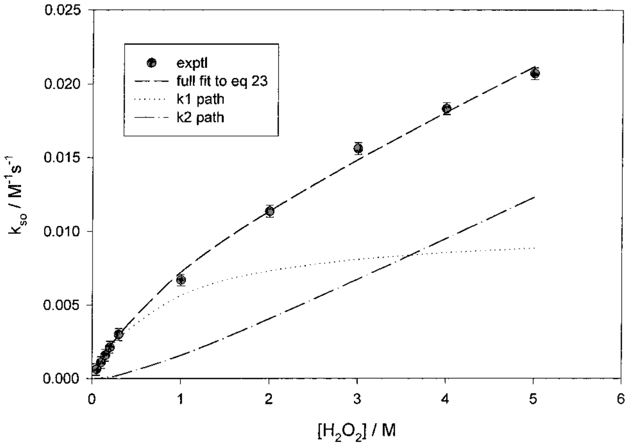

**Figure 6.** Plot of second-order rate constants $k_{so}$ at 25 °C fit by eq 23 for catalytic EPS oxidation in *t*-butanol/water (1.76:1, v/v) as a function of [$H_2O_2$] ([$H_2O$] = 19 M, [*t*-BuOH] = 10.3 M for this fit). The separate contributions of the $k_1$ and $k_2$ paths are shown on the plot (see legend).

agreement between the NMR (27 ± 1) and kinetic values of $K_{14}$ provides further support for the proposed mechanism.

Activation parameters for the $k_1$ pathway were obtained in the temperature range 15−35 °C in *tert*-butyl alcohol/water ($\Delta H^{\ddagger} = 38 \pm 1$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -154 \pm 4$ J mol$^{-1}$ K$^{-1}$) and can be compared to those for other anionic oxidants such as $IO_4^-$ and $HSO_5^-$. In all cases including $HCO_4^-$ the entropy values are strongly negative as expected for a bimolecular reaction (e.g., $IO_4^-$ oxidation of methylphenylsulfide in 1:1 (v/v) ethanol/water: $\Delta H^{\ddagger} = 47 \pm 1$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -113 \pm 4$ J mol$^{-1}$ K$^{-1}$ by reanalysis of published data;[33] $HSO_5^-$ oxidation of methylphenylsulfide in water: $\Delta H^{\ddagger} = 17 \pm 1$ kJ mol$^{-1}$ and $\Delta S^{\ddagger} = -132 \pm 1$ J mol$^{-1}$ K$^{-1}$ by reanalysis of published data[39]). For the oxidants $IO_4^-$ and $HSO_5^-$, variation in rate constants for different sulfides primarily arises from changes in $\Delta H^{\ddagger}$.[33,39] The kinetic advantage of $HSO_5^-$ over $HCO_4^-$ can be traced primarily to the much lower $\Delta H^{\ddagger}$ values for oxidations by $HSO_5^-$.

A molecular interpretation of the catalytic mechanism (eqs 14, 16, and 17) is shown in Figure 7. The $k_1$ path (eq 16) is interpreted as a solvent-assisted oxidation in which alcohol and water (R = alkyl, H) serve as proton donors to facilitate the displacement of carbonate from $HCO_4^-$. Note that the proton transfer from ROH is assumed to be to the carboxylate oxygen of $HCO_4^-$, which is clearly the most basic site on the oxidant (p$K_a$($H_2CO_4$) ≈ 4 by analogy to $H_2CO_3$). In contrast, proton transfer to the leaving group is assumed in Scheme 3 to be at the oxygen α to the electrophilic oxygen attacked by the substrate nucleophile, but in a typical peroxide YOOH another basic site is not available on the leaving group. In addition, $k_1$ contains any contributions from the direct, unassisted displacement of carbonate ion from $HCO_4^-$. The $k_2$ path (eq 17) has an additional $H_2O_2$ in the transition state and predominates at [$H_2O_2$] > 4 M. It is proposed to be essentially the $k_1$ path in Figure 7 with R = OH. The $k_2$ pathway presumably appears even though [$H_2O_2$] < [R″OH], [$H_2O$] since the acidity of $H_2O_2$ is significantly higher than that of alcohol or water.[41]

An intimate role for solvent proton transfer as shown in Figure 7 is consistent with the solvent kinetic isotope effect of 1.5 found for ethanol/water solutions (Table 2). The rather low value for $k_H/k_D$ is consistent with an early transition state for proton transfer from a solvent −OH group and is expected given the significant p$K_a$ difference between the leaving group ($HCO_3^-$, p$K_a$ =10.3) and the solvent (ROH (R = H, Et), p$K_a$ ≈15−16). The value of $k_H/k_D$ is the same for both the observed second-order rate constants ($k_{so}$) and the derived values of $k_1$ (from eq 23) since the values of $K_{14}$ and $K_{15}$ in the deuterated solvent mixture were determined to be within experimental error of those in undeuterated ethanol/water. Therefore, the observed isotope effect is associated primarily with the proposed rate determining step (eq 16) rather than the prequilibria. A similar solvent isotope effect has been reported for the oxidation of thioxane by $H_2O_2$ in water ($k_H/k_D$ = 1.68), for which solvent assistance via the mechanism of Scheme 3 was proposed.[38] In our study, a comparable $k_H/k_D$ value of 1.7 ± 0.1 was determined for the background reaction, that is, direct oxidation of EPS by $H_2O_2$ (Table 2).

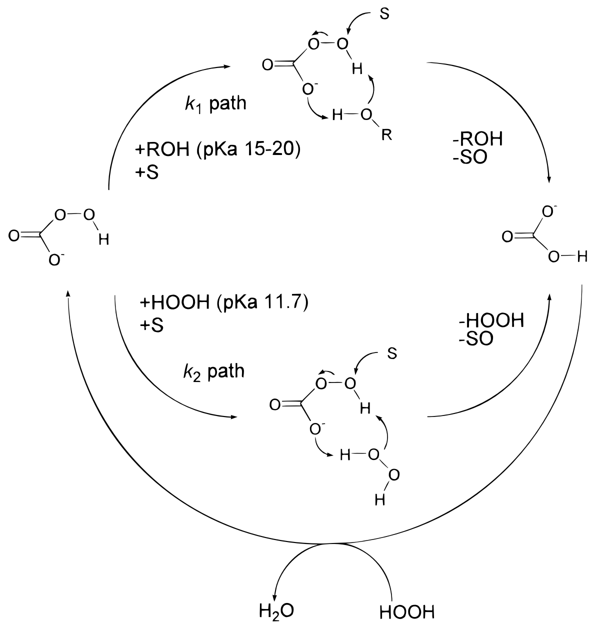

**Figure 7.** Proposed mechanisms for the $k_1$ and $k_2$ paths of eqs 16 and 17 in the text. The $k_1$ path involves solvent catalysis (R = H, alkyl) while the $k_2$ path depends on [$H_2O_2$] via the general acid catalysis shown.

A comparison of the second-order rate constants $k_{01}$ and $k_1$ can also be used to support the proposed mechanism, and the ratios of these rate constants are given in Table 1. For a given substrate oxidation, the second-order rate constant for $HCO_4^-$ is an average of ~300 times larger than that for $H_2O_2$. The typical observation for peroxide and peroxyacid oxidations is that the Brønsted slope is ~0.4 for a plot of log $k_{ox}$ vs p$K_a$(YOH) for halide oxidations, where YOH is the conjugate acid of the leaving group in the oxidant YOOH (Scheme 1).[37] A similar analysis for sulfide oxidations by peroxyacids and peroxides produces a slope of ~0.6.[42] Assuming an average slope of 0.5 ± 0.1, comparison of the p$K_a$ of $H_2O$ (15.7) to the p$K_a$ of $HCO_3^-$ (10.3) would predict that $k_1$ for $HCO_4^-$ should be a factor of $10^{2.2}$−$10^{3.2}$ (~160−1600) times greater than $k_{01}$, the corresponding rate constant for $H_2O_2$. The experimental factor of

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[41] It should be noted that the inclusion of a higher order catalytic pathway is not likely a trivial result of changing polarity of the solvent at high peroxide concentrations. The kinetic experiments we have done were designed to have a constant alcohol/water ratio even at high peroxide concentrations. This means that the concentration of both water and alcohol decline in high [$H_2O_2$] experiments. We wondered if the rate increases arose from the increased polarity of the solvent assuming that $H_2O$ and $H_2O_2$ are comparably polar. Experiments making [ROH] constant even at high [$H_2O_2$] showed only small catalytic rate reductions (<10%) compared to rates using the standard method.

[42] Bruice, T. C.; Noar, J. B.; Ball, S. S.; Venkataram, U. V. *J. Am. Chem. Soc.* **1983**, *105*, 2452−2463.

~300 is within the predicted range, lending further support to the mechanism proposed in eqs 14–17.

**Solvent Effects.** Lower-molecular weight alcohols ROH tend to lead to more rapid BAP reactions for two reasons. First, as a practical matter, the lower-molecular weight alcohols result in greater solubility of bicarbonate salts, so that higher catalyst concentrations can be achieved before saturation is attained (Figure 4). Second, for a given bicarbonate concentration, the smaller R groups lead to greater second-order rate constants for $HCO_4^-$ oxidations. Presumably, the latter effect can be associated with the increased acidity of ROH and the higher polarity of the lighter alcohols.

Increasing water content from 40 to 80% in *tert*-butyl alcohol accelerates the catalytic reaction for EPS oxidation substantially, by a factor of ~5, and a similar effect is observed for ethanol/water reactions (Table 2). The data for ethanol/water media were fit to the Grunwald–Winstein equation[43] for comparison to solvent polarity studies done previously for $IO_4^-$ oxidation of sulfides in the same solvent.[33] A plot of log $k_1$ vs $Y$ for the appropriate data in Table 2 leads to $m = 0.46$, which is substantially lower that the value for $IO_4^-$ oxidation of methylphenylsulfide ($m = 0.722$).[33] Note that the effect of varying water content on the equilibrium reaction of eq 1 has been factored out of our analysis since $k_1$ values are used in the Grunwald–Winstein $Y$ parameter fit. In addition, an overall observed rate increase with increasing water content occurs despite the shift of eq 1 to the left, which reduces the available $HCO_4^-$.

The results of the solvent polarity study imply that the transition state in the $HCO_4^-$ reaction is less polarized than the corresponding state for $IO_4^-$ since $Y$ is a measure of the solvent stabilization of charge separation in the transition state.[43] The difference may be a consequence of the participation of solvent proton transfer in the former case but not the latter. Consistent with this hypothesis, the $IO_4^-$ reaction is not subject to solvent isotope effects,[33] in contrast to the results here for $HCO_4^-$. However, the reduced kinetic dependence on solvent polarity for $HCO_4^-$ compared to $IO_4^-$ could result from other unidentified mechanistic differences.

At pH values above 9, the rate of the bicarbonate catalytic pathway decreases. We tentatively ascribe this decrease to the deprotonation of $HCO_4^-$ by analogy to the known p$K_a$ of $HSO_5^-$ (9.4).

**Numerical Simulations.** Oxidation reactions were done in this study by preequilibrating the peroxide–bicarbonate solutions to allow complete equilibrium formation of $HCO_4^-$. Generally, the sulfide oxidation reactions were assumed to be sufficiently slow that the $HCO_4^-$ concentration was not significantly depleted during the data collection. If the equilibration reaction of eq 1 is not sufficiently rapid to replenish $HCO_4^-$, then nonlinearity would be expected in the pseudo-first-order plots. In such a case the mechanism of eqs 14–17 is inadequate, and the reaction in eq 14 would be replaced by eq 25.

$$HCO_3^- + H_2O_2 \underset{k_r}{\overset{k_f}{\rightleftharpoons}} HCO_4^- + H_2O \qquad (25)$$

The second-order rate constants $k_f$ and $k_r$ have been determined for various solvents and are indeed not too different from the oxidation rate constants. Therefore, we have assessed the possible inadequacy of assuming the preequilibrium of eq 14 in the mechanism by doing a numerical simulation[44] of a mechanism for EPS oxidation consisting of eqs 16, 17, and 25, substituting the estimated rate constants from the NMR study and Table 1.

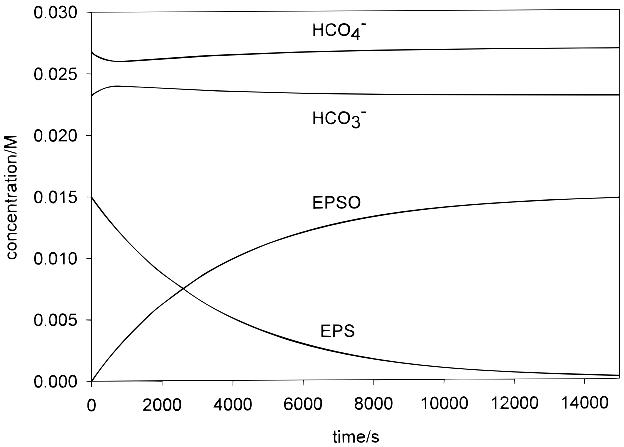

**Figure 8.** Numerical simulation of the oxidation of EPS by $H_2O_2$ catalyzed by $HCO_3^-$ as described in eqs 16, 17, and 24. The simulation is done for *tert*-butyl alcohol/water so the equilibrium of eq 15 is not used. The following parameters were used: $k_f = 1.6 \times 10^{-3}$ $M^{-1}$ $s^{-1}$, $k_r = 7.1 \times 10^{-5}$ $M^{-1}$ $s^{-1}$, $k_1 = 0.010$ $M^{-1}$ $s^{-1}$, $k_2 = 0.00295$ $M^{-1}$ $s^{-1}$, $[HCO_3^-]_0 = 0.0232$ M, $[HCO_4^-]_0 = 0.0268$ M, $[H_2O_2]_0 = 1.0$ M, and $[EPS]_0 = 0.015$ M.

An example of a simulated concentration vs time profile is shown in Figure 8. At the reaction outset, when the substrate concentration is highest, an initial decrease does occur in the amount of $HCO_4^-$. As the substrate oxidation proceeds and the rate of $HCO_4^-$ consumption thereby decreases, the equilibrium of eq 1 recovers. The maximum variation in $[HCO_4^-]$ predicted for the conditions and substrates used in our kinetic studies is <15% (usually much less), and the maximum error of the derived rate constants from first-order plots is <5% (this is the typical error limit for the numerical simulation of this mechanism and thus more precise comparisons could not be made). Insignificant nonlinearity ($R^2 > 0.999$) is predicted in the first-order ln$[R_2S]$ vs $t$ plots due to the variations in the $HCO_4^-$ concentration during the reactions, and the experimental plots were indeed linear. It should be noted that for more nucleophilic substrates, such as dialkylsulfides, the rapid preequilibrium assumption is invalid.

**Implications for Chemical Warfare Agent Decontamination.** Oxidation is a useful strategy for decontamination of certain chemical warfare agents, especially mustard (HD, $(ClCH_2CH_2)_2S$).[10] Bicarbonate catalysis has been shown to significantly lower the $t_{1/2}$ for HD oxidation by $H_2O_2$,[14] and aqueous alcohol provides good agent and oxidant solubility characteristics. We have shown for EPS oxidation that partial replacement of ethanol by propylene glycol accelerates the reaction above that observed for aqueous ethanol as solvent (Figure 4). This observation is of interest since propylene glycol has a wide liquid temperature range and is readily applied on a large scale.

The general BAP formulation is mild and noncorrosive, making it compatible with equipment and relatively safe for human exposure. Aqueous sodium bicarbonate has a pH of 8.3, while solutions of the more soluble ammonium bicarbonate have a pH of 7.9. Upon standing, solid ammonium bicarbonate evaporates, forming $CO_2$, $NH_3$, and $H_2O$. Thus, these solutions could be used without requiring rinsing to remove residual salts

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[43] Grunwald, E.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 846.

[44] Numerical kinetic simulations were done with Kinetica99, a program based on the Gear integration method (D. E. Richardson, University of Florida, 1999).

(however, the ammonium salt has low storage stability). Stable sources of peroxide equivalents are available in solid inorganic peroxides.[45]

The reactivity of mustard (HD) is typically between that of EPS and 2-chloroethylphenylsulfide (CEPS);[46] thus, we examined the oxidation of the latter compound for comparison. The rate constants for background oxidation and the catalytic oxidation of CEPS in ethanol/water are generally a factor of ~5 lower than those for EPS (Table 1). Some difficulty in obtaining data for CEPS at very low [$H_2O_2$] values arose from the observed hydrolysis of the substrate to form 2-hydroxyethylphenylsulfide ($t_{1/2} = 4$ days at 25 °C). We determined the oxidation kinetics for the latter compound (Table 1) and found it was oxidized ~4-fold more rapidly than CEPS. Therefore, kinetic data for CEPS were obtained only under conditions where its hydrolysis was minimal during the data collection.

It has also been reported that the BAP system is effective for rapid decontamination of other agents that can be decomposed by perhydrolysis, such as VX.[14] Apparently the weakly alkaline BAP system has sufficient concentration of the strong nucleophile $HO_2^-$ at equilibrium to decompose these substrates efficiently.

**Synthetic Implications**. The BAP system provides a convenient, high-oxygen efficiency method for the conversion of sulfides to sulfoxides and sulfones. The inexpensive reagents are nominally nontoxic, and organic products can be readily separated. Typical accelerations of 2 orders of magnitude and more for the oxidations can be obtained at moderate bicarbonate and $H_2O_2$ concentrations. For example, with 1 M $H_2O_2$ and 1 M $HCO_3^-$, the catalytic pathway for EPS oxidation is predicted from the data in Table 1 and eqs 6 and 20 to be 190 times faster ($t_{1/2} = 94$ s) than the direct $H_2O_2$ oxidation ($t_{1/2} = 4.9$ h) under the conditions of our *t*-BuOH/water reactions.

In general, we have observed that rates of oxidation by $HCO_4^-$ increase with increasing water content and lighter alcohols as cosolvent (Table 2), and bicarbonate salts have greater solubility in the more polar solvents. Thus, maximizing water in the reaction medium is helpful, at least to the point where solubility limits of the substrate are reached. In addition, alkylated ammonium cations ($RNH_3^+$) can also be used to increase solubility of the catalyst in less polar media.[7]

We have also demonstrated that the BAP system is useful for the epoxidation of alkenes.[15] Thus, the strong acceleration seen in our sulfide kinetics is likely to be found for other substrates, and we have begun a systematic investigation of the synthetic utility of the BAP system in biphasic and monophasic reactions.

**Comparison of Bicarbonate to $CH_3ReO_3$ in Peroxide Activation**. $CH_3ReO_3$ (MTO) is a well-studied example of a transition-metal peroxide activation catalyst, and the kinetics of the catalytic oxidation of sulfides by $H_2O_2$ have been investigated by Espenson and co-workers.[47] Useful comparisons to the present bicarbonate system can be made that illustrate the advantages and disadvantages of the latter. In many respects, the MTO and bicarbonate systems are similar mechanistically. Both feature formation of a peroxy species by initial reaction with $H_2O_2$ (in the case of MTO, both $CH_3Re(H_2O)(O)_2(O_2)$ and $CH_3Re(H_2O)(O)(O_2)_2$ are formed), and these species then act as electrophiles in direct reactions with substrate. The equilibrium constants are somewhat larger for MTO in the peroxide-forming reactions analogous to eq 1.[48] In addition, the second-order rate constants for the reaction of the intermediate peroxy species with substrate are much higher for the MTO case (e.g., $k = 2700\ M^{-1}\ s^{-1}$ for methylphenylsulfide oxidation by $CH_3Re(H_2O)(O)_2(O_2)$ in 1:1 acetonitrile/water at 25 °C; compare to $k_1 \approx 0.05\ M^{-1}\ s^{-1}$ for EPS oxidation (eq 16) in 1:1 ethanol/water here). However, the bicarbonate system has the advantage of being stable and functional at neutral pH, while the MTO peroxides decompose with a half-life of <100 s at pH 7.[48]

## Conclusions

We have shown that bicarbonate ion is an effective activator for hydrogen peroxide in the oxidation of sulfides. The kinetic and spectroscopic results strongly support the formation of peroxymonocarbonate as the oxidant in the catalytic reactions. The reaction of hydrogen peroxide and bicarbonate to form peroxymonocarbonate proceeds rapidly near neutral pH in aqueous solution and alcohol/water mixtures. An equilibrium analysis allows estimation of the electrode potential for the $HCO_4^-/HCO_3^-$ couple.

Solubility of the bicarbonate catalyst is enhanced by use of $NH_4HCO_3$ rather than group 1 salts, which tend to have low solubility in the mixed solvents and can lead to phase separation. The second-order rate constants for sulfide oxidations by peroxymonocarbonate are ~300-fold greater than those for hydrogen peroxide, and this increase is consistent with expectations based on a Brønsted analysis of the kinetics for other heterolytic peroxide oxidations. At high concentrations of $H_2O_2$ (>1 M), a significant pathway that is second order in $H_2O_2$ is observed, and this path is interpreted as a general acid catalysis of carbonate displacement by the substrate attack at the electrophilic oxygen of $HCO_4^-$.

The BAP oxidation system is a simple, inexpensive, and relatively nontoxic alternative to other oxidants, and our experiments indicate that it may have use in a variety of oxidations where a mild, neutral pH oxidant is required. Variation of bicarbonate source and the alcohol cosolvent can allow optimization of substrate solubility and oxidation rates for applications such as organic synthesis and chemical warfare agent decontamination. The lower intrinsic reactivity of $HCO_4^-$ compared to other peroxyacids and metal catalyst systems, such as MTO/$H_2O_2$, can be compensated by significantly increasing the concentration of the inexpensive bicarbonate activator.

Finally, the potential role of peroxymonocarbonate ion as a reactive oxygen species in biology is worthy of further investigation in view of the kinetic and mechanistic results of this study. Given the complexity of biochemical media, the results here argue for a more detailed examination of $HCO_4^-$ formation under typical biochemical conditions and its oxidation of substrates such as amino acids and proteins. Clearly, the heterolytic oxidation of methionine to methionine sulfoxide is a likely process for study, and we have observed bicarbonate-catalyzed oxidation of methionine by peroxide.[27] Further studies of this type are underway in our laboratory.

## Experimental Section

**Materials.** Sulfides (Aldrich), hydrogen peroxide (35%, Aldrich), propylene glycol (Fisher), *tert*-butyl alcohol (Fisher), 2-propanol (Fisher), and ethanol (AAPER), all reagent grade, were used without further purification. High purity sodium bicarbonate (99.99+%, Aldrich) was used to minimize metal contamination. Ammonium bicarbonate (Mallinckrodt), potassium bicarbonate (Mallinckrodt), potassium car-

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[45] Comyns, A. E. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Kroschwitz, J. I., Ed.; Wiley-Interscience: New York, 1997; Vol. 18, pp 202−229.

[46] Wagner, G. W., personal communication.

[47] Vassell, K. A.; Espenson, J. H. *Inorg. Chem.* **1994**, *33*, 5491−5498.

[48] Yamazaki, S.; Espenson, J. H.; Huston, P. *Inorg. Chem.* **1993**, *32*, 4683.

bonate (Baker), analytical reagent, were used as received. The buffer components ammonium dibasic phosphate (Sigma), potassium monobasic phosphate (Fisher), potassium dibasic phosphate (Mallinckrodt), and potassium chloride (Fisher), also analytical quality, were used without further purification. High purity diethylene-triaminepentaacetic acid (DTPA) was obtained from Sigma. For $^{13}$C NMR studies, 99% $^{13}$C-enriched sodium bicarbonate and 99.9% $D_2O$ (Cambridge Isotope Laboratories, Inc.) and 99% $^{13}$C-enriched $K_2CO_3$ (Aldrich) were used. Water was purified using a Barnstead Nanopure system.

**Kinetics.** Alcohol/water solutions of hydrogen peroxide with bicarbonate catalyst were prepared 20−30 min prior to mixing with sulfide substrate to ensure the preequilibration of peroxymonocarbonate formation for each kinetic run. Oxidations of sulfides with hydrogen peroxide in large excess over the sulfide were followed spectrophotometrically with Hewlett-Packer 8453 single-cell or multicell spectrometers with a temperature control of ±0.1 °C. Typically, the concentration of hydrogen peroxide was at least 60-fold over that of the sulfide. Oxidation of sulfides was generally followed by the decreasing absorbance of at $\lambda = 296$ nm. Variation of the sulfide concentration by a factor of up to 5 did not affect the rate constants. Due to the absorbance of hydrogen peroxide at $\lambda \approx 290-300$ nm, cells with shorter optical paths, for example, 0.2 or 0.1 cm, were used for kinetic measurements in 1−5 M hydrogen peroxide solutions.

The concentration of hydrogen peroxide ranged from 0.04 to 5 M in alcohol/water (1.76:1, v:v) binary solvents, and the stock solution of hydrogen peroxide (35%) was regularly standardized iodometrically. Although the ionic strength of the reaction media did not have a significant effect on rate constants at low concentration of bicarbonate salts, kinetic measurements in ethanol/water with ammonium bicarbonate (0−0.05 M) were obtained employing ammonium dibasic phosphate buffer with the total ionic strength maintained at 0.05 in all experiments. The pH range of the corresponding aqueous media with 0.04−5 M hydrogen peroxide was from 7.9 to 7.3 (± 0.1), determined by using either an Orion Research Digital pH/Millivolt Meter 611 or a Fisher AB15 pH Meter.

A pH dependence study on rate constants was performed in ethanol/water solutions of 2 M hydrogen peroxide with a total concentration of 0.05 M potassium bicarbonate/carbonate catalyst, and ionic strength was maintained at 0.12 ± 0.03 (0.05 M potassium carbonate) by the addition of potassium chloride. The pH of the corresponding aqueous media (no alcohol added) of the above solutions ranged from 7.3 (0.05 M potassium bicarbonate) to 9.4 (0.05 M potassium carbonate). Similarly, rate constants of the uncatalyzed oxidation reactions in 2 M hydrogen peroxide solution with the corresponding pH range were measured in potassium phosphate monobasic/dibasic buffer solutions at a total ionic strength 0.1.

In most cases, the oxidations were followed up to 3 half-lives with 30−40 data points, and the absorbance changes were >0.3. In a few cases, the reactions were extremely slow due to a low concentration of hydrogen peroxide and little or no catalyst, data were taken for 0.5−2 half-lives. For kinetic measurements in propylene glycol/ethanol/water solution, minimal ethylphenylsulfide was added due to its poor solubility in the alkaline solution containing glycol, and the change of the absorbance was about 0.1−0.2. Overall, plots of ln $A$ vs time were consistently linear for 3 half-lives with $R^2 > 0.999$ in most cases.

**Equilibria.** $^{13}$C NMR spectral measurements were carried out on a Gemini 300 MHz or a VXR 300 MHz NMR instrument to obtain the kinetic parameters and equilibrium constants for eq 1 in water, ethanol/water and *tert*-butyl alcohol/water media at 25 ± 0.1 °C. Sample solutions were prepared as described for the kinetic studies, except that 10% of $H_2O$ was replaced by $D_2O$. The three components, hydrogen peroxide stock solution, aqueous solution of 99% $^{13}$C-enriched sodium bicarbonate, and alcohol were mixed and injected in an NMR tube immediately before each measurement. Variation of delay parameter *d1* from 5 to 15 s gave similar integral ratios for peaks assigned to $HCO_3^-$, $HCO_4^-$, and $EtOCO_2^-$ in ethanol/water solution, indicating that relaxation times of these species are not appreciably different. Acceptable $^{13}$C NMR spectra were generally obtained with $d1 = 10$ s and 16 acquisitions. The spectra were recorded periodically for 30−40 min automatically. The concentration of hydrogen peroxide varied from 0.2 to 4 M. In most cases, 0.1 M $^{13}$C-enriched sodium bicarbonate was used. Concentrations of sodium bicarbonate <0.05 M decreases the signal/noise level of spectra for obtaining kinetic parameters unacceptably. Higher concentration of the bicarbonate salt usually resulted in difficulty shimming on the instrument due to high ionic strength of the solution.

The rates of the formation of $HCO_4^-$ and $EtOCO_2^-$ were analyzed by the increasing of intensities of these signals using the *kini* program in the Varian VNMR Software. The equilibrium constants were calculated from the integrated intensity ratios of $HCO_3^-$ and $HCO_4^-$ or $HCO_3^-$ and $EtOCO_2^-$. For solutions of 2 M hydrogen peroxide, three duplicate runs were carried out to obtain calculated values for equilibration rate constants and equilibrium constants. Variable-temperature $^{13}$C NMR studies from −20 to 50 °C in ethanol/water with 2 M hydrogen peroxide were performed.

**Products.** The reaction products of sulfide oxidation in the presence of large excess of hydrogen peroxide were examined on a Hewlett-Packard 5890 series II gas chromatography instrument with chlorobenzene as internal standard.

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