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MICELLAR EFFECTS UPON OXIDATION OF ORGANIC SULFIDES BY ANIONIC OXIDANTS

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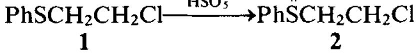
Peroxymonosulfate ion (HSO_5^-) rapidly oxidizes 2-chloroethyl phnyl sulfide (1). Dilute micelle-forming cationic surfactants slightly speed the reaction but the reaction rate decreases sharply with increasing surfactant concentration. Rate-surfactant concentration profiles in solutions of cetyltrimethylammonium hydrogensulfate can be treated quantitatively by estimating concentrations of 1 and HSO_5^- at the micellar surface with allowance for competition between HSO_5^- and HSO_4^-. The second-order rate constant in the micellar pseudo-phase is lower that in water by a factor of *ca* 400. Similar rate–surfactant concentration profiles were observed for the oxidation of di-*n*-propyl sulfide by periodate ion in solutions of cetyltrimethylammonium bromide, chloride and mesylate, and second-order rate constants in the micellar pseudo-phases are lower than in water by factors of *ca* 400. These oxidations are slowed by a decrease in the water content of aqueous acetonitrile and solvent, and micellar rate effects are consistent with transition states in which positive charge builds up on sulfur.

INTRODUCTION

Micellar rate effects on bimolecular aqueous reactions can generally be understood quantitatively in terms of pseudo-phase models that treat water and micelles as distinct regions.[1-4] The overall rate constant depends on the concentrations of the two reactants in each pseudo-phase and on the related second-order rate constants. Calculation of second-order rate constants in the micellar pseudo-phase depends on assumptions regarding the distribution of reactants between water and micelles and the nature of the reaction region at the micellar surface. However, for most bimolecular anionic reactions second-order rate constants at micellar surfaces are within approximately one order of magnitude of those in water. Variations in surfactant structure and concentrations of counter ions have minor effects on second-order rate constants at micellar surfaces. These generalizations also apply to reactions mediated by functional micelles[5] and by microemulsions of alcohol-modified micelles[6] and synthetic vesicles.[7]

The concentrations of both reactants are the key factor in the acceleration of bimolecular reactions by all these colloidal assemblies. We observed qualitatively that oxidation of an organic sulfide with peroxymonosulfate ion, HSO_5^-, is not speeded by cationic micelles, although both reactants should be concentrated at the micellar surfaces. Alkene bromination by Br_3^- is slow at surfaces of cationic micelles.[8] Both HSO_5^- and Br_3^- are anionic electrophiles, so we speculated that reactions of these types of anionic electrophiles with organic substrates might be very slow at micellar surfaces. On this hypothesis, periodate ion oxidation of organic sulfides should also be slower at micellar surfaces than in water.

Reactions of periodate monoanion (IO_4^-) can easily be followed spectrophotometrically,[9-11] so as the substrate we used di-*n*-propyl sulfide, Pr_2S, because it reacts at a convenient rate with IO_4^-.[11] Peroxymonosulfate ion in aqueous solvents reacts very rapidly with many organic compounds, including sulfides,[12] so we used 2-chloroethylphenyl sufide (**1**). The phenyl group deactivates sulfur towards oxidants, and its chromophore allowed us to follow the reaction spectrophotometrically. Initial formation of a sulfoxide (**2**) is followed by a much slower oxidation of the sulfoxide that does not interfere with following the initial reaction.



$$PhSCH_2CH_2Cl \xrightarrow{HSO_5^-} Ph\overset{\overset{O}{\|}}{S}CH_2CH_2Cl$$

1 **2**

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RESULTS

Reaction of HSO_5^-

Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) is the most convenient form of HSO_5^-.[12] It oxidizes many organic compounds, so we followed the oxidation of **1** in the absence of surfactant in aqueous acetonitrile. The first experiments were carried out with HSO_5^- added as Oxone, and we estimated the rate constant in water by extrapolation (see Experimental). Reaction is inhibited by a decrease in the water content of the solvent. We also followed the reaction in aqueous acetonitrile with sufficient H_2SO_4 to convert SO_4^{2-} in Oxone into HSO_4^- (see Experimental). The second-order rate constant for reaction in water, k_W, is then $203\ l\ mol^{-1}\ s^{-1}$. The value obtained by using Oxone is $260\ l\ mol^{-1}\ s^{-1}$, and the difference is probably due to different salt effects of SO_4^{2-} and HSO_4^-.

There is almost no rate increase by cationic surfactants, and with increasing surfactant concentration the rates decrease sharply (Figure 1). The surfactants were cetyltrimethylammonium $X[C_{16}H_{33}NMe_3X$, CTAX; X = NO_3, OMs or $(SO_4)_{0.5}]$.

Quantitative treatments of micellar rate effects on bimolecular ionic reactions involve analysis of the competition between reactive and inert counter ions.[2-4] Solutions of Oxone contain SO_4^{2-} and HSO_4^- as inert anions, and competition also involves the surfactant counter ion (Figure 1). These inert anions compete with HSO_5^- and it is difficult to account for competition involving such a mixture of inert mono- and dianions.[2-4] We simplified the problem of ion exchange by using $CTA(SO_4)_{0.5}$ and adding H_2SO_4 to convert SO_4^{2-}, derived from surfactant and Oxone, into HSO_4^-, so that ionic competition involved only HSO_4^- and HSO_5^-. Observed first-order rate constants with respect to **1** are shown in Figure 2 (the solid lines are from a theoretical simulation). The rate data for reaction in solutions of $CTA(HSO_4)$ (Figure 2) are qualitatively similar to those in solutions that contain mixtures of inert anions (Figure 1), although we did not try to fit these data. Oxone reacts rapidly with Br^- and slowly with Cl^-, so there is a limited choice of surfactant counter ion.

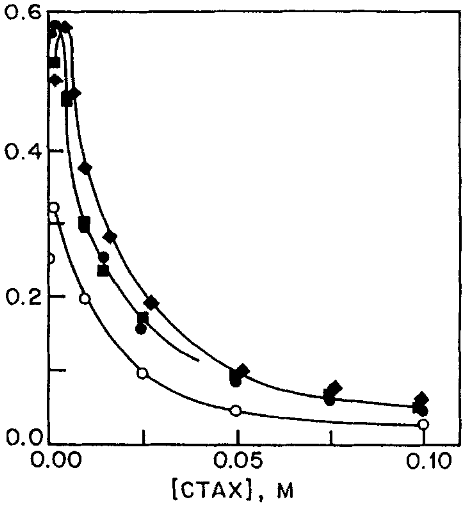


Figure 1. Micellar effects on oxidation of **1** by HSO_5^- in solutions of Oxone. Solid and open symbols $1 \cdot 75 \times 10^{-3}$ and $0 \cdot 88 \times 10^{-3}$ M HSO_5^-, respectively. X = •, ○) $(SO_4)_{0.5}$; (■) NO_3; (◆) OMs

Reaction of IO_4^-

Oxidation of Pr_2S by IO_4^- is inhibited by a decrease in

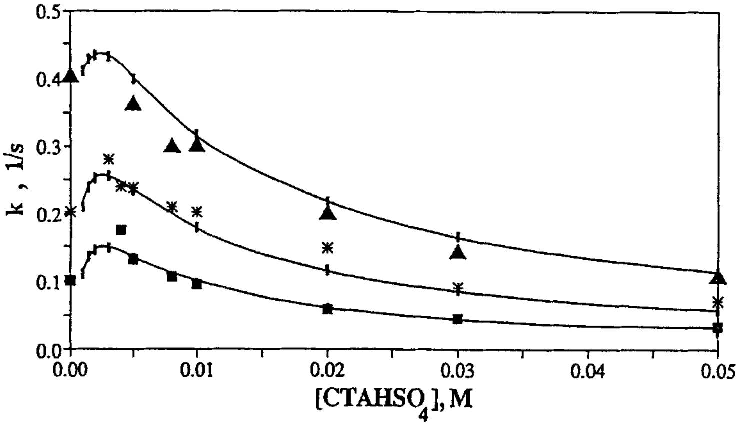


Figure 2. Oxidation of **1** by HSO_5^- in solutions of CTAHSO4. (■) 5×10^{-4} M HSO_5^-; (★) 1×10^{-3} M HSO_5^{a}; (▲) 2×10^{-3} M HSO_5^-. The lines (■) are from a theoretical simulation.

the water content of the aqueous acetonitrile solvents, in agreement with earlier work.[11] We estimated the rate constant for reaction in water by extrapolation and followed the oxidation with Pr_2S in excess over periodate ion, so the observed first-order rate constants are with respect to $[IO_4^-]$ (see Experimental). The second-order rate constant of reaction in water is $3{\cdot}2\ l\ mol^{-1}\ s^{-1}$ at $25{\cdot}0\ ^\circ C$.

Reaction in micellar solutions has to be followed with dilute periodate ion to avoid precipitation of the quaternary ammonium salt, but we were able to use Cl^-, Br^- and OMs^- as surfactant counter ions, because they are inert to periodate ion. First-order rate constants with respect to periodate ion are shown in Figures 3–5. The lines are from a theoretical simulation.

Quantitative treatments of micellar effects

Micellar effects on rates of bimolecular reactions are generally analyzed in terms of pseudo-phase models that consider the distribution of both reactants, e.g. organic substrate, S, and reactive ion, Ox^-, between water and micelles.[1-4]

The distribution of dilute non-ionic substrate follows the equations

$$[S_M]/[S_T] = K_s[D_n]/(1 + K_s[D_n]) \qquad (1)$$

$$[S_W]/[S_T] = 1/(1 + K_s[D_n]) \qquad (2)$$

where subscripts M, W and T indicate material in micelles and water and the total material, respectively. Concentrations are written as molarities in terms of the

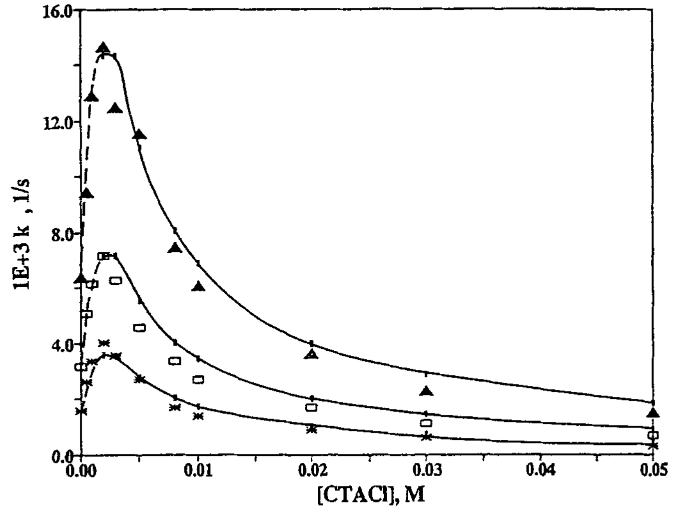


Figure 3. Oxidation of Pr_2S by periodate ion in solutions of CTACl: (★) 5×10^{-4}; (□) 1×10^{-3}; (▲) 2×10^{-3} M Pr_2S

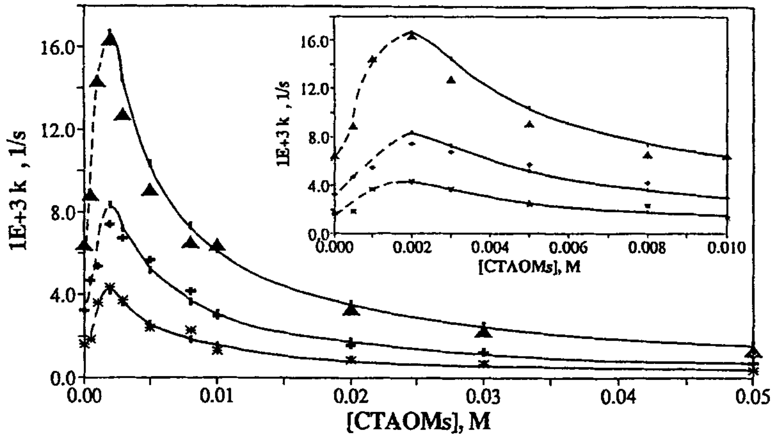


Figure 4. Oxidation of Pr_2S by periodate ion in solutions of CTAOMs: (★) 5×10^{-4}; (+) 1×10^{-3}; (▲) 2×10^{-3} M Pr_2S. Inset shows data in dilute CTAOMs

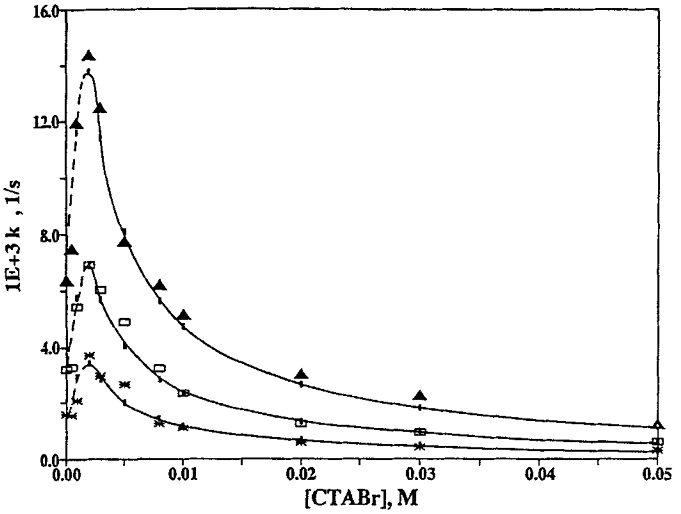


Figure 5. Oxidation of Pr_2S by periodate ion in solutions of CTABr: (★) 5×10^{-4}; (□) 1×10^{-3}; (▲) 2×10^{-3} M Pr_2S

total volume of solution, and $[D_n]$ is the molarity of micellized surfactant (detergent), i.e. the total less the critical micelle concentration (CMC) under kinetic conditions.

Hydrophilic ions compete at the micellar surface, as at ion-exchange resins, and the competition can be described by ion-exchange equations similar to those derived for ion-exchange resins.[2-4] This pseudo-phase ion-exchange (PIE) model has been used extensively to fit data, although it has limitations. An alternative treatment is based on the assumption that ionic distribution is governed by non-specific coulombic interactions and also by specific interactions of ions with micellar head groups.[13,14] These specific interactions neutralize the charge of an equivalent number of head groups and therefore reduce the coulombic attraction of counter ions and repulsion of co-ions.[13]

We used this method to calculate ionic distributions in terms of the cell model of solutions.[13-15] The distribution of ions between the micellar surface and the cell wall is calculated by solving the Poisson–Boltzmann equation (PBE) in spherical symmetry with allowance for a specific ion–micelle interaction for polarizable low-charge density ions such as Br^- or IO_4^-.[13] Specific interactions should be low for very hydrophilic, high charge-density ions whose interactions with micelles are largely coulombic.

We allowed for the specific interactions of two competing counterions by writing the partial coverage, *f*, of the micellar surface in terms of a Langmuir isotherm:

$$f = \frac{\delta_X [X_w^- [+ \delta_{Ox} [Ox_w^-]}{1 + \delta_X [X_w^-] + \delta_{Ox} [Ox_w^-]} \tag{3}$$

where δ is a specificity parameter and X^- is inert counter ion.[13] If only one counter ion is interacting specifically with the micelle, it is convenient to use a Volmer isotherm, which is slightly better than the Langmuir form at high surface occupancy. The Langmuir isotherm is computationally simpler than the Volmer isotherm for two interacting counter ions, and the equations become equivalent at low occupancy, although the values of δ differ by a factor of two.[16].

Calculation of ionic distribution depends on the micellar surface electrical potential and therefore on the charge density, which is reduced by specifically bound counter ions. The charge density of a spherical micelle depends on the aggregation number, *N*, and the radius to the charged interface, *a*. Reasonable values of these parameters are known from direct measurement or by comparison with values for micelles of similar composition.[13] The observed first-order rate constant with respect to an organic substrate for overall reaction is given by

$$k = \frac{k_w [Ox_w^-] + k_2^m K_s [D_n] [Ox^-]_\Delta}{1 + K_s [D_n]} \tag{4}$$

where k_2^m ($l\ mol^{-1}\ s^{-1}$) is the second-order rate constant with concentration written as molarity in a reaction region at the micellar surface. We write this region as a shell of thickness Δ, and fitting of rate data for reactions of nucleophilic anions was based on $\Delta = 2{\cdot}4$ Å,[13] and that value being used here. The second-order rate constant k_w, can be determined by direct measurement.

Reactions of HSO_5^-

For reaction in $CTAHSO_4$ we assumed that *a* and *N* would be similar to values for CTACl,[13] and we took $a = 20$ Å and $N = 80$. We took $\delta_{HSO_4} = 15$ l mol^{-1} and, on the assumption that HSO_5^- should be slightly more polarizable, we took $\delta_{HSO_5} = 20$ l mol^{-1}. The fits of the kinetic data are reasonable (Figure 2). The CMC will be lowered by added electrolytes and apolar solutes,[2,17] but the effect should be small in our experiments because reactants are in low concentrations. The pseudo-phase model, as generally written, involves the assumptions that reaction is in either the aqueous or micellar pseudo-phase, that there is no reaction in submicelles and that substrate does not affect formation of submicelles or the equilibrium between monomer and micelles. For many reactions the rates are so much lower in water than in surfactant solutions that these assumptions cause no problems,[1-4] but the situation may be different for oxidation by HSO_5^-, where there is very little increase in the rate of the overall reaction (Figures 1 and 2). The fitting parameters for oxidation by HSO_5^- are given in Table 1.

Reaction of periodate ion

Equation (4) is written in terms of the first-order rate constant with respect to sulfide,[13] but it is convenient experimentally to follow the micellar reaction with sulfide in excess over periodate ion,[11] where the observed first order rate constant, k_ψ is with respect to periodate ion and designated k^p. We converted this first-order rate constant into a first-order rate constant with respect to sulfide, k^s:

$$\text{rate} = k^p[\text{Per}] = k^s[\text{Pr}_2\text{S}] \tag{5}$$

$$k^s = k^p[\text{Per}]/[\text{Pr}_2\text{S}] \tag{6}$$

Equation (6) is written with initial reactant concentrations and Per represents periodate monoanion. The reactive species of periodate monoanion is IO_4^- and equilibrium strongly favors it over the hydrated form, $H_4IO_6^-$.[10] Cationic micelles may change this equilibrium, but the effect seems to be small because there is no significant change in the strong absorbance at *ca* 235 nm due to IO_4^-.

Table 1. Micellar effects on second-order rate constants[a]

Reactants	Surfactant	$10^2k_2^m$ (l mol^{-1} s^{-1})	k_2^m/k_w
$HSO_5^- + \mathbf{1}$	$CTAHSO_4$[b]	50	0·0025
$IO_4^- + Pr_2S$	CTACl[c]	1·0	0·0031
$IO_4^- + Pr_2S$	CTABr[d]	0·60	0·0019
$IO_4^- + Pr_2S$	CTAOMs[e]	0·65	0·0020

[a] At 25·0 °C with $K_s = 1000$ and 300 l mol^{-1} for Pr_2S and **1**, respectively.

[b] $a = 20$ Å, $N = 80$, CMC $= 9 \times 10^{-4}$ M.

[c] $a = 21$ Å, $N = 80$, CMC $= 1{\cdot}4 \times 10^{-3}$ M.

[d] $a = 24$ Å, $N = 95$, CMC $= 8 \times 10^{-4}$ M.

[e] $a = 23$ Å, $N = 85$, CMC $= 1{\cdot}3 \times 10^{-3}$ M.

We fitted variations of k^s [equation (6)] with changes in concentrations of surfactants and Pr_2S to equation (4) with values of k_2^m given in Table 1 and recalculated k^P (the observed rate constant with excess of Pr_2S) to obtain the plots shown in Figure 3–5.

We based our fitting on values of a and N (Table 1) used earlier in fitting data for micellar effects on reactions of nucleophilic anions.[13] The specificity parameters δ_{Br}, δ_{Cl} and δ_{OMs} were 60, 7·5 and 10 l mol^{-1}, repectively [equation (3)] as used earlier.[13] We took $\delta_{IO_4} = 50$ l mol^{-1} on the basis that periodate ion would interact strongly with cationic micelles, but small changes in this parameters do not significantly affect the simulations.

DISCUSSION

The pseudo-phase model fits micellar effects on oxidations by HSO_5^- and periodate ion over a range of conditions, even though, except in dilute surfactant, reaction of HSO_5^- is micellar inhibited, as is reaction of periodate with [surfactant] >0·01 M (Figures 2–5). Changes in the surfactant counter ion do not significantly affect k_2^m for reaction of periodate ion (Table 1). We could not make this comparison for the reaction of HSO_5^-, but observed overall rate constants in solutions of micellized $CTAHSO_4$ are similar to those in solutions of $CTANO_3$, CTAOMs and $CTA(SO_4)_{0.5}$ (Figures 1 and 2).

Values of k_2^m/k_w are *ca* 0·0025 for reaction of HSO_5^- and are in the range 0·0019–0·003 for reaction of periodate, in marked contrast to values close to unity for many bimolecular reactions of anions.[1-4] Values of k_2^m/k_w depend on the value of Δ [equation (4)], but even if it varied by a factor of two, which is unlikely, the values of k_2^m/k_w would still be unusually low.

Low values of k_2^m/k_w are not typical of oxidations. For example, rate constants of chromic acid oxidations of alcohols are similar in water and at surfaces of anionic micelles,[18] and $k_2^m/k_w \approx 1$ for the oxidations of ferrocene derivatives to ferricenium ions by Fe^{3+}.[19]

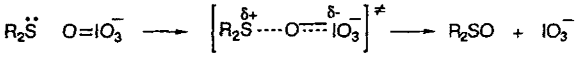
Although for many bimolecular reactions the rate constants are similar in aqueous and micellar pseudophases, the situation is different for spontaneous reactions, where only distribution of the substrate has to be considered. Rate constants are often similar in the two pseudo-phases for bimolecular, water-catalyzed, hydrolyses, but they may differ sharply for unimolecular reactions.[20,21] Spontaneous anionic decarboxylations,[22] dephosphorylations[23] and desulfation[24] are faster at surfaces of cationic micelles than in water, by one to three orders of magnitude. Micelles inhibit S_N1 reactions and the inhibition is much larger in cationic than in anionic micelles.[21] Ruff and Kucsman[11] showed that medium effects on the periodate ion oxidation of sulfides are qualitatively similar to those on S_N

reactions, which suggest that there should be similarities in micellar effects on these reactions.

Solvent effects on the periodate oxidation of sulfides in aqueous ethanol fit the Grunwald–Winstein equation[25] with $m = 0{\cdot}72$,[11] so solvent sensitivity is less than that for an S_N1 reaction. The behavior is similar for oxidation of Pr_2S in aqueous acetonitrile[26] where $m = 0{\cdot}80$. Dependence of m on substrate structure and the solvent pair is well known.[25] The solvent effect on oxidation of **1** by HSO_5^- also follows the Grunwald–Winstein equation, but $m = 1{\cdot}2$ in aqueous acetonitrile,[26] and this high value suggests that there is considerable charge development in the transition state of this reaction.

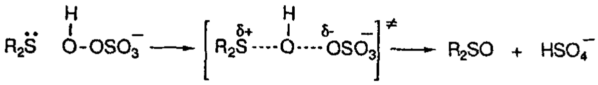
Polarities at micellar surfaces are lower than that of water, based on comparisons of spectral shifts of probes in micelles and in organic solvents.[27,28] However, there is a significant potential gradient at micellar surfaces which may influence reaction rates in this region. For example, an alkyl halide or sulfonate ester at a micelle–water interface will orient itself, on average, with the leaving group in the water-rich region. For an S_N1 reaction occurring in a cationic micelle, ionization generates a carbocation adjacent to quarternary ammonium centers and the coulombic interaction disfavors reaction.[21] The rate enhancements of anionic decarboxylations and dephosphorylations by cationic micelles can be ascribed to favorable coulombic interactions in the transition states and to polarity at the micellar surface.[22,23]

Electron-releasing substituents speed oxidations of sulfides by periodate ion and the reaction rate is increased by polar solvents. Reactions involve overall oxygen transfer to sulfur and the mechanism was written as[11]



$$R_2\ddot{S}\quad O{=}IO_3^- \longrightarrow \left[R_2\overset{\delta+}{S}\cdots O\overset{\delta-}{\cdots} IO_3^-\right]^{\neq} \longrightarrow R_2SO + IO_3^-$$

with build up of positive charge on sulfur in the transition state. A similar mechanism can be written for HSO_5^-:



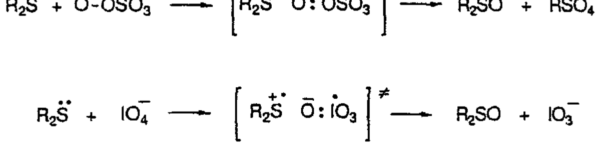
$$R_2\ddot{S}\quad \overset{H}{\overset{|}{O}}{-}OSO_3^- \longrightarrow \left[R_2\overset{\delta+}{S}\cdots\overset{H}{\overset{|}{O}}\cdots\overset{\delta-}{OSO_3^-}\right]^{\neq} \longrightarrow R_2SO + HSO_4^-$$

Build-up up of positive charge on sulfur will be disfavored by cationic micelles because organic substrates will bind in the vicinity of the cationic head groups.

Many ionic substitutions have been described on the assumption that a nucleohile donates a pair of electrons to an electrophilic center to form the new bond and that the electrons of the existing bond leave with the leaving group. However, an alternative model of transition-state formation involves transfer of one electron from a nucleophile,[29,30] and additions and substitutions of electron-rich arenes with electrophiles and of nucleophiles with a variety of electrophiles, especially di- and trinitroarenes and their derivatives, can be written as transfer of a single electron (SET) from the nucleophile (reducant) to the electrophile (oxidant).[31] This transfer generates intermediates or transition states with charge-transfer character. Similar SET descriptions have been applied to ester deacylations[32] and to a variety of nucleophilic[29–32] and electrophilic[33] reactions. For example, Ritchie[34] reported that rates of nucleophilic addition to preformed carbocations do not fit Brønsted relationships, based on either basicities or equilibrium constants of the overall reactions, but follow oxidation potentials of the nucleophiles. In some reactions that had been written as two-electron transfers there is evidence for free radicals generated by SET.[35]

Similar mechanistic models, as applied to our oxidations, are shown in Scheme 1. They involve the donation of an electron from sulfur into an antibonding orbital of the oxidant. The build-up of positive charge on sulfur will be disfavored by carrying out the reaction at the surface of a cationic micelle. For non-micellar reactions the increase in charge in the transition state will be favored by polar hydroxylic solvents. The transition states in Scheme 1 are shown with complete electron transfer from the sulfide to the oxidant and very little breaking of the O—O or O—I bonds. Substituent and solvent effects on oxidations by periodate ion suggest that in these reactions charge development is less than indicated in Scheme 1, i.e. transition-state formation does not require complete electron transfer from the sulfide. However, the large value of m for oxidation by HSO_5^- in aqueous acetonitrile is indicative of extensively charge development in this reaction. As for other reactions, transition-state formation can be described in terms of either the classical model or the SET formalism.

Although these oxidations and many nucleophilic substitutions and additions are anion–molecule reactions, they should behave completely differently in cationic colloidal assemblies. The organic substrate will be adjacent to cationic head groups and nucleophilic attack generates negative charge on it, but, if the organic substrate is the reductant (nucleophile), it will develop positive charge in the transition state and suffer unfavorable interactions with cationic head groups. The



Scheme 1

extent to which these interactions will be offset by those of the anionic reagent with water or micellar head groups and counter ions will depend on reactant structure and the detailed mechanism, in addition to the micropolarity of the reaction environment. Ruff and Kucsmann[11] noted analogies between medium effects on S_N1 reactions and periodate oxidation of sulfides, and the strong inhibition of S_N1 reactions by cationic micelles has been ascribed to the orientation of the bipolar transition state at micelle–water interfaces.[21]

For periodate oxidation of arylmethyl sulfides, $\rho = -1\cdot4$, based on σ.[11] This value of ρ is much lower than those for S_N1 reactions and carbocation equilibria that correspond to build-up of unit positive charge at the reaction center.[36] This difference suggests that there is only limited charge build-up on sulfur in the oxidation, but inefficient orbital overlap between the phenyl group and the bulky sulfur atom may reduce the sensitivity of the reaction to electronic effects of substituents.

Substituent, solvent and micellar effects on alkene bromination by Br_3^- [8,37] can also be explained in terms of single electron transfer from the alkene into an antibonding orbital of the electrophile. In these brominations, as in oxidations by IO_4^- and HSO_5^-, neutral reducing agents (nucleophiles) donate an electron to an anionic oxidant (electrophile) despite unfavourable coulombic interactions. Dioxiranes, derived from ketones and HSO_5^-, are very effective oxidants and transfer oxygen to nitrogen and sulfur nucleophiles and to Cl^-.[38] It has been pointed out that some of their reactions could occur by electron transfer.[39]

EXPERIMENTAL

Materials. Reagents were commercial samples and the sulfides were redistilled. The oxidant content of Oxone and its solutions was measured idiometrically. Preparation and purification of the surfactants have been described.[13]

Kinetics. Slower oxidations were followed spectrophotometrically in Beckmann or Hewlett-Packard spectrometers at 25·0 °C. Faster reactions were followed in a Durrum stopped-flow spectrometer. Disappearance of periodate ion was followed at 235–240 nm with excess of Pr_2S. For reaction in micellar solutions we used 5×10^{-5} M periodate ion and in the absence of surfactant 1×10^{-4} M periodate ion. Disappearance of **1** was followed at 260 nm with excess of HSO_5^-. We used 1×10^{-5} and 2×10^{-5} M **1** in the presence and absence of surfactant, respectively.

The solvent effect on the reaction of **1** with Oxone is shown in Figure 6 and data for reaction of **1** with HSO_5^- in aqueous acetonitrile of high water content are given in Table 2. Extrapolation of the rate constants to pure water gives a second-order rate constant $k_w = 203\ \mathrm{l\ mol^{-1}\ s^{-1}}$. A similar extrapolation of rate constants for reaction with Oxone (Figure 6) gives a second-order rate constant of $260\ \mathrm{l\ mol^{-1}\ s^{-1}}$.

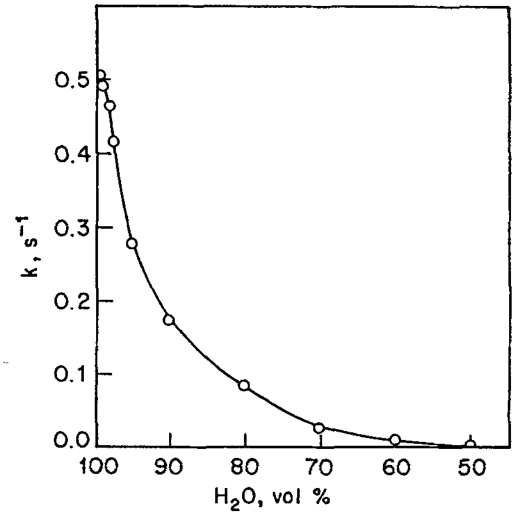


Figure 6. Oxidation of **1** by $1\cdot88 \times 10^{-5}$ M HSO_5^- in solutions of Oxone in aqueous acetonitrile

First-order rate constants with respect to periodate ion with Pr_2S in aqueous acetonitrile are given in Table 3. Extrapolation gives a second-order rate constant of $3\cdot2\ \mathrm{l\ mol^{-1}\ s^{-1}}$ in water at 25·0 °C.

Kinetic simulations. Variations of first-order rate constants, with surfactant concentration were fitted by the simulation procedure already described.[13] Concentrations of reactive anions as functions of distances from the micellar surface to the cell wall are calculated by solving the PBE in spherical symmetry by numerical integration with boundary conditions at the micellar surface and the cell wall. Reaction in the micellar pseudo-phase is assumed to occur in a shell at the

Table 2. Oxidation of **1** by HSO_5^- [a]

H_2O(%, v/v)	100	99	97·5	95	93
$10^2 k_\psi (s^{-1})$	12·7[b]	11·7	11·1	9·19	8·17

[a] At 25·0 °C with $6\cdot27 \times 10^{-4}$ M HSO_5^- and 2×10^{-5} M **1**.
[b] Extrapolated value.

Table 3. Reaction of periodate ion with Pr_2S [a]

H_2O(%, v/v)	100	95	90	80	70
$10^3 k_\psi (s^{-1})$	6·4[b]	5·21	4·31	2·12	0·91

[a] At 25·0 °C with 1×10^{-4} M periodate ion and $2\cdot0 \times 10^{-3}$ M Pr_2S.
[b] Extrapolated value.

water–micelle interface whose thickness is $\Delta = 2{\cdot}4$ Å. Substrate is assumed to locate uniformly in this region and ionic concentrations follow the PBE. The fitting parameters are given in Table 1.

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