

Mechanism of Sulfide Oxidations by Peroxymonocarbonate

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A detailed mechanism for the oxidation of aryl sulfides by peroxymonocarbonate ion in cosolvent/water media is described. Kinetic studies were performed to characterize the transition state, including a Hammett correlation and variation of solvent composition. The results are consistent with a charge-separated transition state relative to the reactants, with an increase of positive charge on the sulfur following nucleophilic attack of the sulfide at the electrophilic oxygen of peroxymonocarbonate. In addition, an average solvent isotope effect of 1.5 ± 0.2 for most aryl sulfide oxidations is consistent with proton transfer in the transition state of the rate-determining step. Activation parameters for oxidation of ethyl phenyl sulfide in *tert*-butyl alcohol/water are reported. From the pH dependence of oxidation rates and ^{13}C NMR equilibrium experiments, the estimated $\text{p}K_{\text{a}}$ of peroxymonocarbonate was found to be ~ 10.6 .

Our recent kinetic investigations of bicarbonate-catalyzed organic sulfide oxidations¹ strongly support the central role of peroxymonocarbonate (HCO_4^-) as the oxidant. Peroxymonocarbonate is formed from bicarbonate and hydrogen peroxide (eq 1) and subsequently oxidizes the sulfide to sulfoxide (eq 2). Previously reported kinetic results¹ are consistent with the



equilibration reaction of eq 1 proceeding via the perhydration of CO_2 formed in equilibrium with HCO_3^- . When mixed cosolvent/water solvents are used for the oxidations, the concentration of water is included explicitly in the equilibrium expressions, so $K = [\text{HCO}_4^-][\text{H}_2\text{O}]/[\text{H}_2\text{O}_2][\text{HCO}_3^-]$. The rate constants k_f and k_r are the second-order rate constants for the forward and reverse reactions of the reaction in eq 1, respectively. In experiments that support the intermediacy of CO_2 in the formation of HCO_4^- , we have demonstrated that the equilibration of eq 1 is accelerated in the presence of catalysts for the dehydration of bicarbonate.² Thermodynamic results for eq 1 give a value of $E^\circ(\text{HCO}_4^-/\text{HCO}_3^-) = 1.8 \pm 0.1 \text{ V}$ (vs NHE), and HCO_4^- is therefore a potent oxidant in aqueous solution.¹ The structure of the ion is that of a true peroxide, i.e., HOOCO_2^- , as shown convincingly by X-ray crystallography ($\text{KHCO}_4 \cdot \text{H}_2\text{O}$).³

Peroxymonocarbonate is a moderately reactive heterolytic oxidant that can be classified as an anionic peracid. The rate constants for oxidation of aryl sulfides¹ are intermediate between those for H_2O_2 and more reactive oxidants such as peroxymonosulfate.⁴ The second-order rate constants for ethyl phenyl

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.

In this continuation of our study of peroxymonocarbonate oxidations we examine the nature of the transition state species for sulfide oxidation in more detail. Hammett correlations, variation of solvent composition, and kinetic isotope effects have been used to characterize the charge distribution and extent of proton transfer in the activated complex. In addition, the pH dependence of the oxidation reaction kinetics was used along with ^{13}C NMR studies of eq 1 to determine the Brønsted acid–base properties of peroxymonocarbonate ion.

Results and Discussion

Kinetics. The oxidation of various aryl sulfides in alcohol/water mixtures was monitored spectrophotometrically as described previously¹ by following the loss of absorbance in the 290–400 nm range. The sulfide was added to pre-equilibrated solutions of hydrogen peroxide and NH_4HCO_3 catalyst at the start of the reaction. $(\text{NH}_4)_2\text{HPO}_4$ was used to maintain a constant ionic strength and to set a comparable pH in background kinetic studies, and pseudo-first-order conditions were used with H_2O_2 in large excess. Bicarbonate-catalyzed reactions were followed for the three most reactive methyl phenyl sulfides for at least 2 half-lives, and no evidence for deviation from first-order behavior was observed. For the least reactive two sulfides, 30–50% of the catalyzed reaction was followed since some decomposition of peroxide becomes evident after 24 h. For the background reactions with no bicarbonate added only a small percentage of the reaction could be recorded (2–25%), but the background contribution in the catalyzed reactions was small ($\leq 12\%$).

In previous work¹ we suggested that the mechanism for the bicarbonate activation of hydrogen peroxide is that given in eqs 1 and 2 above along with eqs 3 and 4. In cases where the

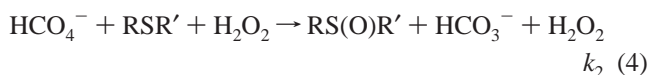
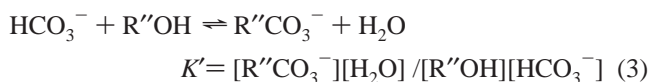
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cosolvent is a primary alcohol, a correction for carbonate ester formation (eq 3) is necessary when deducing the rate constants k_1 and k_2 . At high concentration of hydrogen peroxide ($> 1 \text{ M}$), hydrogen peroxide itself is significantly catalytic, and this is the k_2 path (eq 4). If the first-order rate constant for oxidation ($k_1[\text{RSR}']$) is comparable in magnitude to the rate constant for the reverse of eq 1 ($k_r[\text{H}_2\text{O}]$), then eq 1 cannot be considered a preequilibrium reaction and a steady state rate law applies (eq 5).

$$\frac{d[\text{RS(O)R}']}{dt} = \frac{(k_1 + k_2[\text{H}_2\text{O}_2]_0)[\text{H}_2\text{O}_2]_0[\text{HCO}_3^-]_0[\text{RSR}']}{k_r[\text{H}_2\text{O}] + k_1[\text{RSR}'] \left(1 + \frac{K'[\text{R}''\text{OH}]}{[\text{H}_2\text{O}]} \right) + [\text{H}_2\text{O}_2]_0} \quad (5)$$

When $k_r[\text{H}_2\text{O}] \gg k_1[\text{RSR}']$, eq 5 reduces to the preequilibrium rate law of eq 6.¹

$$-\frac{d[\text{RSR}']}{dt} = \frac{(k_1 + k_2[\text{H}_2\text{O}_2]_0)K[\text{H}_2\text{O}_2]_0[\text{HCO}_3^-]_0[\text{RSR}']}{[\text{H}_2\text{O}] + K[\text{H}_2\text{O}_2]_0 + K'[\text{R}''\text{OH}]} = k_{\text{obs}}[\text{RSR}'] \quad (6)$$

When the concentration of hydrogen peroxide is low, the k_2 term can be ignored.

From previous studies,¹ in 1.76:1 ethanol/water (v/v) at 25 °C, $K = 27 \pm 1$, $K' = 1.8 \pm 0.2$, $k_r \approx 9 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$, and $k_1 \approx 3 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. We note that the equilibrium constants given are effective constants rather than strict thermodynamic quantities and were obtained under conditions that are similar to those of the kinetic studies here. The catalytic rate constants k_1 were determined for aryl sulfides in this work by substituting known values for the relevant equilibrium constants K and K' and the observed rate constants into eq 6, assuming $k_1 \gg k_2[\text{H}_2\text{O}_2]$ under our conditions.

The values for k_1 along with the background rate constants k_{01} for a variety of methyl phenyl sulfides are given in Table 1. Rate constants for oxidation by peroxymonocarbonate were found to be 250–300 times greater than those for the uncatalyzed reaction with H_2O_2 , and this result is consistent with previous observations¹ for ethyl phenyl sulfides.

Dialkyl sulfides are usually stronger nucleophiles than aryl sulfides in reaction with electrophilic oxidants. The value of k_1 for the dialkyl sulfide $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ is ~ 25 times greater than that of methyl phenyl sulfide, and the reaction was therefore analyzed via eq 5 by nonlinear regression of ¹H NMR data as described elsewhere for the oxidation of methionine.² The value of k_{01} for the reaction of $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ with H_2O_2 ($0.0066 \text{ M}^{-1} \text{ s}^{-1}$) in ethanol/water is comparable in magnitude to that reported for CH_3SCH_3 in water by Amels et al. ($0.018 \text{ M}^{-1} \text{ s}^{-1}$).⁵

Solvent Effects. An increase in the water content of the water/alcohol medium for bicarbonate-activated peroxide oxidations

results in an increase in the rate of the reactions despite the resulting shift of eq 1 to the left.¹ A fit of k_1 values to the Grunwald–Winstein equation⁶ gave an m value of 0.46.

To explore solvent effects in more detail, we examined the trends in oxidation rates for ethyl phenyl sulfide (EPS) as a function of the cosolvent used in the mixed aqueous reaction medium. A plot of $\log k_1$ against the Kirkwood solvent dielectric parameter⁷ has a positive slope (Figure 1), which is indicative of a transition state that is more polar than the reactants. The Kirkwood parameter closely parallels the $1/\epsilon$ values for the various solvents used. Increasing the polarity of the solvent, as measured by the static dielectric constant, results in an increase in the rate of oxidation of the sulfides. Such an increase in rate in a more polar medium is expected for displacement reactions involving an uncharged nucleophile (sulfide) and an anionic leaving group (carbonate).⁸

Hammett Correlation. Changing the para substituent on an aryl sulfide from an electron-donating group, such as $-\text{OMe}$, to one which is electron withdrawing, such as $-\text{CN}$, leads to a decrease in the value of k_1 (Table 1). A Hammett plot was made (Figure 3) to determine the correlation coefficient ($\rho = -1.4 \pm 0.2$). The observation that an electron-donating substituent accelerates the oxidation rate is consistent with stabilization of positive charge buildup at sulfur in the transition state. Similar results were reported for the oxidation of para-substituted methyl phenyl sulfides by periodate ($\rho = -1.4$),⁹ suggesting that both systems have a similar charge at sulfur in the activated complex. A somewhat lower ρ value (ca. -1) was reported by Bunton et al.,⁴ for the oxidation of aryl sulfides with peroxymonosulfate.

Activation Parameters. The rates of oxidation for EPS at various temperatures (15 – 25 °C) in 60:40 v/v *tert*-butyl alcohol/water were compared to those in a medium with higher water content (30:70 v/v *tert*-butyl alcohol/water). The resulting activation parameters are given in Table 2. The activation parameters for the system do not change significantly with an increase in the water content. Although the reaction rate was approximately 5 times higher in the higher water medium, the increase could not be associated with changes in either activation parameter with any statistical significance. In general, more reactive peracids such as peroxymonosulfate are characterized by lower enthalpies of activation for the oxidation reaction.⁴

Solvent Kinetic Isotope Effects. In previous work a solvent isotope effect of 1.5 ± 0.15 was obtained for ethyl phenyl sulfide oxidation by peroxymonocarbonate ion in an ethanol/water medium.¹ We concluded that there is participation of proton transfer involving the solvent in the transition state. Further studies carried out here on several methyl phenyl sulfides having para-substituted electron-withdrawing or -donating groups (Table 3) yield consistent solvent isotope effects of $k_{\text{H}}/k_{\text{D}} = 1.5 \pm 0.2$ for the catalytic pathway with most substrates. We conclude that most of the aryl sulfides have comparable participation of hydrogen transfer in the transition state.

An exception was observed for the case involving an electron-donating substituent, *p*-methoxyphenyl ethyl sulfide, which did not display a significant solvent kinetic isotope effect ($k_{\text{H}}/k_{\text{D}} = 1.10 \pm 0.25$). However, the 95% confidence interval on the value of this isotope effect is rather large, and the result must therefore be interpreted with caution.

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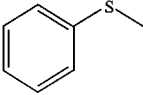
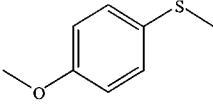
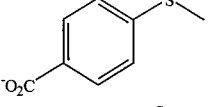
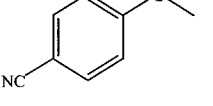
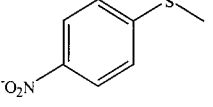
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Table 1. Kinetic Parameters for Sulfide Oxidations by Bicarbonate-Activated Hydrogen Peroxide^a

Substrate	Solvent (composition)	$10^5 k_0 / \text{M}^{-1} \text{s}^{-1}$ ^b	$10^3 k_1 / \text{M}^{-1} \text{s}^{-1}$	k_1/k_0
	EtOH/H ₂ O (60:40)	7.3 ± 1.6	22.8 ± 0.8	312
	EtOH/H ₂ O (60:40) EtOH/H ₂ O (30:70)	20.0 ± 2.0 113 ± 15	54.1 ± 1.1 320 ± 14	271 283
	EtOH/H ₂ O (60:40)	4.9 ± 1.2	11.4 ± 0.6	233
	EtOH/H ₂ O (60:40)	1.25 ± 0.12	2.60 ± 0.06	208
	EtOH/H ₂ O (60:40)	0.40 ± 0.04	1.30 ± 0.03	325
CH ₃ SCH ₂ CH ₂ OH ^c	EtOH/H ₂ O (30:70)	660 ± 80	670 ± 20	102

^a Conditions: 25 °C, [H₂O₂] = 0.10 M, [HCO₃⁻] = 0–0.050 M. The k_1 values were derived from k_{obs} values and eq 6 (with correction for the background reactions) assuming $k_2[\text{H}_2\text{O}_2]$ is negligible. ^b k_0 is the second-order rate constant for the background reaction $\text{RSR}' + \text{H}_2\text{O}_2 \rightarrow \text{RS(O)R}' + \text{H}_2\text{O}$. ^c Oxidation reaction studied by using ¹H NMR spectroscopy. k_1 and k_0 values are derived from fitting of the data to numerical simulations using Kinetic99. Errors shown are quoted as standard errors.

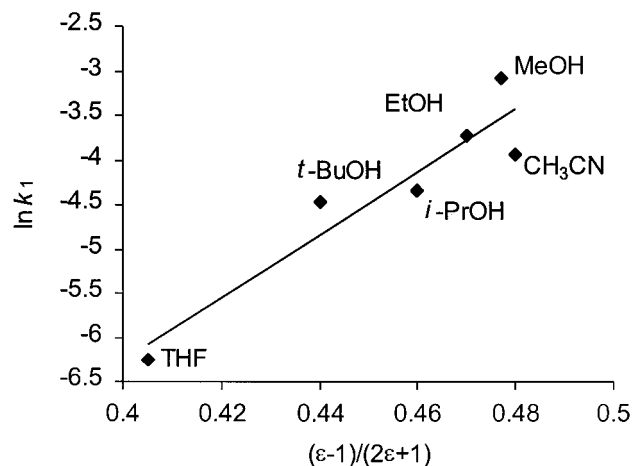


Figure 1. Plot for $\ln k_1$ versus $\{(\epsilon - 1)/(2\epsilon + 1)\}$ for ethyl phenyl sulfide oxidations in several mixed aqueous solvents. Reaction conditions: 25 °C, [H₂O₂] = 0.1 M, [HCO₃⁻] = 0–0.05 M, solvent/water = 1.76:1 v/v. The small discrepancy between the entry for ethanol in this figure and ref 1 arises from the neglect of the k_2 pathway in analyzing the rate constants here.

We examined the origin of the isotope effect by using an approximate model as described by Schowen.¹⁰ It is important to note that the solvent kinetic isotope effect also must include any effect associated with the deuteration of HCO₄⁻, since DCO₄⁻ will be formed by hydrogen/deuterium exchange in D₂O/EtOD media. Thus, the hydrogen donor producing the isotope effect can be the peroxide –OOH, solvent ROH (R = Et, H), or both. Given the weak acidity of water and alcohols and the high acidity of their conjugate acids, hydrogen transfer from solvent to HCO₄⁻ and to solvent from HCO₄⁻ is not expected to be extensive in the transition state (estimated $\text{p}K_a(\text{HCO}_4^-)$

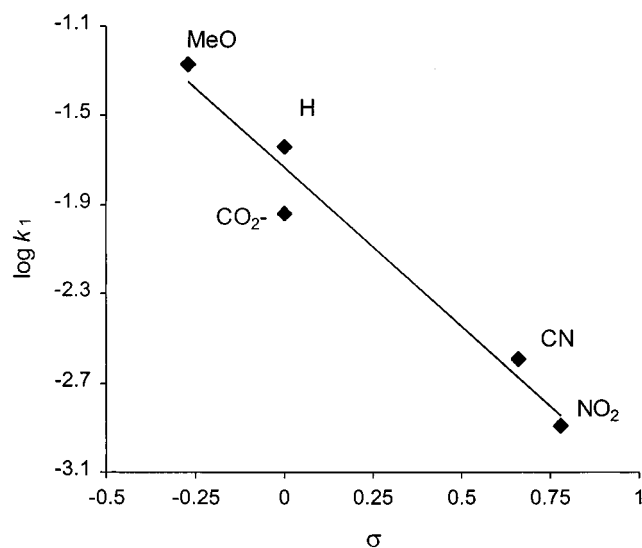


Figure 2. Plot for the $\log k_1$ versus σ for ethyl phenyl sulfide oxidations. Reaction conditions: 25 °C, [H₂O₂] = 0.1 M, [HCO₃⁻] = 0–0.05 M, ethanol/water = 1.76:1 v/v.

~ 10.6 (see below), $\text{p}K_a(\text{H}_2\text{CO}_4) \sim 4$ (estimated from that of carbonic acid)). Maximum primary isotope effects for O–H–O transfers are high (~ 10 – 15) since the reactant O–H stretching frequencies are in the range 3300–3700 cm^{-1} . Secondary isotope effects are expected to be negligible here, and the experimental values of K for eq 1 in D₂O and D₂O/EtOD are not significantly different from those in water and H₂O/EtOH. The extent of transfer is expected to be low in the transition state, thus accounting for a low $k_{\text{H}}/k_{\text{D}}$ of ~ 1.5 . An x value $\ll 0.1$ is deduced for the transfer by the treatment of Schowen (x describes the extent of H transfer in the transition state, with possible values from 0 to 1).¹⁰

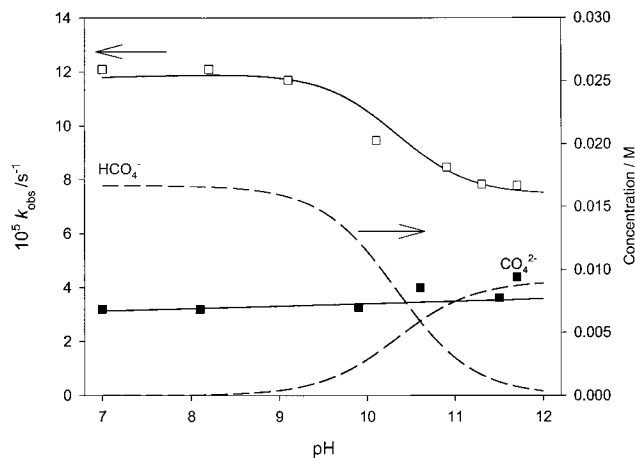


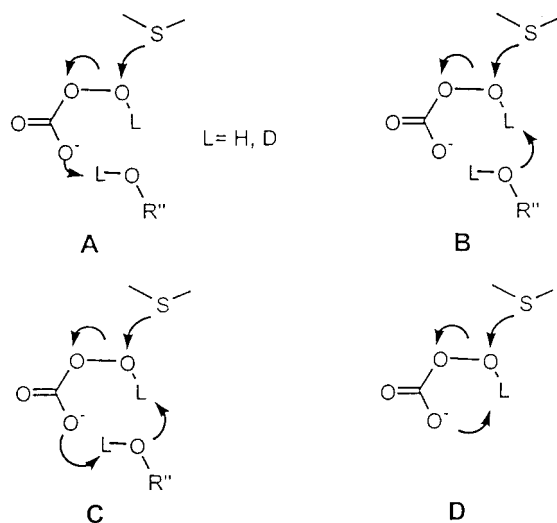
Figure 3. Variation of observed first-order rate constants for 2-hydroxyethyl phenyl sulfide oxidations at different pH values. Reaction conditions: 25 °C, pH = (7.3–11.7), $[H_2O_2] = 0.10$ M, ethanol/water = (20:80 v/v). \square : Observed rate constants with $[HCO_3^-] + [CO_3^{2-}] = 0.025$ M (left axis). \blacksquare : Observed background rate constants with no bicarbonate (left axis). Solid lines: fits as described in text. Dashed lines: concentrations of peroxycarbonate species (right axis) based on $pK_a(HCO_4^-) = 10.6$ and equilibrium constants given in the text.

Table 2. Activation Parameters^a

oxidant	solvent	ΔH^\ddagger kJ/mol	ΔS^\ddagger J/mol K
peroxymonocarbonate ^b	60:40 <i>t</i> -BuOH/H ₂ O	38 ± 1	-154 ± 4
peroxymonocarbonate	30:70 <i>t</i> -BuOH/H ₂ O	37 ± 3	-146 ± 11
H ₂ O ₂ ^b	60:40 <i>t</i> -BuOH/H ₂ O	55 ± 5	-145 ± 17
H ₂ O ₂	30:70 <i>t</i> -BuOH/H ₂ O	59 ± 2	-119 ± 7

^a Conditions: $[H_2O_2] = 0.10$ M, $[HCO_3^-] = 0-0.050$ M, $T = 15.4-35$ °C. Errors shown are quoted as standard errors. The substrate is ethyl phenyl sulfide. ^b Reference 1.

Structure **A** shows one possible origin of the solvent isotope effect, where protonation of the leaving carbonate by water or alcohol assists in its displacement by sulfide. This proton shift



is a strongly disfavored process energetically given the weak acidity of the solvent. Structure **B** describes another possible contributor to the solvent isotope effect, in which the solvent accepts a proton from the peroxide. Again, only a small primary effect is expected given the low extent of transfer expected in the transition state. Structure **C** combines both transfers in a concerted mechanism and avoids significant charge separation associated with **A** and **B**. Although **C** depicts a single solvent

Table 3. Kinetic Isotope Effect Studies for Methyl Aryl Sulfides^a

substrate	k_H/k_D	
	H ₂ O ₂	HCO ₄ ⁻
methyl 4-(methoxyphenyl) sulfide	1.63 ± 0.46	1.10 ± 0.25
ethyl phenyl sulfide ^b	1.67 ± 0.10	1.50 ± 0.15
methyl phenyl sulfide	1.42 ± 0.26	1.51 ± 0.07
4-(methylthio)benzotriole	1.45 ± 0.39	1.52 ± 0.24
methyl 4-(nitrophenyl) sulfide		1.5 ± 0.3

^a Conditions: 25 °C, $[H_2O_2] = 0.10$ M, $[HCO_3^-] = 0-0.050$ M, ethanol/water = 1.76:1 v/v. k_H and k_D values are values of k_{01} (Table 1, note b) and k_1 (eq 6 assuming $k_2[H_2O_2]$ is negligible). Errors shown are 95% confidence levels. ^b Reference 1.

molecule, additional solvent molecules can be involved. An analysis of the observed isotope effects cannot be used to distinguish the extent to which any of these three mechanisms contribute to the reaction pathway as all are expected to have small k_H/k_D values.

A mechanism with the same net result as **C** is shown as **D**, in which intramolecular proton transfer produces the products. An analogous five-membered-ring transition state is widely invoked for epoxidation by peracids in aprotic solvents, and small primary isotope effects ($k_H/k_D < 1.2$) have been reported for such epoxidation reactions.^{11,12}

A solvent isotope effect of $k_H/k_D = 1.7 \pm 0.1$ was obtained for the oxidation of ethyl phenyl sulfide by H₂O₂.¹ In this study we observed an average value of $k_H/k_D = 1.5 \pm 0.2$ for the H₂O₂ oxidation of all the aryl sulfides studied (Table 3). This value is comparable to that found for the oxidation of thioxane ($k_H/k_D = 1.68$) by hydrogen peroxide.¹³

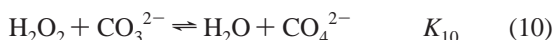
pH Dependence. It was noted in our previous publication that increasing the solvent pH to >9 leads to a decrease in the oxidation rates for bicarbonate-activated peroxide.¹ We tentatively suggested that this decreased oxidation rate resulted from the deprotonation of HCO₄⁻ to form CO₃²⁻, which presumably is a less electrophilic oxidant. We have now examined the pH dependence of the oxidation of 2-hydroxyethyl phenyl sulfide in detail (Figure 3). This sulfide was chosen to maintain buffer and substrate solubility under all of the experimental conditions with a minimal ethanol content in the medium (20%). The background reaction with H₂O₂ shows little dependence on the change in pH from 7 to 11.7, which is surprising in view of the decrease in reaction rate observed for dimethyl sulfide oxidation at pH values near the pK_a of H₂O₂.⁵ However, we have carefully investigated this region for 2-hydroxyethyl phenyl sulfide oxidation and find no evidence for a reduced oxidation rate in this pH region. The presence of 20% ethanol does not have a large effect on the effective pH of the solution as shown by potentiometric measurements. We conclude that, unlike the case for dimethyl sulfide, H₂O₂ and HO₂⁻ have comparable reactivities with 2-hydroxyethyl phenyl sulfide.

For the catalyzed reaction, an increase in the pH from 7 to ~12 shows a steady decrease in observed rate constants above pH 9 which appears to level off at pH values >11 (Figure 3). This dependence is consistent with a deprotonation of a reactive species or a species involved in the formation of the active species with $pK_a \approx 10-11$. The observation of an effective pK_a for the catalyzed reaction cannot be directly associated with

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the deprotonation of HCO_4^- since its concentration is linked by the labile equilibrium of eq 1 to the concentration of bicarbonate, which has a $\text{p}K_a$ value of 10.3.

To resolve the uncertainty in the interpretation of the kinetically effective $\text{p}K_a$, we carried out ^{13}C NMR experiments for eq 1 over the pH range used in the kinetic studies. At high pH values, deprotonation of HCO_3^- , HCO_4^- , and H_2O_2 will lead to the formation of CO_3^{2-} , CO_4^{2-} , and HO_2^- , respectively. The effective equilibrium constant determined by the integration of peaks for $\text{H}^*\text{CO}_3^-/\text{CO}_3^{2-}$ and $\text{H}^*\text{CO}_4^-/\text{CO}_4^{2-}$ can then be analyzed with respect to the equilibria of eq 1 and eqs 7–10.



If it is assumed that $K_9 < K_8$ and K_7 and that the influence of the deprotonation of H_2O_2 is negligible at pH 10.3 (the $\text{p}K_a$ of HCO_3^-), then it is easy to show that eq 11 applies at pH = 10.3. In eq 11, $[\text{HCO}_3^-]_t = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$ and $[\text{HCO}_4^-]_t$

$$K + K_{10} = \frac{2[\text{H}_2\text{O}][\text{HCO}_4^-]_t}{[\text{H}_2\text{O}_2][\text{HCO}_3^-]_t} \quad (11)$$

$= [\text{HCO}_4^-] + [\text{CO}_4^{2-}]$, and the ratio $[\text{HCO}_4^-]_t/[\text{HCO}_3^-]_t$ is determined from the integration of NMR peaks corresponding to the percarbonate and carbonate carbons. If the $\text{p}K_8$ value were equal to that of HCO_3^- (10.3), then this ratio of peak intensities would be independent of pH. On the other hand, if the $\text{p}K_8$ value were to be substantially larger than 10.3, the peak ratio would decrease rapidly as the pH is raised to >10 . It was observed that $[\text{HCO}_4^-]_t/[\text{HCO}_3^-]_t$ decreases 25% as pH is raised from 8 to 10.3. At pH 8, the value $K = 18$ is obtained from the NMR data. From the pH 10.3 data and eq 11, we estimate $K_{10} \approx 9$. It is readily shown that $K_8 = K_{10}K_7/K$, and we obtain $\text{p}K_8 \approx 10.6$. It should be emphasized that this acid dissociation constant for HCO_4^- was obtained from data for 20% ethanol solution.

We have examined the pH dependence of the ^{13}C NMR chemical shifts as an independent method for estimating the $\text{p}K_8$ value (data not shown). Useful NMR data are also available from the work of Griffith and co-workers.¹⁴ A fit of the chemical shifts for the carbonate and percarbonate resonances in the range pH 7–14 leads to $\text{p}K_7 \approx 10.3$ and $\text{p}K_8 \approx 10.8$, in agreement with the known value for HCO_3^- and the estimate above for HCO_4^- .

The inflection in the observed rate constants as the pH is raised (Figure 3) does not lead to complete loss of reactivity in the bicarbonate-activated case, and the residual activity over background above pH 11 is still $\sim 50\%$ of that at pH 7–8. The most straightforward explanation for this result is that CO_4^{2-} has significant reactivity with sulfides. A fit of the observed rate constants to a simple three-term rate law (eq 12) with the calculated equilibrium concentrations of peroxy species suggests that the effective second-order rate constant for CO_4^{2-} (k'') is only about 20% lower than that estimated for HCO_4^- . The fits are shown in Figure 3. It can be concluded that the reduction in oxidation rate at higher pH results both from the deprotonation

$$k_{\text{obs}} = k'[\text{HCO}_4^-] + k''[\text{CO}_4^{2-}] + k'''[\text{H}_2\text{O}_2]_t \quad (12)$$

of HCO_4^- to form its somewhat less reactive conjugate base and from a decrease in the total concentration of the peroxy-carbonate species that arises from the difference in the acidities of HCO_3^- and HCO_4^- .

Transition States for Oxygen Transfer. Sulfide oxidations by peroxides are generally considered to proceed by nucleophilic attack of the sulfide on an electrophilic oxygen. Examples include sulfide oxidation by periodate ion,⁹ peracids,¹⁵ and peroxymonosulfate.⁴ In the oxidations of sulfides, neither periodate nor peroxymonosulfate displays significant solvent isotope effects. An analogous mechanism has been proposed for sulfide oxidations by peroxymonocarbonate,¹ and we suggested that in protic solvents the solvent assists in the nucleophilic displacement of the carbonate (left structure in Scheme 1 with $\text{R}'' = \text{H}$, alkyl, OH, and structure C).

The formal transition state in Scheme 1 is consistent with the data presented in this work. An early transition state is anticipated since the oxidation of organic sulfides to sulfoxides by a peroxide has significant exoergicity (e.g., the estimated exothermicity for the oxidation of $(\text{CH}_3)_2\text{S}$ to $(\text{CH}_3)_2\text{SO}$ by aqueous H_2O_2 or HCO_4^- is -200 kJ/mol). The increased polarity of the activated complex relative to the reactants results in more rapid oxidations in solvents with increased water content or cosolvents of higher polarity (Figure 1). The buildup of positive charge on sulfur is consistent with the substituent effects (Table 1), which have a negative Hammett correlation coefficient (Figure 2). It is also consistent with the observation of a solvent isotope effect, and the ordered cyclic structure is consistent with the large, negative entropy of activation (Table 2). As expected for a nucleophilic attack at an electrophilic oxidant, a more rapid oxidation is observed for the more nucleophilic dialkyl sulfides $\text{CH}_3\text{SCH}_2\text{CH}_2\text{OH}$ (Table 1) and methionine.²

Experimental Section

Materials. The sulfides and hydrogen peroxide (35%) were purchased from Sigma-Aldrich. Reagent grade solvents, ethanol (AAPER), *tert*-butyl alcohol (Aldrich), isopropyl alcohol (Fisher), methanol (Fisher), and tetrahydrofuran (Fisher) were purchased and used without further purification. Ammonium bicarbonate (Mallinckrodt) and ammonium dibasic phosphate (Sigma) were purchased as analytical grade reagents and used without further purification. High-purity sodium bicarbonate (99.99 +%, Aldrich) was used, and water was purified by using a Sybron/Barnstead water purification system. 99% ^{13}C -enriched sodium bicarbonate (Cambridge Isotope Laboratories, Inc.) and 99% ^{13}C -enriched K_2CO_3 (Aldrich) were used in ^{13}C NMR studies.

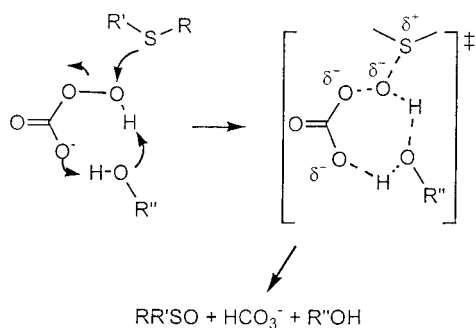
Kinetics. Sulfide oxidations were carried out in cosolvent/water media. Solutions containing hydrogen peroxide and ammonium bicarbonate were allowed to pre-equilibrate for approximately 20 min prior to the addition of the sulfides. The study was carried out spectrophotometrically by following the decreasing absorbance of the aryl sulfide peak in the 290–400 nm range on a Hewlett-Packard 8453 multicell spectrometer with a temperature control of ± 0.1 °C. The hydrogen peroxide concentration (0.10 M) was at least 60-fold higher than that of the sulfide, and the ammonium bicarbonate concentration was in the range 0–0.050 M. The 35% H_2O_2 stock solution was regularly standardized iodometrically. Ionic strength was maintained at 0.050 (ammonium dibasic phosphate), and pH measurements were taken as described previously.¹

A pH dependence study for the oxidation of 2-hydroxyethyl phenyl sulfide was performed in ethanol/water (20:80, v/v) solutions of 0.10 M hydrogen peroxide with a total concentration of 0.025 M of catalyst as potassium bicarbonate and potassium carbonate. The ionic strength

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Scheme 1



was maintained at 0.075 ± 0.005 by addition of potassium chloride. The pH of the corresponding aqueous media (no alcohol added) for the above solutions ranged from 7.3 to 11.7. Hydrochloric acid and potassium hydroxide were used to adjust the pH below 7.3 (0.025 M $KHCO_3$) or above 11.3 (0.025 M K_2CO_3), respectively. Rate constants for the uncatalyzed oxidation reactions, in 0.10 M hydrogen peroxide solution and within the corresponding pH range, were measured in potassium phosphate monobasic/dibasic or dibasic/tribasic media at a

total ionic strength of 0.075. The substrate concentration used was 0.0020 M. Depending on the pH of the solution the mixture was allowed to stand for 0.5–2.5 h before kinetic measurements were taken. Reactions were usually followed for at least 1 half-life with an absorbance change of ~ 0.3 (20–30 data points). In the case of the uncatalyzed reaction at low concentration of hydrogen peroxide the reactions were extremely slow; in such cases data for only a small percentage of the reaction were obtained.

Equilibrium constants K and K_{10} in ethanol/water (20:80, v/v) were determined by ^{13}C NMR spectral measurements as described in previous work.¹ D_2O (10%) was employed for instrument locking. The concentration of hydrogen peroxide was 0.50 M, and 99% ^{13}C -enriched sodium bicarbonate (0.050 M) and potassium carbonate (0.050 M) were used for measurements at pH = 8 and pH = 10.3, respectively. The rate of equilibration was followed by the increasing intensity of the NMR signal due to peroxymonocarbonate. After the equilibrium reaction was completed on the basis of ^{13}C NMR measurements, the ratio of the integrations of relevant NMR peaks was determined.

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