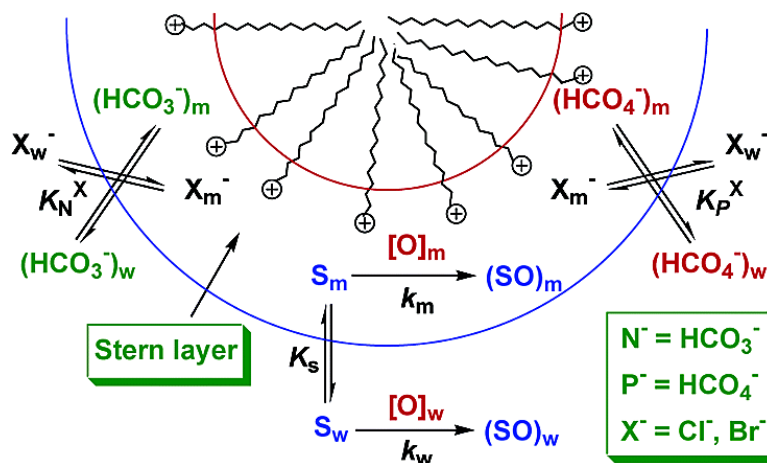


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Bicarbonate Surfoxidants: Micellar Oxidations of Aryl Sulfides with Bicarbonate-Activated Hydrogen Peroxide

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Abstract: The mechanism and kinetics of bicarbonate-catalyzed oxidations of sulfides by H_2O_2 at the aqueous/cationic micellar interface have been investigated. The general term *surfoxidant* is introduced to describe the combination of an ionic surfactant with a reactive counterion that is itself an oxidant or activates an oxidant from the bulk solution to form an oxidant counterion. It is shown that the new catalytic cationic surfoxidant CTAHCO_3 (cetyltrimethylammonium bicarbonate) significantly enhances the overall oxidation rates as compared to the addition of bicarbonate salts to CTACl and CTABr, for which the halide counterions must undergo equilibrium displacement by the oxidant anion (peroxymonocarbonate, HCO_4^-). General equations based on the classic pseudophase model have been derived to account for the preequilibrium reaction in the aqueous and micellar phases, and the resulting model can be used to describe any micellar reaction with associated preequilibria. Rate constants and relevant equilibrium constants for HCO_4^- oxidations of aryl sulfides at micellar surfaces have been estimated for CTAHCO_3 , CTACl, and CTABr. The second-order rate constants in the Stern layer (k_2^m) for sulfide oxidations by HCO_4^- are estimated to be ~ 50 -fold (PhSEtOH) and ~ 180 -fold (PhSEt) greater than the background rate constant k_m^0 for oxidation by H_2O_2 at the micellar surface. The estimated values of k_2^m are lower than the corresponding values in water by a factor of 20–70 depending on the substrate, but the high local concentration of the bicarbonate activator in the surfoxidant and the local accumulation of substrate as a result of strong binding to the micelle lead to a net increase in the observed reaction rates. Comparisons of CTAHCO_3 -activated peroxide to other highly reactive oxidants such as peroxymonosulfate (HSO_5^-) in aqueous surfactant media suggest a wide variety of potential applications for this green oxidant.

Introduction

Water offers many advantages as a solvent for organic reactions.^{1–5} In particular, its nontoxic character and tendency to accelerate reactions with polar transition states demonstrate that it can have both environmental and kinetic advantages over organic solvents. The low solubility of many hydrophobic reactants and reagents in water is a major limitation, however, and cosolvents must often be used to increase substrate solubilities, thereby reducing the environmental and kinetic benefits. Surfactants have been investigated as alternatives to organic cosolvents for the promotion of transformations of hydrophobic substrates in water.^{6,7} The concentrations of surfactants needed in a typical emulsion reaction are low as compared to the usual level of organic cosolvents used in mixed solvents, and surfactants are also nonvolatile and recyclable.

Many studies have shown how ionic surfactants with reactive counterions (*reactive ion surfactants*) can accelerate chemical

reactions because of high local concentrations of reactant ions and substrates in the micellar pseudophase.^{8–15} Recent reports illustrate the promise of approaches in which a catalyst such as a metal ion is used as the counterion.^{12–16} For example, Kobayashi and co-workers¹⁴ investigated anionic surfactants with Lewis acid counterions (scandium(III)) and showed that aldol, allylation, and Mannich-type reactions could be carried out efficiently in water. In another example, Engberts and co-workers have shown that Diels–Alder reactions can be promoted significantly (10^6 -fold) in water by anionic surfactants with copper(II) counterions.¹⁶

We have been developing a general class of reactive ion surfactants for use in the oxidation of hydrophobic substrates, for example, organic sulfides and alkenes. We use the general

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term *surfoxidant* to describe the combination of an ionic surfactant with a reactive counterion that is itself an oxidant or activates an oxidant from the bulk solution to form an oxidant counterion. As shown in this work, surfoxidants can offer significant kinetic advantages over the combination of ionic surfactants (with nonreactive counterions) with the same ionic oxidants or activators added separately.

In this article, we describe the preparation and oxidative reactivity of bicarbonate surfoxidants (CTAHCO₃, CTA = cetyltrimethylammonium) combined with H₂O₂ as the primary oxidant. It was our hypothesis that the bicarbonate counterion of a cationic micelle could be converted into an active oxidant by reaction with H₂O₂ to form a reactive peroxy carbonate anion (HCO₄⁻) concentrated at the micellar surfaces. Under these circumstances, it was expected that micelle-bound substrates might be more rapidly oxidized due to concentration of substrate and oxidant in the micelle. Our recent studies on bicarbonate-catalyzed oxidations of aryl sulfides by H₂O₂ have identified peroxy moncarbonate (HCO₄⁻) or its kinetic equivalent as an active electrophilic oxidant.^{17,18} In this model, peroxy moncarbonate, a true peroxide with a structure of HOOCO₂⁻, is formed from bicarbonate and hydrogen peroxide (eq 1) and subsequently oxidizes nucleophilic substrates (eq 2). The equilibration of eq 1 most likely proceeds via the intermediacy of CO₂,¹⁹ and HCO₄⁻ is essentially a CO₂ adduct of the hydroperoxide anion, OOH⁻.



Equilibrium analysis of eq 1 by ¹³C NMR leads to a K_{eq} value of 0.33 M⁻¹ in water (K_{eq}^{w}), and $E^\circ(\text{HCO}_4^-/\text{HCO}_3^-) = 1.8 \pm 0.1$ V (vs NHE) at 25 °C. The second-order rate constants k_1 for aryl sulfide oxidations by HCO₄⁻ are consistently about 300-fold greater than those for H₂O₂ in cosolvent/water media.^{17,18} Epoxidation of alkenes can also be achieved by using bicarbonate-activated peroxide solutions.²⁰

Bicarbonate-activated peroxide (BAP) oxidations have many advantages over other peroxyacids or metal-catalyzed peroxidations, such as an environmentally friendly oxidant/catalyst combination, a stable and recyclable catalyst (HCO₃⁻), and water as the reaction byproduct. The formation and use of the active oxidant (HCO₄⁻) at neutral pH values can reduce acid- or base-catalyzed product decomposition reactions. Our cosolvent composition studies have shown that pure water is the most desirable solvent for BAP oxidations,¹⁷ as introduction of an organic cosolvent usually retards the nucleophilic displacement reaction at the active oxygen. A surfactant-based BAP system could be used as a green oxidant for applications including organic synthesis,²¹ chemical warfare agent decontamination,^{22–24} and bleaching.²⁵ We have investigated micellar effects in BAP oxidations from a mechanistic point of view to help define factors that would increase its utility as a green oxidant.

The goal of the present study was to model the mechanism and kinetics of bicarbonate-catalyzed oxidations of sulfides by

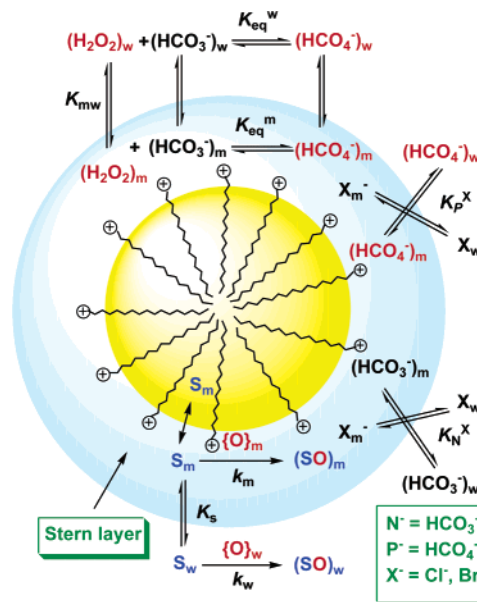


Figure 1. Pseudophase model for BAP oxidations in aqueous cationic micelles. Reactants are distributed rapidly between water and micelles. Kinetic treatments are based on the assumption that reactions occur in both the Stern layer and the bulk aqueous medium.

H₂O₂ in cationic micellar solutions. We also show that the new catalytic cationic surfoxidant CTAHCO₃ can offer a significant rate enhancement for oxidation of aryl sulfides. We have compared the surfoxidant approach to the addition of reactive anions to CTACl and CTABr in water, where the halide counterions must undergo equilibrium displacement at the micelle interface by the oxidant anion. General equations based on the classic pseudophase model have been derived to account for the preequilibrium reaction (eq 1) in both the aqueous and the micellar phases (Figure 1), and the resulting model can be used to describe any micellar reaction with associated preequilibria. The experimental and modeling approaches used here involve the determination of substrate and reactant affinities for the micellar pseudophase, measurement of the relevant kinetic parameters in water and aqueous micelle media for both uncatalyzed peroxide and BAP reactions, and fitting of the data to the modified pseudophase model. In this way, rate constants and relevant equilibrium constants for HCO₄⁻ oxidations of aryl sulfides at micellar surfaces have been estimated for CTA surfactants. Furthermore, some of the kinetically derived equilibrium parameters have been confirmed by direct spectroscopic measurements. It is shown that surfoxidants can offer significant kinetic advantages by providing both substrate solubility and enhancement of oxidation rates.

Results

Determination of Critical Micelle Concentration (CMC) Values and Substrate Binding Constants. The value of the

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Table 1. CMCs (M) of CTA Micellar Solutions Determined by Surface Tensiometry

	CTACl	CTABr	CTAHCO ₃
$\mu = 0$	1.4×10^{-3}	9.5×10^{-4}	1.4×10^{-3}
$\mu = 0.20^a$	2.0×10^{-4}	1.0×10^{-4}	

^a Ionic strength established with (NH₄)₂HPO₄.

substrate binding constant K_s for 2-(phenylthio)ethanol (PhSEtOH) in CTACl was determined by following its UV spectral shifts as a function of CTACl concentration and fitting the data to eq 3.²⁶

$$\frac{A - A_w}{A_m - A} = K_s([D] - \text{CMC}) = K_s[D_n] \quad (3)$$

In eq 3, A is the observed absorbance at the monitored wavelength, A_w and A_m are the absorbances in water and in micellar pseudophases, respectively, CMC is the critical micellar concentration, and $[D]$ is the total surfactant concentration. The CMC values were determined by using surface tensiometry, and the resulting values for CTACl and CTABr are close to literature values.²⁷ CMC values decreased with addition of electrolyte,²⁸ and the results are listed in Table 1.

UV absorbance studies for PhSEtOH in CTACl solutions were performed in the absence and in the presence of electrolyte. The K_s value determined for PhSEtOH is $120 \pm 30 \text{ M}^{-1}$ (error limits are given at the 95% confidence level unless otherwise stated) without addition of electrolyte. A higher K_s value of $170 \pm 30 \text{ M}^{-1}$ is obtained when (NH₄)₂HPO₄ ($\mu = 0.20$) is used to set the ionic strength. It is assumed that the K_s value of a substrate is the same for all of the CTA surfactants in this work regardless of the counterions (e.g., Cl⁻, Br⁻, or HCO₃⁻). The K_s value for ethylphenyl sulfide (PhSEt) in CTACl aqueous micelles is estimated to be $700 \pm 130 \text{ M}^{-1}$ in the presence of (NH₄)₂HPO₄ ($\mu = 0.20$). These K_s values are listed in Table 2 and will be compared to those obtained independently from kinetic studies in the Discussion section.

Partitioning of Hydrogen Peroxide between Aqueous and Micellar Phases. The partition coefficient K_{mw} of H₂O₂ between water and micelles was evaluated by using the micellar chromatography method developed by Armstrong and Nome.²⁹ The retention volumes (V_e) of H₂O₂ were measured by using micellar solutions containing various concentrations of CTACl. The calculation of K_{mw} is based on eq 4

$$\frac{V_s}{V_e - V_0} = \frac{V_m(K_{mw} - 1)}{K_{sw}}[D_n] + \frac{1}{K_{sw}} \quad (4)$$

where V_s and V_0 are the stationary and void volumes, respectively, and K_{sw} is the partition coefficient between the stationary phase and water. No significant change in V_e was found whether H₂O₂ was eluted with pure water or with a micellar solution of CTACl up to 0.20 M. A linear plot of $V_s/(V_e - V_0)$ versus $[D_n]$

gave a slope indistinguishable from zero (-0.3 ± 0.6) and an intercept of 1.29 ± 0.07 . From eq 4, the value of K_{mw} has an upper limit of ~ 2.0 based on experimental error analysis.

Oxidations in Water. Oxidations of PhSEtOH and PhSEt were followed by monitoring the loss of substrate absorbance at $\sim 290 \text{ nm}$ in the presence of excess hydrogen peroxide as described previously.¹⁷ Ionic strength and pH values for the uncatalyzed (H₂O₂ only) reactions were controlled by (NH₄)₂HPO₄ and were equivalent to the reaction conditions for bicarbonate-catalyzed reactions. Normally, sulfide was added to a preequilibrated solution of hydrogen peroxide and bicarbonate (or hydrogen peroxide solution with (NH₄)₂HPO₄ for the background reaction) for each kinetic run. For PhSEt, the sulfide substrate was predissolved in water by using ultrasonic mixing and was added to the preequilibrated H₂O₂/NH₄HCO₃ solution or H₂O₂/(NH₄)₂HPO₄ solution. The oxidation was usually followed for three half-lives, and good linear first-order plots ($r^2 > 0.99$) were obtained. The contribution of the uncatalyzed oxidation by H₂O₂ was subtracted from the overall observed pseudo first-order rate constant to obtain the rate constants attributed to the catalytic pathway.

The rate law for the oxidation in water is given by eq 5 under the conditions of low concentrations of hydrogen peroxide ($K_{eq}^w[\text{H}_2\text{O}_2] \ll 1$), where k_w^0 and k_w are second-order rate constants of the uncatalyzed and bicarbonate-catalyzed oxidations, respectively.^{17,18}

$$-\frac{d[S]}{dt} = k_w^0[\text{H}_2\text{O}_2]_0[S] + k_w K_{eq}^w[\text{H}_2\text{O}_2]_0[\text{HCO}_3^-]_0[S] \quad (5)$$

No higher order pathways were observed for either hydrogen peroxide in the uncatalyzed and catalyzed oxidations in water under the conditions examined. The values of k_w^0 and k_w for PhSEtOH and PhSEt were calculated from eq 5 by linear regressions and are given in Table 3 ($K_{eq}^w = 0.33 \text{ M}^{-1}$).¹⁷ The rate constants for PhSEt in pure water are $k_w = 0.14 \pm 0.02 \text{ M}^{-1} \text{ s}^{-1}$ and $k_w^0 = 2.2 \pm 0.1 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, and these values are consistent with extrapolations of the Grunwald–Winstein analysis in water/alcohol solvents reported previously¹⁸ to pure water (the extrapolation of the published plot gives values of $k_w = 0.3 \text{ M}^{-1} \text{ s}^{-1}$ and $k_w^0 = 1.5 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$).³⁰

Oxidations by H₂O₂ in CTA Media. Oxidations of PhSEtOH and PhSEt by H₂O₂ in CTABr solutions were followed with H₂O₂ (0.20 M) in the presence of (NH₄)₂HPO₄ ($\mu = 0.20$) to control pH and ionic strength. The observed oxidation rate constant k_{obs}^0 (s⁻¹) decreases sharply as the concentration of surfactant increases (Figure 2). The rates of oxidation reactions were also analyzed at various concentrations of H₂O₂ with [CTABr] = 0.050 M under similar conditions. Figure 3 shows that the rate increases with concentration of hydrogen peroxide up to 2.0 M.

Oxidation of PhSEtOH by H₂O₂ in Aqueous CTAHCO₃. Reactions for the aqueous surfoxidant CTAHCO₃ were followed by addition of PhSEtOH to preequilibrated solutions of H₂O₂ and CTAHCO₃. Oxidation kinetics were determined with variation of surfactant concentration (Figure 4) and variation of hydrogen peroxide concentration (Figure 5). The catalytic first-order rate constants were obtained by subtracting the

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Table 2. Equilibrium Parameters in Cetyltrimethylammonium Surfactant Solutions

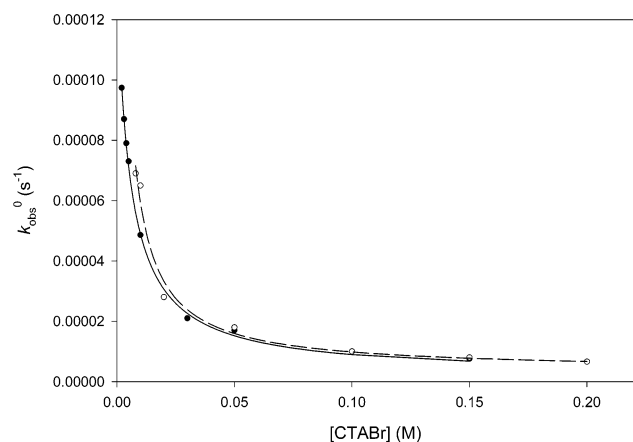
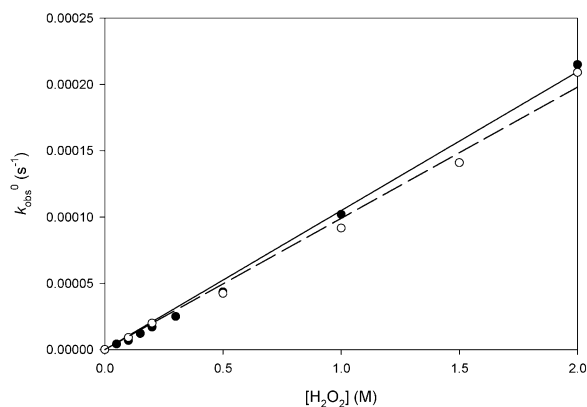
substrate	K_s (M^{-1})		${}^a K_{\text{eq}}^m$ (M^{-1})		K_N^X		K_P^X		
	UV	kinetic fit	${}^{13}\text{C}$ NMR	kinetic fit	${}^{a,c} K_N^P$	$X^- = \text{Cl}^-$	$X^- = \text{Br}^-$	$X^- = \text{Cl}^-$	$X^- = \text{Br}^-$
PhSEtOH	120 ± 30 ($\mu = 0$)	170 ± 20 ($\mu = 0.2$)	$0.9^b \pm 0.3$	0.6 ± 0.3	1.8 ± 0.6	2.0 ± 0.3^d	12 ± 2^d	1.1 ± 0.4	6.7 ± 2.5
PhSEt	170 ± 30 ($\mu = 0.2$)	700 ± 120 ($\mu = 0.2$)							

^a $K_{\text{mw}} = 1$ is assumed. K_{eq}^m is one-half of the reported value if $K_{\text{mw}} = 2$ (see Discussion). ^b Addition of NaHCO_3 in CTA bicarbonate solutions may increase β , depending on the relative concentration of CTA and NaHCO_3 . $K_{\text{eq}}^m \approx 0.7$ is obtained when assuming β increases gradually with addition of NaHCO_3 and approaches 1.0 with excess NaHCO_3 ($[\text{NaHCO}_3]:[\text{CTA}] \geq 3:1$). ^c $\text{N}^- = \text{HCO}_3^-$, $\text{P}^- = \text{HCO}_4^-$. The reported value is based on $K_{\text{eq}}^m = 0.6$ and can vary by a factor of 2 due to the uncertainty of K_{mw} . ^d Estimated from simulations.

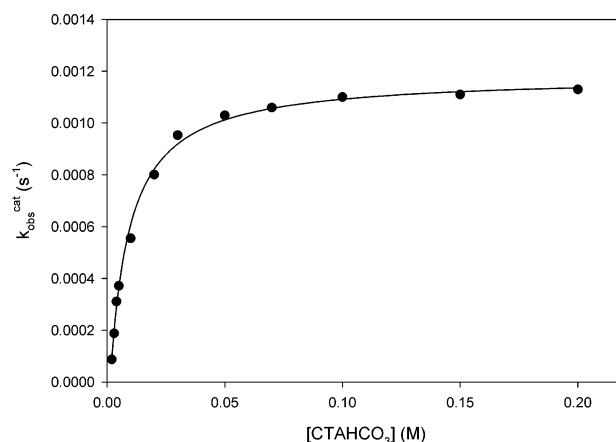
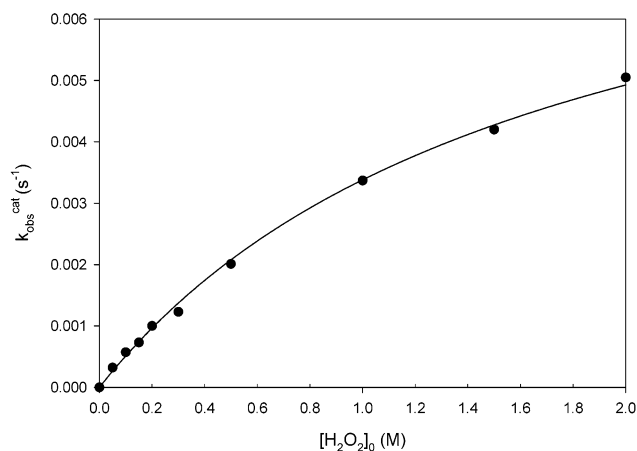
Table 3. Rate Constants of Background and Catalytic Reactions in Water and CTA Micelle Pseudophases

substrate	k^0 ($M^{-1} s^{-1}$)			k^{cat} ($M^{-1} s^{-1}$)			
	k_w^0	${}^a k_m^0$	${}^a k_w^0/k_m^0$	k_w	${}^b k_2^m$	${}^b k_w/k_2^m$	${}^b k_2^m/k_m^0$
PhSEtOH	$(6.5 \pm 0.5) \times 10^{-4}$	$(3.9 \pm 0.7) \times 10^{-5}$	18 ± 4	0.14 ± 0.02	$(2.0 \pm 0.2) \times 10^{-3}$	70 ± 12	51 ± 11
PhSEt	$(2.2 \pm 0.2) \times 10^{-3}$	$(3.9 \pm 0.7) \times 10^{-5}$	56 ± 11	0.14 ± 0.02	$(7.0 \pm {}^c 0.8) \times 10^{-3}$	20 ± 4	180 ± 40

^a Values are based on the assumption of $K_{\text{mw}} = 1$; for example, k_m^0 is one-half of the value in the table if $K_{\text{mw}} = 2$. The reported deviations are simple mathematical propagation. ^b $k_2^m \approx k_m \times 0.14 M^{-1}$. Reaction volume V_m is $0.14\text{--}0.3 M^{-1}$, the estimated k_2^m could be twice of those in the table, and the values of k_w/k_2^m and k_2^m/k_m^0 may vary by a factor of 2 and 4, respectively. See Discussion. ^c Estimated from simulations.

**Figure 2.** Oxidations by H_2O_2 (0.20 M) in CTABr: (●) PhSEtOH, (○) PhSEt. Lines are from model fits (see text). (—) PhSEtOH; (---) PhSEt.**Figure 3.** Oxidations by H_2O_2 in CTABr (0.050 M): (●) PhSEtOH, (○) PhSEt. Lines are from model fits (see text). (—) PhSEtOH; (---) PhSEt.

corresponding rate constants for H_2O_2 oxidations in CTABr, although the contribution from the uncatalyzed reactions was usually negligible as compared to that of the catalytic pathway. In Figure 4, the observed catalytic rate constant $k_{\text{obs}}^{\text{cat}}$ (s^{-1}) is plotted as a function of $[\text{CTAHCO}_3]$ with $[\text{H}_2\text{O}_2] = 0.20 M$. The rate plateau at high concentration of CTAHCO_3 is typical for binuclear reactive ion reactions,^{8,31} indicating full micellization of the substrate.

**Figure 4.** Dependence of catalytic rate constants on surfactant concentration for PhSEtOH oxidation by H_2O_2 (0.20 M) in CTAHCO_3 . Line is from preequilibrium pseudophase model fit (see text).**Figure 5.** Dependence of catalytic rate constants on peroxide concentration for PhSEtOH oxidation by H_2O_2 in CTAHCO_3 (0.050 M). Line is from preequilibrium pseudophase model fit (see text).

BAP Oxidations of PhSEtOH in Aqueous CTACl or CTABr. Oxidations with bicarbonate-activated hydrogen peroxide in solutions of CTACl or CTABr were followed by using methods similar to those used for reactions in CTAHCO_3 media, except that NH_4HCO_3 (0.20 M) was added in solutions of H_2O_2

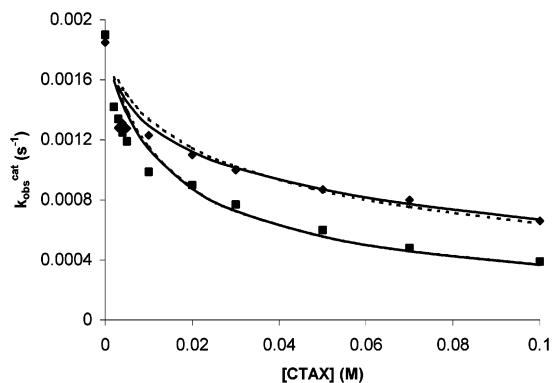


Figure 6. Catalytic oxidations of PhSEtOH in CTAX ($X^- = \text{Cl}^-, \text{Br}^-$); $[\text{H}_2\text{O}_2]_0 = 0.20 \text{ M}$ and $[\text{NH}_4\text{HCO}_3]_0 = 0.20 \text{ M}$. (\blacklozenge) CTACl; (\blacksquare) CTABr. Lines are from preequilibrium pseudophase model fits. (—) $\beta = 0.75$, $K_N^{\text{Cl}} = 2.0$, and $K_N^{\text{Br}} = 12$; (---) $\beta = 0.85$, $K_N^{\text{Cl}} = 3.5$, and $K_N^{\text{Br}} = 18$.

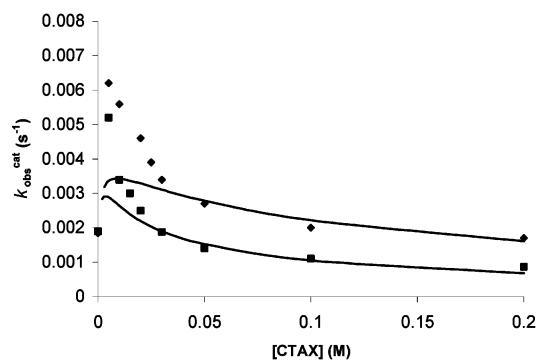


Figure 7. Catalytic oxidations of PhSEt in CTAX ($X^- = \text{Cl}^-, \text{Br}^-$); $[\text{H}_2\text{O}_2]_0 = 0.20 \text{ M}$ and $[\text{NH}_4\text{HCO}_3]_0 = 0.20 \text{ M}$. (\blacklozenge) CTACl; (\blacksquare) CTABr. Lines are predicted values from the preequilibrium pseudophase model.

(0.20 M) with various concentrations of CTACl or CTABr for preequilibrium formation of peroxymonocarbonate. Figure 6 shows the catalytic rate constant versus surfactant concentration profiles for oxidations in CTACl and CTABr. Deceleration of oxidations by adding CTAX ($X = \text{inert ion}$) is observed and suggests a lower second-order rate constant k_2^m ($\text{M}^{-1} \text{s}^{-1}$) at micellar surfaces as compared to bulk water.

BAP Oxidations of PhSEt in Aqueous CTACl or CTABr.

PhSEt was dissolved completely in aqueous surfactant solutions of CTA by ultrasonic mixing or shaking prior to its reactions with preequilibrated solutions of H_2O_2 (0.20 M) and NH_4HCO_3 (0.20 M). The oxidation kinetics were recorded with various concentrations of CTA surfactants, and the resulting catalytic oxidation rate versus surfactant concentration profiles are plotted in Figure 7. The reactions are faster in diluted CTA micellar solutions ($< 0.03 \text{ M}$) than in water, but rates decrease sharply at higher concentrations of the surfactants.

NMR Studies on Equilibrium Formation of Peroxymonocarbonate. The apparent equilibrium constants, $K_{\text{eq}}^{\text{app}}$ (M^{-1}), for HCO_4^- formation (eq 1) in surfactant solutions were measured by using a ^{13}C NMR spectroscopic method. With a fixed total concentration of bicarbonate (0.20 M, adjusted by addition of ^{13}C -enriched NaHCO_3) in CTAHCO_3 solutions, $K_{\text{eq}}^{\text{app}}$ (M^{-1}) for HCO_4^- formation varies with the CTA surfactant concentration in the presence of excess hydrogen peroxide (2.0 M) (Supporting Information).

Discussion

Pseudophase Model for Reactions in Surfactant Media.

A kinetic model for sulfide oxidations by bicarbonate-activated peroxide in aqueous micelles considers preequilibrium formation of HCO_4^- in water and micellar pseudophases, oxidation reactions in water and micellar pseudophases, and ion exchanges at the micelle–water interfaces (Figure 1). To our knowledge, a catalytic bimolecular reaction with a preequilibrium reaction in micellar media has not been modeled previously using a quantitative pseudophase approach. The present study employs a pseudophase model^{32,33} to fit the kinetic data for bicarbonate-catalyzed sulfide oxidations by H_2O_2 in aqueous solutions of CTA cationic micelles. The general equations and assumptions of the pseudophase model are given in this section, and new equations for the preequilibrium pseudophase model are presented in subsequent sections as experimental data are analyzed.

The distribution of organic substrates between water and micelles is described by a binding constant K_s (M^{-1}) as in eq 6.

$$K_s = \frac{[S_m]}{[S_w][D_n]} \quad (6)$$

In eq 6, D_n is the concentration of micellized surfactant ($[D_n] = [D] - \text{CMC}$),³² and S_w and S_m represent substrates in the aqueous and micellar pseudophases, respectively. The first-order rate constant of overall reaction (rate = $k_{\text{obs}}[S]$) can be written as in eq 7.^{33,34} In eq 7, the second-order rate constant in the micellar pseudophase, k_2^m ($\text{M}^{-1} \text{s}^{-1}$), is defined in terms of the local molarity of oxidant, $\{O\}_m$, in the micelle reactive region (local molarities are indicated by $\{\}$ brackets).

$$k_{\text{obs}} = \frac{k_w[O]_w + k_2^m K_s [D_n] \{O\}_m}{1 + K_s [D_n]} \quad (7)$$

This approach allows the direct comparison of k_2^m ($\text{M}^{-1} \text{s}^{-1}$) with the second-order rate constant in water, k_w ($\text{M}^{-1} \text{s}^{-1}$), which is conventionally written in terms of molarity of oxidant in the aqueous phase, $[O]_w$. (The volume of aqueous phase is approximately the total solution volume, and the local concentration of oxidant in water, $\{O\}_w$, is therefore usually not distinguished from the conventional concentration in bulk, $[O]_w$.) Equation 7 requires information on the distribution of oxidant between micellar and aqueous pseudophases to determine $\{O\}_m$ values.

Another approach is to define the first-order rate constant in the micellar pseudophase, k_m (s^{-1}), in terms of a mole ratio, m_{ox}^s , defined by eq 8. The observed first-order rate constant is written as eq 9.³⁵

$$m_{\text{ox}}^s = \frac{[O]_m}{[D_n]} \quad (8)$$

$$k_{\text{obs}} = \frac{k_w[O]_w + k_m m_{\text{ox}}^s K_s [D_n]}{1 + K_s [D_n]} \quad (9)$$

In eq 8, $[O]_m$ is the concentration of micellar-bound oxidant in

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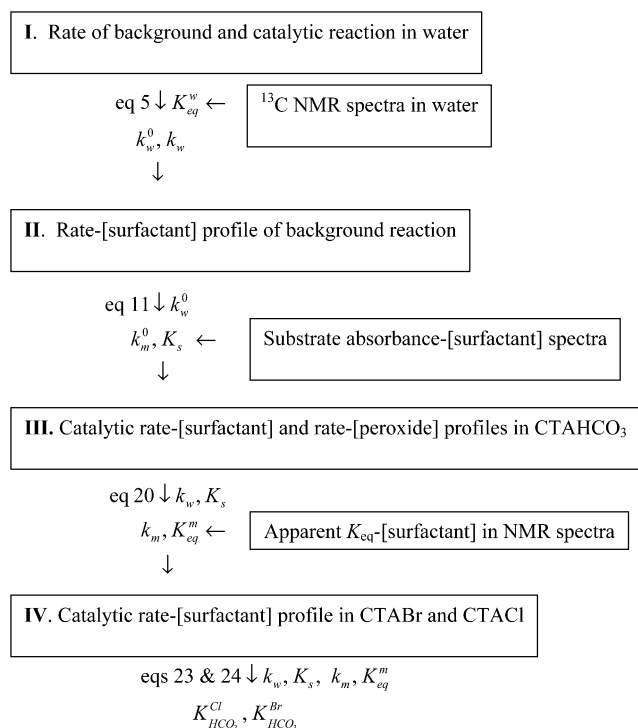


Figure 8. Flowchart illustrating fitting procedures used to determine various equilibrium and kinetic parameters obtained in this work. All constants are determined by using kinetic models and are checked when possible by independent spectroscopic measurements.

terms of total solution volume, which is approximately that of the aqueous pseudophase. This approach does not require preknowledge of oxidant distribution between micellar and aqueous pseudophases. However, a molar volume for the micellar reactive region, for example, the Stern layer, is assumed to compare the micellar rate constant with k_w ($\text{M}^{-1} \text{s}^{-1}$) in the aqueous phase. The rate constant k_m (s^{-1}) is converted to k_2^m ($\text{M}^{-1} \text{s}^{-1}$) by multiplying the molar volume, V_m^s , of the Stern layer (eq 10).

$$k_2^m = k_m V_m^s \quad (10)$$

The rate laws of the pseudophase model in expressions of eqs 7 and 9 are identical provided that distribution of the oxidant between micellar and aqueous pseudophases is known. We have derived the rate laws for BAP oxidations in CTA cationic micellar solutions on the basis of eqs 7 and 9 for an uncatalyzed reaction and a catalyzed reaction, respectively. The binding constants K_s (M^{-1}) of the substrates (PhSetOH or PhSet), ion exchange constants K_N^X ($N^- = \text{HCO}_3^-$, $X^- = \text{Cl}^-$, Br^-), equilibrium constant K_{eq}^m (M^{-1}) of micellar HCO_4^- formation, and micellar rate constant k_m (s^{-1}) can then be obtained by nonlinear regression using the derived pseudophase models. The flowchart in Figure 8 illustrates the fitting procedures used to obtain the kinetic and equilibrium parameters. As indicated in Figure 8, the equilibrium parameters from kinetic models can be compared to those obtained independently by spectroscopic

methods in this work (for K_s and K_{eq}^m) or to literature values³⁶ (for K_N^X).³⁷

Hydrogen Peroxide Partitioning between Pseudophases.

A pseudophase model based on eq 7 is used directly to describe oxidations of organic sulfides by hydrogen peroxide. The observed first-order rate constant for the overall reaction is given by eq 11.

$$k_{obs}^0 \text{ (s}^{-1}\text{)} = \frac{k_w^0 [\text{H}_2\text{O}_2]_w + k_m^0 K_s [\text{D}_n] \{ \text{H}_2\text{O}_2 \}_m}{1 + K_s [\text{D}_n]} \quad (11)$$

Extraction of rate constants from eq 11 therefore requires a quantitative determination of the partitioning of H_2O_2 between bulk water and the micellar pseudophase.

The ratio of $\{ \text{H}_2\text{O}_2 \}_m$ to $\{ \text{H}_2\text{O}_2 \}_w$ is defined as partition coefficient K_{mw} for hydrogen peroxide between micelle and water pseudophases (eq 12), and K_{mw} is the thermodynamic parameter reflecting the relative solubility of a nonionic reactant in the micellar phase and water.²⁶

$$K_{mw} = \frac{\{ \text{H}_2\text{O}_2 \}_m}{\{ \text{H}_2\text{O}_2 \}_w} \quad (12)$$

Thus, $\{ \text{H}_2\text{O}_2 \}_m$ and $\{ \text{H}_2\text{O}_2 \}_w$ (or $[\text{H}_2\text{O}_2]_w$) can be expressed in terms of molar volume of micelles V_m (M^{-1}), K_{mw} , and $[\text{D}_n]$. The values of V_m are about 0.36 M^{-1} for CTABr and 0.31 for CTACl.^{40,41} In dilute surfactant solutions ($[\text{D}_n] \leq 0.1 \text{ M}$), $\{ \text{H}_2\text{O}_2 \}_m$ and $\{ \text{H}_2\text{O}_2 \}_w$ (or $[\text{H}_2\text{O}_2]_w$) are given in terms of the total analytical concentration $[\text{H}_2\text{O}_2]_0$ by eqs 13 and 14, respectively, if K_{mw} is not large.

$$\{ \text{H}_2\text{O}_2 \}_m = \frac{K_{mw} [\text{H}_2\text{O}_2]_0}{1 + K_{mw} [\text{D}_n] V_m} \approx K_{mw} [\text{H}_2\text{O}_2]_0 \quad (13)$$

$$\{ \text{H}_2\text{O}_2 \}_w = [\text{H}_2\text{O}_2]_w = \frac{[\text{H}_2\text{O}_2]_0}{1 + K_{mw} [\text{D}_n] V_m} \approx [\text{H}_2\text{O}_2]_0 \quad (14)$$

It is difficult to measure K_{mw} (or K_s) for H_2O_2 by conventional spectroscopic methods or by ultrafiltration,^{26,35} because the observed physical properties for the hydrophilic neutral solute H_2O_2 are not highly sensitive to the added surfactant.

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(37) It should be noted that the local concentration of oxidant IO_4^- and HSO_5^- in the micellar pseudophase is estimated by solving the Poisson–Boltzmann equation (PBE) in Bunton's work (refs 38, 39). The pseudophase PBE model is mostly applied to small anionic reactants, for example, OH^- , and includes an adjustable thickness of Stern layers (refs 9, 11). The pseudophase ion exchange (PIE) model has advantages over the PBE method in terms of simplicity, fewer assumptions, and the ability to resolve multiple parameters. The PIE model assumes that the micellar surfaces are always saturated with counterions and the mole ratio of counterions to micellar headgroup in the Stern layer is a constant, β . The β value is in the range of 0.6–0.9 depending on different surfactants (ref 33). The second-order rate constant k_2^m ($\text{M}^{-1} \text{s}^{-1}$) is calculated by assuming a molar volume of the Stern layer V_m^s (eq 10). The value of k_2^m therefore has an uncertainty within a factor of 2, which is the estimated uncertainty of the Stern layer volume (ref 33). Despite different approaches in estimating the reactive ion concentration at micellar surfaces, the results are reasonably self-consistent for the two methods, and the calculated second-order rate constants by various methods are generally comparable (ref 32).

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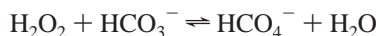
A value of $K_{mw} = 8$ for H_2O_2 in CTA micelles was reported by Encinas and Lissi, who used a fluorescence probe method where H_2O_2 served as a quencher of the bound donor.⁴² Considering the lower polarity of the micellar phase,^{43,44} we doubted that the relative solubility of H_2O_2 in CTA micelles as compared to that in water would be that high. Our experiments with a C-18 reverse phase column have shown no significant changes of retention time for H_2O_2 using micellar solvents with [D] up to 0.20 M, implying that K_{mw} is small, and a statistical analysis at the 95% confidence level gave a maximum K_{mw} value of 2. Given the uncertainties arising from the estimated Stern layer volume and the hypothesis of unaffected micelle nature with addition of solutes or variation of surfactant concentrations in the pseudophase model, a value of $K_{mw} = 1$ for H_2O_2 will be used in this work (i.e., H_2O_2 does not partition preferentially into one pseudophase).

Kinetic Parameters for Hydrogen Peroxide Oxidations in the Micellar Pseudophase. Following the determination of oxidation rate parameters in pure water (part I in Figure 8), the second-order rate constant for oxidation of the substrate by H_2O_2 in the micelle pseudophase can be estimated by fitting of data obtained for surfactant solutions, that is, the analysis in part II in Figure 8. The rate constant k_m^0 ($M^{-1} s^{-1}$) can be determined by fitting observed rate constants with $[H_2O_2]_w = \{H_2O_2\}_m = [H_2O_2]_0$ in eq 11. Figure 2 gives calculated curves of rate constants versus [D] profiles. It is noted that the fit of eq 11 in Figure 2 is not sensitive to the values of k_m^0 due to an insignificant contribution from the micellar reaction relative to the aqueous reaction in dilute surfactant solutions. A fit of rate constant versus $[H_2O_2]_0$ in Figure 3 is used to obtain the estimated values of k_m^0 . The results for K_s (M^{-1}) and k_m^0 ($M^{-1} s^{-1}$) are listed in Tables 2 and 3, respectively.

The micelle binding constants K_s (M^{-1}) for PhSEtOH and PhSEt were obtained from nonlinear regression fitting of the kinetic data to eq 11 (Figure 2). The input parameters in eq 11 were $K_{eq}^w = 0.33 M^{-1}$, $CMC = 1 \times 10^{-4} M$, and $k_w^0 = 6.5 \times 10^{-4} M^{-1} s^{-1}$ and $k_w^0 = 2.2 \times 10^{-3} M^{-1} s^{-1}$ for PhSEtOH and PhSEt, respectively. The K_s values for PhSEtOH ($170 \pm 20 M^{-1}$) and PhSEt ($700 \pm 100 M^{-1}$) obtained from kinetic fits agree with those from independent UV spectroscopic studies (Table 2). The higher value of K_s for PhSEt is consistent with its greater hydrophobicity as compared to that of PhSEtOH. The rate constants k_m^0 ($M^{-1} s^{-1}$) for both PhSEtOH and PhSEt are $(4 \pm 1) \times 10^{-5} M^{-1} s^{-1}$ as a result of fits to the rate profiles in Figure 3, taking K_s values of PhSEtOH and PhSEt to be 170 and 700 M^{-1} , respectively. The ratios of second-order rate constants in micellar and aqueous pseudophases are estimated and listed in Table 3. Sulfide oxidation by H_2O_2 is estimated to be 60 ± 40 times faster in water than in micelles, with the range reflecting the uncertainty of K_{mw} for H_2O_2 . Because the distribution of H_2O_2 in aqueous and micellar pseudophases is similar, the oxidation of sulfides is inhibited by substrate binding to micelles in aqueous surfactant solutions (assuming the substrate is soluble in water).

Catalytic Oxidation Kinetics in CTAHCO₃ and Determination of K_{eq}^m , k_m , and k_2^m . Referring to the chart in Figure

8, we now consider part III of the analysis. A rate law for sulfide oxidations is derived below for the mechanism of eqs 1 and 15–17, assuming $[H_2O_2]_w = \{H_2O_2\}_m = [H_2O_2]_0$.



$$K_{eq}^m = \frac{m_{HCO_4^-}^s}{\{H_2O_2\}_m m_{HCO_3^-}^s} = \frac{[HCO_4^-]_m}{\{H_2O_2\}_m [HCO_3^-]_m} \quad (15)$$



Equations 16 and 17 refer to oxidations in water and micelle, respectively. The equilibrium constant for peroxy carbonate formation K_{eq}^m (M^{-1}) at micellar surfaces is defined in terms of mole ratios m^s of bound HCO_3^- and HCO_4^- (e.g., $m_X^s = [X]/[D]$), analogous to the definition of the basicity constant in acid–base equilibrium at CTA micellar surfaces^{31,35}. K_{eq}^m (M^{-1}) can be compared directly to the equilibrium constant K_{eq}^w ($= [HCO_4^-]_w / ([H_2O_2]_w [HCO_3^-]_w)$) in water. In addition, the ratio of K_{eq}^m / K_{eq}^w is the ion exchange constant of HCO_3^- and HCO_4^- between water and micelles (eq 18), with the assumption that the concentration of hydrogen peroxide is equivalent in the aqueous and micellar pseudophases. In eq 18, $N^- = HCO_3^-$, $P^- = HCO_4^-$.

$$K_N^P = \frac{m_{HCO_4^-}^s [HCO_4^-]_w}{m_{HCO_3^-}^s [HCO_3^-]_w} = \frac{K_{eq}^m}{K_{eq}^w} \quad (18)$$

In solutions of CTAHCO₃ and H_2O_2 , the two counterions HCO_3^- and HCO_4^- are in equilibrium via eq 1 (Figure 1), and the sum of the mole ratios (m) of HCO_3^- and HCO_4^- to $[D]_n$ is equal to β (i.e., the fractional extent of counterion binding to the micelle from 0 (no binding) to 1 (complete binding)). On the basis of the pseudophase kinetic model of eq 19 (or eq 9) and an assumed constant β value, the apparent catalytic oxidation rate constant k_{obs}^{cat} (s^{-1}) is given by eq 20 (see Supporting Information for derivation).

$$k_{obs}^{cat} = \frac{k_w [HCO_4^-]_w + k_m m_{HCO_4^-}^s K_s [D]_n}{1 + K_s [D]_n} \quad (19)$$

$$k_{obs}^{cat} = [(k_w K_{eq}^w / K^w) [H_2O_2]_0 ([D] - \beta [D]_n) + (k_m K_s K_{eq}^m / K^m) \beta [H_2O_2]_0 [D]_n] / (1 + K_s [D]_n) \quad (20)$$

In eq 20, $K^w = 1 + K_{eq}^w [H_2O_2]_0$, and $K^m = 1 + K_{eq}^m [H_2O_2]_0$. Equation 20 has the general form of a pseudophase reactive ion model,^{8,45} except that it contains equilibrium parameters for HCO_4^- formation in micelles and water. A value of $\beta = 0.75$ is usually used for CTA micelles.^{8,46} With $k_w = 0.14 M^{-1} s^{-1}$, $K_{eq}^w = 0.33 M^{-1}$, $CMC = 1 \times 10^{-3} M$, and $K_s = 120 M^{-1}$ for PhSEtOH (values from above), k_m (s^{-1}) and K_{eq}^m (s^{-1}) are obtained by a complete fit of the k_{obs} versus [D] (Figure 4) and versus $[H_2O_2]_0$ (Figure 5) profiles for oxidations in CTAHCO₃

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by using eq 20. The results for K_{eq}^{m} and k_{m} values are listed in Tables 2 and 3, respectively. The kinetic equilibrium constant for HCO_4^- formation at micellar surfaces ($K_{\text{eq}}^{\text{m}} = 0.6 \pm 0.3 \text{ M}^{-1}$) is found to be about twice the value of K_{eq}^{w} in water. Assuming that the molar volume of the Stern layer of CTAHCO_3 is similar to that of CTABr ($V_{\text{m}}^{\text{s}} = 0.14 \text{ M}^{-1}$),⁴⁷ we estimated the second-order rate constant k_2^{m} ($\text{M}^{-1} \text{ s}^{-1}$) for PhSEtOH oxidation by HCO_4^- to be $2 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ (eq 10), which is ~ 70 -fold lower than that in water. The relative reduction in reactivity of HCO_4^- in the Stern layer versus bulk water is comparable to the reduction in H_2O_2 reactivity estimated above.

The rate versus CTA concentration profile in Figure 4 has the general form of a pseudophase reactive ion model (in which the counterion is reactive with micelle-bound substrate) because the HCO_3^- ion has an equilibrium relationship with the reactive ion HCO_4^- . For oxidations in aqueous solutions of CTAHCO_3 , our kinetic model shows that the contribution from oxidation in the aqueous phase is small relative to the overall rate of catalyzed oxidations. In dilute solutions of CTAHCO_3 , $[\text{HCO}_4^-]_{\text{w}}$ (or $[\text{HCO}_3^-]_{\text{w}}$) is so low that the oxidation of sulfide in the aqueous phase is negligible, although the second-order rate constant k_{w} in the aqueous phase is ~ 70 times higher than the estimated value of k_2^{m} in the micellar pseudophase. At higher concentrations of CTAHCO_3 , sulfide is largely bound to micelles, and oxidation occurs in the micellar phase almost exclusively (at $[\text{CTAHCO}_3] = 0.1 \text{ M}$, 92% of the PhSEtOH oxidation and $>99\%$ of the PhSEt oxidation occur in the micelle under our conditions). In Figure 4, full micellization of the sulfide is indicated by the maxima approached at CTA concentration values $>0.1 \text{ M}$. At high concentrations of CTA, the rate law of eq 20 is written as eq 21, which is independent of CTA concentrations once all of the substrate is bound ($1 \ll K_{\text{s}}[\text{D}_n]$). Values for k_{m} (s^{-1}) and K_{eq}^{m} (s^{-1}) can be simply obtained by fitting rate constant versus $[\text{H}_2\text{O}_2]_0$ profiles with eq 21 in concentrated solutions of CTAHCO_3 ($>0.1 \text{ M}$).

$$k_{\text{obs}}^{\text{cat}} = \frac{k_{\text{m}}K_{\text{eq}}^{\text{m}}\beta[\text{H}_2\text{O}_2]_0}{1 + K_{\text{eq}}^{\text{m}}[\text{H}_2\text{O}_2]_0} \quad (21)$$

The ion exchange constant K_{N}^{P} ($\text{N}^- = \text{HCO}_3^-$, $\text{P} = \text{HCO}_4^-$) is estimated to be 1.8 ± 0.6 from the ratio of K_{eq}^{m} to K_{eq}^{w} (eq 18 and Table 2). The values suggest that HCO_4^- binding is slightly favored at micellar surfaces relative to HCO_3^- . However, it should be noted that the parameter K_{eq}^{m} obtained from kinetic fittings includes a factor of K_{mw} , the partition coefficient of H_2O_2 between water and micelles. If $K_{\text{mw}} \neq 1$, the true equilibrium constant K_{eq}^{m} is equal to $K_{\text{eq}}^{\text{m}}/K_{\text{mw}}$. The value of K_{mw} is <2 based on micellar HPLC analysis. Therefore, the lowest value for K_{eq}^{m} is $\sim 0.3 \text{ M}^{-1}$ counting for the uncertainty of the K_{mw} value.

To validate further our assumption that $K_{\text{mw}} = 1$, a ^{13}C NMR study on the equilibrium formation of HCO_4^- was performed in a medium that mimics the Stern layer. It is well known that the micellar Stern layer is highly polar, consisting of charged headgroups and counterions.³² The local molarities of headgroups and counterions are very high in the Stern layer, ~ 7 and $\sim 5 \text{ M}$ for CTA micelles, respectively. As a model for the Stern layer, an aqueous solution of tetramethylammonium

chloride (5 M) was prepared, and the equilibrium constant of HCO_4^- formation (K_{eq}) was determined to be $0.5 \pm 0.1 \text{ M}^{-1}$ by using the standard ^{13}C NMR technique described previously. The value is close to that of K_{eq}^{m} obtained from the kinetic fit. Although the organized headgroups at the micellar surface are not identical to the randomly distributed tetraalkylammonium groups in the experiment, the equilibrium reaction of HCO_4^- formation should be affected similarly. The agreement between the K_{eq} values determined by the independent kinetic and NMR experiments suggests that $K_{\text{mw}} = 1$ for H_2O_2 is a reasonable assumption in the kinetic fitting.

Catalytic Oxidation Kinetics in CTAX ($\text{X}^- = \text{Cl}^-$, Br^-) and Determination of K_{N}^{X} . Part IV of the scheme in Figure 8 is now considered. The mechanism of HCO_4^- oxidations in CTACl or CTABr is similar to that in CTAHCO_3 (eqs 14–17), except that the unreactive ion X^- is involved in ion exchange with reactive ions between micelles and water. The ion exchange constant K_{N}^{X} ($\text{N}^- = \text{HCO}_3^-$, $\text{X}^- = \text{Cl}^-$ or Br^-) is given by eq 22.

$$K_{\text{N}}^{\text{X}} = \frac{m_{\text{X}}^{\text{s}}[\text{HCO}_3^-]_{\text{w}}}{m_{\text{HCO}_3^-}^{\text{s}}[\text{X}]_{\text{w}}} \quad (22)$$

In the pseudophase model analysis in the presence of X^- , β is the sum of mole ratios for three counterions, for example, HCO_4^- , HCO_3^- , and X^- . The rate law based on eq 19 of the pseudophase kinetic model is given by eq 23 (see Supporting Information for derivation).

$$k_{\text{obs}}^{\text{cat}} = [(k_{\text{w}}K_{\text{eq}}^{\text{w}}/K^{\text{w}})[\text{H}_2\text{O}_2]_0([\text{HCO}_3^-]_0 - K^{\text{m}}m_{\text{HCO}_3^-}^{\text{s}}[\text{D}_n]) + k_{\text{m}}K_{\text{s}}K_{\text{eq}}^{\text{m}}[\text{H}_2\text{O}_2]_0m_{\text{HCO}_3^-}^{\text{s}}[\text{D}_n]] / (1 + K_{\text{s}}[\text{D}_n]) \quad (23)$$

To simplify the notation in eq 23, $K^{\text{w}} = 1 + K_{\text{eq}}^{\text{w}}[\text{H}_2\text{O}_2]_0$, and $K^{\text{m}} = 1 + K_{\text{eq}}^{\text{m}}[\text{H}_2\text{O}_2]_0$. The mole ratio m_{N}^{s} ($\text{N}^- = \text{HCO}_3^-$) in eq 23 can be expressed as a function of $[\text{D}]$ by eq 24 (see Supporting Information for derivation).

$$(K_{\text{HCO}_3^-}^{\text{X}}K^{\text{w}} - K^{\text{m}})K^{\text{m}}[\text{D}_n](m_{\text{HCO}_3^-}^{\text{s}})^2 + [K_{\text{HCO}_3^-}^{\text{X}}K^{\text{w}}([\text{X}]_0 - \beta[\text{D}_n]) + K^{\text{m}}([\text{HCO}_3^-]_0 + \beta[\text{D}_n])]m_{\text{HCO}_3^-}^{\text{s}} - \beta[\text{HCO}_3^-]_0 = 0$$

$$([\text{X}]_0 = [\text{D}]) \quad (24)$$

When eq 24 is compared to standard quadratic equations for a reactive ion model,^{8,46} the only difference is that it contains equilibrium parameters K^{w} and K^{m} . If the values of both K^{w} and K^{m} have unit values (i.e., no preequilibrium reactions are present), eq 24 reduces to the known form for exchange involving two ions. Equations 23 and 24 were combined to fit the observed kinetic data. Assuming the rate constant k_{m} (s^{-1}) and equilibrium constant K_{eq}^{m} (M^{-1}) at micellar surfaces do not vary with different counterions, we found that the only unknown parameter in the kinetic model of eqs 23 and 24 is the ion exchange constant K_{N}^{X} ($\text{N}^- = \text{HCO}_3^-$, $\text{X}^- = \text{Cl}^-$ or Br^-). The rate versus $[\text{D}]$ profiles for catalytic oxidation in CTA solutions were fit by using assumed values of K_{N}^{X} in eq 23. It was assumed that $K_{\text{s}} = 170 \text{ s}^{-1}$, and the CMC values were set as 1.0×10^{-4} and $2.0 \times 10^{-4} \text{ M}$ for CTACl and CTABr in the presence of electrolyte, respectively. Other parameters used in eqs 23 and 24 were $k_{\text{w}} = 0.14 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}}^{\text{w}} = 0.33 \text{ M}^{-1}$, and

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$K_{\text{eq}}^{\text{m}} = 0.6 \text{ M}^{-1} \text{ s}^{-1}$. The best fits of rate versus $[D]$ curves in solutions of CTACl or CTABr were given by using K_{N}^{Cl} ($\text{N}^- = \text{HCO}_3^-$) = 2.0 ± 0.3 and K_{N}^{Br} ($\text{N}^- = \text{HCO}_3^-$) = 12 ± 2 , respectively (Figure 6). These results are close to the literature values for carbonate anion, determined by an independent UV spectroscopic method.³⁶ The values of K_{P}^{X} ($\text{P}^- = \text{HCO}_4^-$, $\text{X} = \text{Cl}^-$ or Br^-) can be derived from the ratios of K_{N}^{X} and K_{N}^{P} ($K_{\text{N}}^{\text{P}} = K_{\text{eq}}^{\text{m}}/K_{\text{eq}}^{\text{w}}$). The ion exchange constants are included in Table 2.

We have considered that the β value may not be independent of the concentration of counterions.⁴⁸ Addition of electrolyte may cause structural changes in micelles and affect ion binding. In the presence of excess electrolyte, the β value may increase.^{10,49} The typical literature values of $K_{\text{OH}}^{\text{Br}}$ and $K_{\text{OH}}^{\text{Cl}}$ are 20 and 4, respectively.³⁶ A larger anion such as HCO_3^- should have lower K_{N}^{X} values as compared to that of K_{OH}^{X} . The consistency of the results suggests that $\beta \approx 0.75$ (for CTA micelles) and that the β value remains relatively constant in the presence of NH_4HCO_3 (0.20 M) electrolyte.

It is noted that the rate-surfactant profiles for PhSEtOH oxidation by BAP in CTAX ($\text{X}^- = \text{Cl}^-$, Br^-) do not go through maxima, as do typical bimolecular reactions in surfactant solutions with both inert and reactive counterions.^{33,34,45} The rate-surfactant profile for a particular reaction is determined by the binding constant, ion exchange constants, and the difference in rate constants for reactions in the micellar and aqueous pseudophases.³⁴ In the case of PhSEtOH oxidations by BAP in aqueous CTA solutions, a much lower second-order rate constant in the micellar pseudophase relative to that in water ($k_{\text{w}}/k_2^{\text{m}} \approx 70$) causes the oxidation rates to decrease with no maxima for increasing concentration of surfactant.

Catalytic Oxidation of PhSEt in CTAX ($\text{X}^- = \text{Cl}^-$ or Br^-). The fit for PhSEt oxidation in dilute CTAX solutions shown in Figure 7 is poor, and observed rates for $[\text{CTAX}] < 0.03 \text{ M}$ are higher than predicted, presumably due to variations in micelle structure and properties from those at higher concentrations. In published studies, the observed rate constants for oxidation of 1-methoxy-4-methylthio benzene (ArSMe) by IO_4^- in CTACl were simulated on the basis of the pseudophase model by Bunton and co-workers.³⁹ Simulated rates were also much lower than the observed rates in dilute CTACl solutions in that study.

The value of $K_{\text{s}} = 700 \text{ M}^{-1}$ of PhSEt from both kinetic fits of uncatalyzed reactions and UV spectroscopic measurements shows that PhSEt is bound somewhat more strongly by CTA micelles than is ArSMe ($K_{\text{s}} = 340 \text{ M}^{-1}$ by UV spectroscopy³⁹). The rate versus $[D]$ profiles are simulated by a combination of eqs 23 and 24. Because all of the equilibrium constants and ion exchange constants are independent of substrates, k_{m} (s^{-1}) for PhSEt can be obtained by fits using eq 22. The following parameters were used in simulations of PhSEt oxidations: $k_{\text{w}} = 0.14 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{eq}}^{\text{w}} = 0.33 \text{ M}^{-1}$, $K_{\text{eq}}^{\text{m}} = 0.6 \text{ M}^{-1} \text{ s}^{-1}$, $K_{\text{s}} = 700 \text{ M}^{-1}$, $\text{CMC} = 1 \times 10^{-4} \text{ M}$ and $2 \times 10^{-4} \text{ M}$ for CTACl and CTABr, and $K_{\text{N}}^{\text{Cl}} = 2$ and $K_{\text{N}}^{\text{Br}} = 12$ for CTACl and CTABr, respectively. A value of $k_{\text{m}} = 0.05 \text{ s}^{-1}$ at high surfactant concentrations was found to fit the experimental data (Figure 7). The value of k_2^{m} was estimated to be $0.007 \text{ M}^{-1} \text{ s}^{-1}$ on the

basis of eq 10. A ratio of $k_{\text{w}}/k_2^{\text{m}} = 20$ is therefore obtained for oxidation of PhSEt by HCO_4^- . The results are listed in Table 3.

K_{eq}^{m} Determined by ^{13}C NMR. Experiments were done to provide information on the formation constant for HCO_4^- in the presence of micelles. The apparent equilibrium constants $K_{\text{eq}}^{\text{app}}$ for peroxy carbonate formation were determined from ^{13}C NMR spectra of preequilibrated solutions of bicarbonate (0.20 M) and excess hydrogen peroxide (2.0 M) at various concentrations of CTA surfactant (0.05, 0.10, and 0.15 M) by using the method reported previously.¹⁷ The equation of $K_{\text{eq}}^{\text{app}}$ as a function of $[D]$ is given by eq 25 (see Supporting Information for derivation).

$$\frac{1}{K} = \frac{(K^{\text{w}} - K^{\text{m}})\beta[\text{D}_{\text{n}}]}{[\text{HCO}_3^-]_0 K^{\text{w}} K^{\text{m}}} + \frac{1}{K^{\text{w}}} \quad (25)$$

In eq 25, $K = 1 + K_{\text{eq}}^{\text{app}}[\text{H}_2\text{O}_2]_0$, $K^{\text{w}} = 1 + K_{\text{eq}}^{\text{w}}[\text{H}_2\text{O}_2]_0$, and $K^{\text{m}} = 1 + K_{\text{eq}}^{\text{m}}[\text{H}_2\text{O}_2]_0$. To provide appropriate experimental data for eq 25, the concentration of bicarbonate $[\text{HCO}_3^-]_0$ was fixed by adding ^{13}C -enriched NaHCO_3 in CTAHCO₃ solutions. As the CMC decreases with addition of electrolyte,²⁸ $[\text{D}_{\text{n}}] = [\text{D}] - \text{CMC}$ is equal to $[\text{D}]$ in the range of surfactant concentrations we used, and $K_{\text{eq}}^{\text{app}} = K_{\text{eq}}^{\text{w}}$ if the surfactant concentration $[\text{D}] \leq \text{CMC}$. From a plot for $1/K$ versus $[\text{D}]$ (eq 25), K_{eq}^{m} (M^{-1}) is calculated from the slope as $0.9 \pm 0.3 \text{ M}^{-1}$, assuming that $\beta = 0.75$ (Supporting Information). The mean value is higher than that obtained from our kinetic study (0.6 ± 0.3), but the values are not statistically different. It is possible that the assumption of a constant β value in eq 25 is not appropriate in reaction media with variation of electrolyte (NaHCO_3) concentrations.^{10,49}

Comparison of Reactivities for HCO_4^- , IO_4^- , and HSO_5^- at Micellar Surfaces. Consistent with our results, previous reports have shown that rate constants for reactions of anionic peroxidants in a cationic micelle pseudophase can be significantly lower than those for the aqueous phase. Bunton and co-workers have studied micellar effects on the oxidation of organic sulfides by anionic oxidants in the presence of CTA surfactants (HSO_5^- , IO_4^-).^{38,39,50} The observed oxidation rates with HSO_5^- and IO_4^- are not accelerated by cationic micelles, although both reactants should be concentrated at the micellar surfaces. The much lower values of second-order rate constants at micellar surfaces as compared to those in bulk water are evidently responsible for the reduced oxidation rates by HSO_5^- and IO_4^- in aqueous CTA solutions. The second-order rate constants at CTA micellar surfaces are lower than those in water by a factor of ~ 400 and ~ 1000 , respectively.^{38,39} The low values of k_2^{m} relative to k_{w} are attributed by Bunton and co-workers to the unfavorable interactions between the increased positive charge on sulfur in the proposed transition state and the positive charge on micellar headgroups. The polarity of the Stern layer is generally considered to be lower than that of bulk water,^{43,44} but the effect was suggested to be less important by Bunton and co-workers than the charge-charge interaction.⁵⁰

In contrast, the value of $k_{\text{w}}/k_2^{\text{m}}$ for aryl sulfide oxidations by HCO_4^- is < 100 (Table 3). Solvent effect studies on sulfide oxidations by HCO_4^- have shown that the oxidation is favored

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in polar solvents, and Hammett correlation studies indicate a transition state having increased positive charge on sulfur.^{17,18} Therefore, the mechanism of HCO_4^- oxidations at micellar surfaces should be very similar to those of HSO_5^- and IO_4^- oxidations. However, sulfide oxidation rates for HCO_4^- at CTA micellar surfaces are not decelerated to as large of an extent. For example, the value of k_w/k_2^m of PhSEtCl oxidation by HSO_5^- was ~ 400 , while a value of $k_w/k_2^m \approx 70$ was found for PhSEtOH oxidation by HCO_4^- .

The lower reactivity of anionic oxidants when transferred from water to micelles is consistent with the kinetic observations for mixed aqueous solvents. The kinetic parameters in mixed solvents have been fit to the Grunwald–Winstein equation for sulfide oxidation by IO_4^- and HCO_4^- in aqueous ethanol and for sulfide oxidation by HSO_5^- in aqueous acetonitrile. The m values for oxidation by HSO_5^- , IO_4^- , and HCO_4^- were reported to be 1.0 (in aqueous acetonitrile),⁵¹ 0.72 (in alcohol/water),⁵² and 0.46 (in alcohol/water),¹⁷ respectively. The lower value of m for HCO_4^- oxidations implies a less polarized transition state than the corresponding transition states for HSO_5^- and IO_4^- oxidations. The charged sulfur in the transition state of HCO_4^- oxidation is expected to induce less repulsion with the positive charges on micellar headgroups. In addition, the decrease in rate as a consequence of the medium upon transfer from water to the less polar micelle pseudophase will be less for HCO_4^- oxidations than for those oxidants with higher m values. This rationalizes why the deceleration of oxidation at micellar surfaces for HCO_4^- is not as large as those for HSO_5^- and IO_4^- oxidations.

The reactivity of HSO_5^- is typically $\sim 10^3$ – 10^4 times higher than that of HCO_4^- in water or organic solvents based on a Brønsted plot analysis.^{53,54} For example, k_w for oxidation of PhSEtCl by HSO_5^- (203 – $260 \text{ M}^{-1} \text{ s}^{-1}$) is ~ 1500 – 2000 -fold higher than that for PhSEtOH oxidation by HCO_4^- ($0.14 \text{ M}^{-1} \text{ s}^{-1}$). The marked difference in the corresponding rate constants between HSO_5^- and HCO_4^- oxidations in water is significantly reduced to ~ 250 -fold at micellar surfaces. Hence, the interaction between the anionic oxidant, substrate, and the cationic micellar headgroups can strongly affect the reaction kinetics, and the electrophilicity of the oxidant is not the only important parameter in the determination of micellar oxidation rates.

A value of $k_m^0 = 3.9 \pm 0.7 \text{ M}^{-1} \text{ s}^{-1}$ was determined for both PhSEtOH and PhSEt oxidations by H_2O_2 , and the ratios of k_w^0/k_m^0 are found to be < 100 (Table 3). These results are also consistent with a less polarized transition state of sulfide oxidations by H_2O_2 than that of oxidations by anionic oxidants, HSO_5^- and IO_4^- , which have better leaving groups than H_2O_2 , for which OH^- is displaced.⁵³

Comparison of HCO_4^- to H_2O_2 Oxidations. The second-order rate constants k_2^m ($\text{M}^{-1} \text{ s}^{-1}$) for sulfide oxidations by HCO_4^- are estimated to be 50-fold (PhSEtOH) and ~ 180 -fold (PhSEt) greater than k_m^0 ($\text{M}^{-1} \text{ s}^{-1}$) for H_2O_2 at micellar surfaces (Table 3). These values could be up to 4 times higher, considering the uncertainties of the Stern layer volume and the value of K_{mw} . The corresponding values of k_w/k_w^0 in water are

in the range of 50–200. The average value of k_1/k_0 for HCO_4^- oxidations of aryl sulfides in mixed solvents is ~ 300 .^{17,18} The consistency of estimated comparative rate constants for HCO_4^- and H_2O_2 in micelles and homogeneous solution suggests that the assumptions used in this work are valid. Thus, HCO_4^- is more reactive than H_2O_2 by a factor of $\sim 10^2$ regardless of the reaction media, and this result is consistent with a Brønsted analysis of the kinetics for heterolytic peroxide oxidations.¹⁷

Surfactant versus Mixed Water/Solvents as Reaction Media. The apparent rate constant for sulfide oxidation by HCO_4^- in ethanol/water solvent has been compared to that in CTA micelles to explore the feasibility of replacing organic cosolvents with surfactants in oxidations of a variety of organic substrates. With respect to oxidation of PhSEtOH by HCO_4^- in concentrated CTAHCO_3 solutions ($[\text{D}] \geq 0.050 \text{ M}$), the apparent rate constant is up to 2.4 times that in pure water in the presence of the same amount of bicarbonate catalyst. However, the surfactant media can dissolve much more of the substrate than pure water, in which hydrophobic organic substrates have limited solubility. The relatively higher rates in CTA micelles result from the much higher concentration of anionic activator ($\sim 5 \text{ M}$) and a larger equilibrium constant for peroxycarbonate formation at CTA micellar surfaces. For example, the concentration of oxidant HCO_4^- is $\sim 2 \text{ M}$ in the Stern layer with 1 M of H_2O_2 in the bulk water. Even in the solutions of CTACl and CTABr with unreactive ions largely present at micellar surfaces, the apparent rate constants of oxidations are only reduced by a factor of 2–4 in concentrated surfactant solutions relative to that in water under similar reaction conditions. Overall, the rates of oxidation by HCO_4^- are not lowered much by addition of CTA surfactant, although the second-order rate constant k_2^m is ~ 70 -fold less than the value of k_w in water. In contrast, the observed rate of oxidation by HCO_4^- in ethanol/water (1.76:1, v:v) is ~ 6 -fold slower than that in water due to a lower second-order rate constant ($k_1 = 0.012 \text{ M}^{-1} \text{ s}^{-1}$) in the mixed solvent under the experimental conditions.¹⁷ Therefore, *the observed rate constants for aryl sulfide oxidations are approximately 14 times higher in the surfoxidant media as compared to in ethanol/water with similar concentrations of bicarbonate activator.*

These results show that cationic micelles, in particular, CTAHCO_3 , are excellent reaction media and can be superior to organic cosolvents in oxidations of organic sulfides by bicarbonate-activated hydrogen peroxide. For the bicarbonate surfoxidant, the combination of reactive ion micellar catalysis and the increase in equilibrium formation of HCO_4^- at micellar surfaces overwhelms the less favorable kinetics of HCO_4^- oxidations caused by the nature of the micellar environment.

Experimental Section

Materials. Sulfides and hydrogen peroxide (35%) were purchased from Aldrich. Stock solutions of hydrogen peroxide were standardized iodometrically. Cetyltrimethylammonium bromide (CTABr) obtained from Sigma was purified by recrystallization from Et_2O – EtOH . Aqueous solutions of 25% cetyltrimethylammonium chloride (CTACl) and 10% cetyltrimethylammonium hydroxide (CTAOH) were purchased from Aldrich and used without further purification. Cetyltrimethylammonium bicarbonate (CTAHCO_3) was prepared by bubbling CO_2 through an aqueous solution of CTAOH for $\sim 1 \text{ h}$. The completion of the reaction was indicated by a stable pH of ~ 7.8 for the surfactant solution. The concentration of CTAHCO_3 was then determined by

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titration using the standard barium chloride method. Ammonium bicarbonate (Mallinckrodt), ammonium dibasic phosphate (Sigma), and tetramethylammonium chloride (Aldrich) were analytical grade and were used as received. For ^{13}C NMR studies, 99% ^{13}C -enriched sodium bicarbonate and 99.9% D_2O (Cambridge Isotope Laboratories, Inc.) were used. Water was purified by using a Barnstead Nanopure system.

Physical Properties. Critical micellar concentrations (CMC) were determined from the variation of surface tension with surfactant concentration $[\text{D}]$ by using a Tante ST-PLUS tensiometer. No minima were found in a plot of surface tension against $\log[\text{D}]$ for all of the CTA surfactants. For CTACl and CTABr, the CMC was measured in the absence and presence of ammonium dibasic phosphate ($\mu = 0.20$). It was reported that there was no change of CMC of CTACl in the presence of up to 2.0 M hydrogen peroxide.⁴² Our measurements of CMC of CTACl found a lower value of CMC with 0.20 M hydrogen peroxide, possibly due to the additive stabilizer in the stock solution of hydrogen peroxide. However, the change of CMC by addition of hydrogen peroxide was not as significant as the change caused by addition of phosphate ($\mu = 0.20$).

Partitioning of Hydrogen Peroxide. A Varian model 320 liquid chromatography system equipped with a UV 254 nm_{max} was used in measurements of retention volumes (V_r) of hydrogen peroxide at a variety of CTACl concentrations (0–0.20 M), following published procedures. The reverse phase column used was a Phenomenex Jupiter, 5- μm C18 300A packing (25 cm long \times 4.6 mm i.d.). The total volume (V_t) was 4.15 mL, the void volume (V_0) was 1.7 mL, and the volume of the stationary phase (V_s) was taken as the difference of V_t and V_0 . The void volume was not significantly different using eluting solvents containing various surfactant concentrations.

Kinetics. Oxidations were followed spectrophotometrically with hydrogen peroxide in large excess over the sulfide using HP 8453 single-cell or multicell spectrophotometers with cell holders at 25.0 ± 0.1 °C.¹⁷ Solutions of hydrogen peroxide with bicarbonate catalyst were prepared 20–30 min prior to mixing with sulfide substrate to ensure preequilibration of peroxycarbonate formation. The concentration of surfactant ranged from 2.0×10^{-3} to 2.0×10^{-1} M. In a typical study of rate constants as a function of $[\text{D}]$, the concentrations of both H_2O_2 and NH_4HCO_3 were 0.20 M. The oxidation kinetics were also investigated at various concentrations of hydrogen peroxide (0.10–2.0 M) for uncatalyzed oxidations in CTABr (0.050 M) and catalytic oxidations in CTAHCO₃ (0.050 M). Sulfide concentration was usually 2.0×10^{-4} M, although variation of sulfide concentration from 2×10^{-4} to 8×10^{-4} M did not affect the rate constants even in dilute surfactant solutions. Oxidation of sulfide was followed by decreasing absorbance at $\lambda \approx 290$ nm. For PhSEtOH, the substrate was added in a 1 cm cuvette with the preequilibrated mixture of H_2O_2 and CTAHCO₃ solutions, or $\text{H}_2\text{O}_2/\text{NH}_4\text{HCO}_3$ and CTAX ($\text{X}^- = \text{Cl}^-, \text{Br}^-$) solutions,

for each kinetic run. For PhSEt, the sulfide was dissolved completely in water by using a Fisher ultrasonic bath. The preequilibrated surfactant solution of H_2O_2 and NH_4HCO_3 was mixed with an aqueous solution of sulfide in a 1 cm cuvette at each run. The background reactions were followed with addition of $(\text{NH}_4)_2\text{HPO}_4$ to control the $\text{pH} \approx 8$ and an ionic strength comparable to 0.20 M NH_4HCO_3 . The reactions were generally recorded for ~ 3 half-lives. For the background reactions in concentrated surfactant solutions, the reactions were extremely slow, and the data were taken for only 0.3–1 half-life.

Substrate Binding. The micellar binding constant (K_s) of PhSEtOH was obtained spectrophotometrically from the variation of substrate absorbance (A) at 257 nm with surfactant concentration $[\text{D}]$.²⁶ The absorbance at 257 nm increased due to spectral shifts upon addition of CTA surfactant until the limiting value (A_m) was reached. The values of K_s were calculated in terms of eq 3 with the corresponding CMC values in the absence and presence of electrolyte (Table 1).

A similar method was used to determine the K_s value of PhSEt in CTA solutions, in which the spectra shifts were followed at 259 nm. Because the solubility of PhSEt is too low in water, a stock solution of PhSEt in CTACl was prepared for measurements of absorbance of PhSEt in aqueous CTACl solutions. The concentration of CTA in each cuvette was corrected for the added CTACl from the stock solution. CTACl (~ 0.001 M) from the stock solution does not affect absorbance in the interested region.

Equilibrium Constant Determination. Equilibrium constants $K_{\text{eq}}^{\text{app}}$ for peroxycarbonate formation in surfactant solutions were measured by using a ^{13}C NMR spectroscopic method as described in previous work.¹⁷ The concentration of hydrogen peroxide was 2.0 M, and the total concentration of bicarbonate was 0.20 M. 99% ^{13}C -enriched sodium bicarbonate (0.05–0.20 M) was added in corresponding CTAHCO₃ solutions of various concentrations (0.15–0.0 M). The equilibrium constants $K_{\text{eq}}^{\text{app}}$ were calculated on the basis of the ratio of the integration of relevant NMR signals after equilibrium reactions were completed.

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Supporting Information Available: Derivations of key equations in the preequilibrium pseudophase model (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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