Micellar Effects upon Alkene Bromination. The Role of Micellar Charge

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The observed effects of aqueous micelles on overall rates of alkene bromination (Lennox, R. B.; McClelland, R. A. *J. Am. Chem. Soc.* **1986**, *108*, 3771) are due largely to a micellar charge effect and to a change in the equilibrium between Br_2 and Br_3^-. In micelles of cetyltrimethylammonium bromide (CTABr) the equilibrium favors the less reactive Br_3^-, and overall reaction is therefore slower than in nonionic micelles of Brij 35 or in anionic micelles of sodium dodecyl sulfate (SDS). Addition of $(n\text{-}Bu)_4NBr$ to anionic or nonionic micelles perturbs their surface, which assists binding of anions, e.g., Br^- or Br_3^-, and slows reaction. Variations of T_1 relaxation times for [81]Br show that Br^- interacts with the polyoxyethylene residues of nonionic micelles, and there is qualitative evidence for binding of Br_3^- to Brij 35.

Aqueous micelles affect rates of bimolecular, nonsolvolytic reactions by acting as a pseudophase, i.e., as a reaction medium distinct from bulk solvent.[1] Rate effects can be analyzed quantitatively, provided that account is taken of the distribution of both reactants between water and micelles.[2-5] Rate effects upon spontaneous reactions provide evidence on the nature of micellar surfaces,[6-8] and they are consistent with spectroscopic evidence that the polarity of these surfaces is lower than that of water.[9]

Changes in *overall* second-order rate constants do not necessarily provide evidence on the nature of the micellar surface, because they may be due to changes in both reactant distribution and second-order rate constants at the surface.[2-5] It is therefore necessary to separate these factors. This separation is difficult for alkene bromination in the presence of Br^-, because Br_2 and Br_3^- are brominating agents related by the equilibrium:[10-13]

$$Br_3^- \xrightleftharpoons{K_d} Br_2 + Br^- \tag{1}$$

This equilibrium is medium dependent, and K_d decreases markedly with decreasing solvent polarity.[12] It

should also be affected by micelles, which regardless of charge may bind Br_2, whereas Br^- and Br_3^- bind readily to cationic micelles but less readily to anionic or nonionic micelles.[1-4,13]

Micellar effects upon alkene bromination by Br_2 + LiBr have recently been examined as potential probes of micellar structure.[14] Very hydrophobic alkenes were used to ensure that reaction was wholly in the micellar pseudophase, which was made up of cetyltrimethylammonium bromide (CTABr) or sodium dodecyl sulfate (SDS) or Brij 35, which is poly(oxyethylene)(23) lauryl ether. The rate data were discussed on the assumption that reaction involved only Br_2 in the micelles. The distribution of Br_2 and Br_3^- between water and micelles and reactions of both agents were not considered. The only situation in which overall rate constants could provide information on structures of the different micelles would be that in which relative concentrations of the different brominating agents in the micelles were identical—a most improbable condition in view of differences in micellar charge and the equilibrium between Br_2 and Br_3^-.[10-13]

In water, Br_2 is more reactive than Br_3^- toward most alkenes, but reactivity differences are not large, and with some alkenes, Br_3^- is more reactive than Br_2.[10,11] Reaction is strongly assisted by polar solvents, which is consistent with the transition state having a structure similar to that of a bromonium ion.[10-15]

In this paper we consider these questions and present an explanation of micellar effects upon alkene bromination that differs from that given in ref 14. We also provide evidence on interactions of Br^- and Br_3^- with micelles and estimate rate constants of reactions in micelles of CTABr from published data.[14] Values of T_1 for [81]Br show that Br^-, and by inference Br_3^-, interact with polyoxyethylene residues of nonionic micelles. These results and the known effects of micellar charge upon the equilibrium between Br_2 and Br_3^-[13] show that earlier conclusions regarding micellar effects upon alkene bromination[14] should be reconsidered.

Results

The absorbance at 270 nm of Br_3^- obtained by rapidly mixing Br_2 and LiBr was reported to increase in Brij 35

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Table I. Effect of Added Solutes on Relaxation Times[a]

salt	added solute	T_1 (^{81}Br), μs	T_1 (^{23}Na), ms
LiBr		860 ± 10	
LiBr	0.01 M Brij	614 ± 7	
LiBr	0.04 M Brij	345 ± 6	
LiBr	0.01 M Solulan	615 ± 7	
LiBr	0.04 M Solulan	334 ± 3	
NaBr		880 ± 10	56.0 ± 0.4
NaBr	0.01 M Brij	655 ± 10	50.1 ± 0.2
NaBr	0.04 M Brij	356 ± 4	37.7 ± 0.3
NaBr	0.01 M PEG 400	797 ± 10	54.6 ± 0.8
NaBr	0.04 M PEG 400	596 ± 8	49.9 ± 0.5
NaBr	0.01 M PEG 1540	582 ± 10	49.2 ● 0.4
NaBr	0.04 M PEG 1540	285 ± 5	33.4 ± 0.3
NaBr	0.4% v/v MeOH	860 ± 15	55.3 ± 0.4
NaBr	2% v/v MeOH	800 ± 10	53.9 ± 0.2
RbBr[b]		860 ± 10	
RbBr[b]	0.01 M Brij	591 ± 11	
RbBr[b]	0.04 M Brij	343 ± 4	
Bu$_4$NBr		190 ± 7	
Bu$_4$NBr	0.01 M Brij	156 ± 10	

[a] At 25 °C in H_2O/D_2O (4:1, v/v) and 0.1 M Br$^-$. [b] Values of T_1 (ms) for ^{87}Rb are 2.51, 1.95, and 1.17 in 0, 0.01, and 0.04 M Brij, respectively.

Table II. Effects of Salts on Relaxation Times[a]

salt	added solute	T_1 (^{81}Br), μs	T_1 (^{23}Na), ms
LiBr 0.01 M		856 ± 20	
LiBr 0.05 M		861 ± 18	
LiBr 0.1 M		860 ± 10	
LiBr 0.05 M	0.7 M LiCl	802 ± 13	
LiBr 0.05 m	0.7 M LiCl + 0.05 M SDS	799 ± 15	43.9 ± 0.2
LiBr 0.05 M	0.05 M SDS		29.1 ± 0.4
NaBr 0.01 M			55.9 ± 0.3
NaCl 0.05 M			56.1 ± 0.2
NaCl 0.05 M	0.05 M SDS		28.5 ± 0.3
SDS 0.05 M			23.3 ± 0.2
NaBr 0.1 M	0.01 M Brij[b]		49.8 ± 0.3
NaBr 0.1 M	0.04 M Brij[b]		37.0 ± 0.2
NaBr 0.1 M	0.01 M PEG 400[b]		53.8 ± 0.2

[a] At 25 °C in H_2O/D_2O (4:1, v/v). [b] With 0.4% MeOH by volume.

and decrease in CTABr and SDS, relative to the value in water.[14] This observation does not necessarily mean that Brij preferentially solvates Br$_3$$^-$ and that the ionic micelles preferentially solvate Br$_2$, as was suggested; micelles frequently change extinction coefficients and λ_{max} in electronic absorption spectra.[1,16] We examined the spectra in CTABr and SDS by using a conventional spectrometer (see the Experimental Section). The spectrum of Br$_3$$^-$ in mixtures of Br$_2$ and LiBr in CTABr is red-shifted and absorbance increases relative to aqueous Br$_2$ + LiBr, because equilibrium formation of Br$_3$$^-$ is strongly favored.[13] There is no shift of λ_{max} in SDS, but the absorbance decreases, probably because the anionic micelles tend to exclude Br$^-$ and Br$_3$$^-$ and bind Br$_2$ and shift the equilibrium, eq 1, in its favor. Consistently, the absorbance at 380 nm due to Br$_2$ increases. We did not examine the effects of nonionic surfactant on these spectra, because of reactions of the brominating agents with the surfactant in the time required to run the spectra, cf. ref 14.

Evidence for interaction of Br$^-$ with nonionic micelles of Brij 35 and Solulan-24[17] was obtained by examining values of T_1 for the NMR signal of ^{81}Br$^-$ (Tables I and II). Values of T_1 are decreased by these nonionic surfactants

Scheme I

$$Br_2W + D_n = Br_2M \xrightarrow[k_M]{alkene} product$$
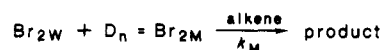
and also by polyethylene glycol (PEG). Alkali metal cations do not affect T_1, although it is decreased by tetra *n*-butylammonium ions in water and aqueous surfactant (Table I). These results suggest that Br$^-$ is binding to the polyethylene oxide groups of the surfactants or PEG. The changes in T_1 are similar for PEG 400 and 1540, on the basis of the numbers of ethylene oxide units, and are also similar for micelles of Brij 35 and Solulan-24, which have similar numbers of ethylene oxide units, but different hydrophobic groups. The binding may be via the cations, because if they bind to the ethylene oxide groups of the polymer or the micelle, Coulombic attractions will also bind Br$^-$. Consistently, values of T_1 for ^{23}Na and ^{87}Rb are lower in the aqueous surfactants or aqueous PEG than in water (Tables I and II).

As expected, anionic micelles of SDS have very little effect upon the value of T_1 for ^{81}Br$^-$ (Table II), although they decrease T_1 for ^{23}Na$^+$, and their effect is reduced by Li$^+$, which competes with Na$^+$ for the micelle.

We did not examine the NMR spectrum of ^{81}Br$^-$ in solutions of the nonionic surfactants with Br$_2$ or Br$_3$$^-$ because of the possibility of decomposition, but the binding of Br$^-$ to nonionic micelles suggests the Br$_3$$^-$ will bind readily.

These effects of polyethylene oxide upon T_1 are due to direct interactions with the ions, which affects their coordination or mobility,[18] rather than to a general solvent effect because T_1 values are affected only slightly by added methanol, and SDS has no effect, even at high [Li$^+$]. Changes in ionic concentrations do not markedly affect T_1 values of either ^{81}Br or ^{23}Na in water.

Formation of a dark orange solid from an aqueous solution of Brij 35, Br$_2$, NaBr, and HCl is evidence for an interaction between the nonionic surfactant and Br$_3$$^-$, because this solid does not form in the absence of Br$^-$ (see the Experimental Section). This material brominates 1-hexene, but we did not attempt to characterize it because there is some loss of brominating agent, probably due to reaction with Brij.

Discussion

Lennox and McClelland assumed that Br$_2$ was the only brominating agent in their micellar solutions.[14] This condition should be reasonably well satisfied with no added Br$^-$, because then only small amounts of Br$^-$ would be present due to formation of bromohydrin. But in CTABr, and especially with added LiBr, the solution contains both Br$_2$ and Br$_3$$^-$,[13] although it is possible that in SDS only reaction of Br$_2$ has to be considered, and this situation may also apply to reactions in Brij. As a test of this possibility, we attempted to analyze the reaction kinetics in Brij quantitatively on the basis of a pseudophase model.[2-5,19]

Reactions had not been followed in the absence of LiBr, but the rate constants in 0.01 M Brij in the absence of Br$^-$ can be calculated from the linear plots of $1/k_{app}$ against [LiBr],[14] by extrapolation to [LiBr] = 0. (The *overall* second-order rate constant k_{app} is the observed first-order rate constant with respect to stoichiometric bromine di-

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vided by [alkene].) We confirmed that the plots are linear, except for slight curvature at low [LiBr], on the basis of values of k_{app} in Table IV of ref 14. Extrapolated values of $10^{-4} k_{app}$ in the absence of Br⁻ are:[20] 18Δ6c, 33, 18Δ9c, 30; 18Δ9t, 4.8; 20Δ13c, 9.1 $M^{-1} s^{-1}$. These rate constants depend upon the second-order rate constants for reaction *in the micellar pseudophase* and a term for the distribution of brominating agent between water and micelles.

Providing that, as postulated,[14] Br_2 is the only brominating agent in Brij micelles, even in the presence of LiBr, Scheme I should represent the chemical and physical processes for reaction of fully micellar bound alkene.

In Scheme I, D_n is micellized Brij, subscripts W and M denote aqueous and micellar pseudophases, respectively, and k_M is the second-order rate constant in the micellar pseudophase with alkene concentration written as a mole ratio with respect to micellized Brij.[2b,4] Scheme I gives:

$$k_{app} = k_M K_s f / (1 + K_s[D_n]) \qquad (2)$$

where $f = [Br_2]/([Br_2] + [Br_3^-])$, and K_s is the binding constant of Br_2, written in terms of micellized surfactant.

Equations of the form of eq 2 fit rate–surfactant profiles for many micellar-assisted bimolecular reaction[2–5,19] (we neglect the contribution of monomeric surfactant because nonionic surfactants have very low critical micelle concentrations).

Equation 2 gives

$$1/k_{app} = 1/(k_M K_s f) + [D_n]/k_M f \qquad (3)$$

If Brij does not affect the equilibrium between Br_2 and Br_3^-, Br_2 is the sole brominating agent, cf. ref 14, and f is constant, then eq 2 or 3 should fit variations of k_{app} with [Brij] at *constant* [LiBr]. However, the kinetic data in Table IV of ref 14 do not fit eq 3. Plots of $1/k_{app}$ against [Brij] curve with increasing [Brij], so that the assumptions regarding Br_2 as the *sole* brominating agent[14] are incorrect. This failure is understandable because in the absence of surfactant both Br_2 and Br_3^- are effective brominating agents,[10,11] and this situation probably holds for reaction at the micellar surface. Added LiBr almost certainly affects the equilibrium between Br_2 and Br_3^- (eq 1) in Brij solutions. Our NMR data show that Br⁻ can bind to nonionic micelles (see Results), and Br_3^- should bind even more readily, so the equilibrium between Br_2 and Br_3^- in Brij micelles must be affected by added LiBr. An additional problem is that relative reactivities of Br_2 and Br_3^- depend upon the nature of the alkene and upon the reaction medium.[9–11] The premise on which the data in ref 14 are discussed is incorrect for nonionic micelles of Brij, and it is safe to assume that the equilibrium between Br_2 and Br_3^- (eq 1) will depend upon the charge of ionic micelles (see Results).

The higher overall rates of bromination in anionic as compared with cationic micelles were ascribed to a favorable interaction of the transition state with a structure-breaking cation, such as Na^+, at the surface of the anionic micelle,[14] although Li^+ will be the dominant cation in 0.75 M LiBr.[2] The slow reaction in CTABr was ascribed to destabilization of the transition state by Br⁻. The alternative explanation that an incipient bromonium ion would interact favorably with an anionic sulfate head group and unfavorably with a cationic head group was consid-

ered, but rejected. This second explanation is not unreasonable because differences between rates of S_N1 reactions in anionic and cationic micelles are understandable in terms of interactions of forming carbocations with micellar ionic head groups.[6b] In these reactions, anionic leaving groups will be solvated by water molecules at the micellar surface, and solvation effects should be similar in alkene bromination. Solvent effects upon alkene brominations and S_N1 reactions are very similar, e.g., values of m in the Grunwald–Winstein equation are close to unity for both reactions.[15]

However, in addition to this medium effect upon transition state stability, there are effects on the equilibrium between Br_2 and Br_3^-, and their distribution between water and micelles. Cationic micelles bind Br⁻ and bind Br_3^- so strongly that $CTABr_3$ is a stable crystalline solid, and its aqueous solutions can be heated to 90 °C without loss of Br_2.[13] Therefore Br_3^- is present at the surface of CTA^+ micelles, especially with added LiBr. Concentrations of counterions at the surface of an ionic micelle are estimated to be ca. 5 M or larger.[2] Values of K_d (eq 1) decrease with decreasing medium polarity,[12] and the polarity at the surface of a CTABr micelle,[9] together with the high surface concentration of Br⁻, will strongly favor conversion of Br_2 into Br_3^-, as is observed.[13]

Anionic micelles should not strongly bind Br⁻ and therefore in SDS the predominant brominating agent is probably Br_2, although even here the micelles might bind Br_3^-, which is a bulky, polarizable anion. There is evidence for micellar binding of co-ions induced by high electrolyte concentration or hydrophobicity of the co-ion.[21,22] This binding is consistent with Romsted's ion-exchange model[2] and is also predicted by calculation of the surface electrical potential of a micelle in high [electrolyte].[23] However, it is reasonable to assume that under similar conditions Br_3^- will bind more readily to cationic than to anionic micelles, but charge should have less effect on the binding of nonionic Br_2.

Insofar as Br_2 is more reactive than Br_3^- toward most alkenes,[10,11] conversion of Br_2 into Br_3^- will slow reaction. Bromination in SDS containing Br_2 + LiBr is inhibited by n-Bu_4N^+ [14] because it binds strongly to SDS micelles and reduces their surface potential.[23] As a result, Br⁻ and Br_3^- will be less strongly repelled and Br_2 will be converted into Br_3^-.

The lower overall rate of bromination in cationic than in anionic micellar solutions and the inhibition by n-Bu_4N^+ [14] are understandable qualitatively in terms of the equilibrium between Br_2 and Br_3^- (eq 1) and the charge effect of the micelles upon a bromonium ion like transition state.

Ion binding to ionic micelles is qualitatively straight forward,[2–4,19,23] but we have less evidence as regards nonionic micelles (cf. Results). The outer palisade region of a polyoxyethylene oxide micelle should be water-rich and therefore accessible to ions. Consistently nonionic micelles do not inhibit reactions of hydrophilic anions, e.g., OH⁻, with moderately hydrophobic organic substrates,[24] but they inhibit reactions of very hydrophobic substrates that go deeply into the micelle.[25]

(20) The substrates discussed here are:[14] 18Δ6c, (*Z*)-6-octadecenoic acid; 18Δ9c, (*Z*)-9-octadecenoic acid; 18Δ9t, (*E*)-9-octadecenoic acid; 20Δ13c, (*Z*)-13-docosenoic acid; 18Δ9c(OH), (*Z*)-9-octadecen-1-ol; 18Δ9t(12OH), [(*R*)-(*E*)]-12-hydroxy-9-octadecenoic acid; 26Δ13t (diester), dimethyl (*E*)-13-hexacosendioate; 11Δ10, undecenoic acid; monoolein, 1-monooleoyl-*rac*-glycerol.

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Table III. Comparison of Second-Order Rate Constants of Bromination[a]

	CTABr[b]		HOAc[c]	H₂O	
alkene	$10^{-2}k_M$, s^{-1}	k_2^m, M^{-1} s^{-1}	k_{app}, M^{-1} s^{-1}	$10^{-5}k_{app}$, M^{-1} s^{-1}	$10^4 k_2^m/k_{app}$
18Δ6c	1.4	20	2.54	2.54	0.8
18Δ9c	0.7	10	2.40	2.40	0.4
18Δ9t	0.06	1	1.24	1.24	0.1
11Δ10	0.1	1.4	0.11	0.11	1.3
26Δ13t (diester)	0.11[d]	1.5[d]	1.18	1.18	1.2

[a] At 25 °C. [b] Rounded-off values calculated from data in ref 14 and eq 4. [c] In 0.05 M KBr, ref 14. [d] In CTACl + 0.75 M LiBr.

Nonionic micelles bind Br$^-$ to some extent (see Results), and they should bind Br$_3^-$ more strongly. This binding will increase on addition of n-Bu$_4$N$^+$ and inhibition of bromination by n-Bu$_4$NBr in Brij micelles[14] could be due to conversion of Br$_2$ into Br$_3^-$ (eq 1) and an unfavorable medium effect as positive charge builds up in the micelle due to binding of n-Bu$_4$N$^+$. Our NMR data on ^{81}Br$^-$ in the presence of n-Bu$_4$N$^+$ show that these ions interact with each other even in water (Table I), and there should be strong association between n-Bu$_4$N$^+$ and Br$_3^-$, because both ions are of low charge density. Therefore, they could readily enter the palisade layer of a nonionic micelle as an ion pair.
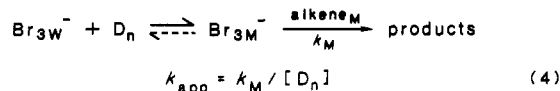
Values of overall second-order rate constants (k_{app}) for reactions of alkenes with Br$_2$ + LiBr in aqueous surfactants[14] are inconsistent with bromination only by Br$_2$. This hypothesis does not fit variations of k_{app} with [Brij], and it is therefore unlikely to be valid for reactions in CTABr. It is difficult to explain the effects of micelles of different charge except on a qualitative basis for the following reasons. (i) The equilibrium between Br$_2$ and Br$_3^-$ depends upon the structure and concentration of the surfactant. The lower polarity of micelles, relative to water,[9] will favor Br$_3^-$ over Br$_2$,[12] but there will also be a significant charge effect on reaction rate. (ii) The relative electrophilicities of Br$_2$ and Br$_3^-$ depend upon alkene structure and the reaction medium.[10,11] (iii) Structural effects upon rates of bromination of different alkenes are similar in polar, hydroxylic solvents, but this generalization fails for nonpolar solvents,[26] and it could fail for reactions at micellar surfaces.

We attempted to apply the widely used pseudophase model of micellar rate effects[2-5] to alkene bromination in CTABr + LiBr by making various simplifying assumptions. In the presence of added Br$^-$ the predominant brominating agent at the surface of a cationic micelle will be Br$_3^-$.[13] This reagent is generally less reactive than Br$_2$ by factors of less than 10,[10,11] and it should be fully bound to the micelles.[13] The hydrophobic alkene should also be fully micellar bound,[14] and if we make the reasonable assumption that Br$_2$ is converted almost completely into Br$_3^-$ in both the aqueous and micellar pseudophase,[10-13] we obtain eq 4 based on Scheme II:

$$k_{app} = k_M/[D_n] \qquad (4)$$

where, as in eq 2, k_M, s^{-1}, is a second-order rate constant written in terms of the mole ratio of alkene to surfactant.[2b,4] (Equation 4 fits reactions of Br$_3^-$ with 1-alkenes in CTABr.)[13b] This rate constant can be rewritten as k_2^m, M^{-1} s^{-1}, by considering the molar volume of the shell at the micellar surface in which reaction takes place. Esti-

Scheme II

$$Br_{3W}^- + D_n \; \underset{\longleftarrow}{\overset{\longrightarrow}{\rightleftharpoons}} \; Br_{3M}^- \; \xrightarrow{\frac{alkene_M}{k_M}} \; products$$

$$k_{app} = k_M/[D_n] \qquad (4)$$

mates of this volume range from 0.14 to 0.37 L,[2-5] and we take the lower limit so that

$$k_2^m = 0.14k_M \qquad (5)$$

Values of k_2^m for various alkenes are in Table III and are based on values of k_{app} in 0.01 M CTABr, 0.75 M LiBr, and 0.01 M HOAc.[14] To the extent that Br$_3^-$ is not full micellar bound, or that the molar volume is greater than 0.14 L, these values will be too low, but not markedly so.

It is usual to compare second-order rate constants at the micellar surface with those in water, but it is impossible to examine bromination of hydrophobic alkenes in water. Solvent effects upon rates of alkene bromination follow the Grunwald–Winstein equation reasonably well with $m \approx 1$.[15] Values of Y are 3.49 and -1.64 for water and acetic acid, respectively, and bromination in water should be faster than that in acetic acid by a factor of ca. 10^5, and we apply this correction factor to values of k_{app} in acetic acid. The values of k_{app} in Table V of ref 14 were measured in acetic acid containing 0.05 M KBr. The equilibrium constant for formation of Br$_3^-$ (eq 1) is 92 M^{-1},[12b] so that there should be a significant reaction of Br$_3^-$ in acetic acid, and for the purpose of calculation we assume that it is the dominant brominating agent (cf ref 10–13). These estimated rate constants for reaction in water are in Table III, and their magnitude is reasonable because the second-order rate constant for reaction of propene with Br$_3^-$ in water is 3.2 × 10^5 M^{-1} s^{-1} at 25 °C.[10] In Table III, values of k_M and k_2^m for reaction of 26Δ13t (diester) are for reaction in CTACl, but with 0.75 M LiBr, the small amount of Cl$^-$ will not affect the situation. Table III includes values of $k_2^m/k_{app}^{H_2O}$. They vary with alkene structure by approximately 1 order of magnitude. The variation is due in part to our assumption that reaction in acetic acid involves only Br$_3^-$ and that kinetic solvent effects upon bromination are independent of alkene structure.[15,26]

Relative rate constants in CTABr micelles and water are subject to large uncertainties, as noted earlier, but reaction is very much slower at the micellar surface than in water, as expected on the basis of a charge effect on formation of a bromonium ion and micellar polarity. The differences in relative reactivities of the alkenes may be significant, but such differences of this magnitude are not unusual for reactions of different substrates in micelles.[2-5] The inhibition of bromination by Br$_3^-$ by CTABr micelles by factors of ca. 10^4, relative to reaction in water (Table III), is qualitatively similar to that for S$_N$1 hydrolyses.[6b]

We did not apply this analysis to reactions in SDS or Brij because we cannot estimate the distribution of the brominating agents between these micelles and water. Reaction in SDS may involve only Br$_2$, as was assumed,[14] but even this conclusion is suspect because OH$^-$, which is

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very hydrophobic, binds to SDS micelles at high concentrations of inert salt.[21] Therefore such polarizable ions as Br^- and Br_3^- may bind in solutions of SDS containing 0.75 M LiBr.

The alkene brominations were followed in 0.75 M LiBr for the ionic surfactants and up to 0.2 M LiBr for Brij.[14] It is necessary to consider the way in which these high salt concentrations may influence discussion of micellar structure on the basis of kinetic evidence, including our estimations of k_2^m (eq 4 and Table III). High concentrations of LiBr induce a sphere to rod transition in CTABr, and probably also in SDS,[28] so any conclusions on micellar structure may not apply to the approximately spherical micelles that form in dilute surfactant, and electrolyte solutions of 0.01 M CTABr and 0.75 M LiBr are not stable and CTABr crystallizes out at 25 °C (see the Experimental Section). We do not know what metastable structures are formed when these components are rapidly mixed, as in a stopped flow spectrometer.

Variations in overall second-order rate constants, relative to those in nonmicellar conditions, can be misleading as probes of micelle structure unless the distribution of reagents is taken into account. The presence of Br^- inevitably compounds the problem because of formation of Br_3^-,[10-13] but the situation is simpler if the alkene has a chromophore, as with stilbene,[29,30] because then reaction can be followed in the absence of Br^-. Caution should be exercised when changes in activation parameters for the overall reaction are cited as evidence for changes in microaggregate structure. The estimated values of activation entropy will depend directly upon reagent distribution between water and the microaggregates, and activation enthalpy will depend, in part, upon the temperature effect upon this distribution. The structure of microaggregates also depends upon temperature.

These general problems of interpretation of kinetic data are especially acute for alkene bromination in mixtures of Br_2 and Br_3^-, because reaction can then involve both Br_2 and Br_3^-, depending upon micellar charge and the presence of inert ions, including such hydrophobic cations as R_4N^+.

Experimental Section

Materials. Brij 35 (Aldrich), Solulan 24,[17] and PEG 400 and 1540 (Fluka) were used without purification, but their NMR spectra were consistent with the specified structures. Purification of the other surfactants has been described,[6,13] and the salts were reagent grade from Merck, Fluka, or Carlo-Erba.

Absorbance Spectra. The absorbance spectrum of a mixture of Br_2 and 0.75 M LiBr was examined on a Cary 210 spectrometer, and ϵ_{max} increased by ca. 70% on addition of CTABr, cf. ref 14 (solutions of 0.01 M CTABr and 0.75 M LiBr are unstable and CTABr gradually separates at 25 °C). On the assumption that Br_2 in aqueous 0.75 M LiBr is ca. 92% converted into Br_3^-, our value of the apparent extinction coefficient in water is 2.3×10^4. The increase in the apparent extinction coefficient on addition of CTABr is consistent with solvent effects upon ϵ_{max}, which is 5.5×10^4 in MeCN,[31] which suggests that a medium of lowered polarity, e.g., a micelle, will give an increased extinction coefficient even if there are no shifts in the equilibria.

The absorbance of Br_2 in 0.75 M LiBr at 267 nm decreases in going from H_2O to 0.05 M SDS, but there is no change in λ_{max} and there is a small increase in the absorbance at ca. 380 nm due to formation of Br_2. Solutions of Br_2 in SDS appeared to be stable for the time required to run a spectrum, but we cannot exclude the possibility that there was some reaction with small amounts of adventitious impurities, e.g., alcohol or alkene, because these reactions would be fast in an SDS micelle.[14]

NMR Spectra. Relaxation times were measured at 25 °C in H_2O/D_2O (4:1, v/v) on a Varian XL 300 spectrometer at 80.984 MHz for ^{81}Br, 79.346 MHz for ^{23}Na, and 98.163 MHz for ^{87}Rb. Values of T_1 were estimated by using the inversion–recovery method, and each is an average of three to six measurements that were within the quoted limits. Values of T_2 from line width agreed with the T_1 values within 5–10%. The 90° pulse was measured directly on the sample to eliminate possible errors due to ionic conductivity. Values of T_1 depend upon the quadrupole relaxation[18,32,33] and are not affected by more than 20% in going to 100% D_2O.

Qualitative Observations. A dark orange solid separates from an aqueous solution of 0.01 M Brij 35, 0.05 M Br_2, 0.05 M NaBr, and 0.1 M HCl. The mixture is an effective brominating agent and retains ca. 95% of the brominating capacity of the original Br_2, on the basis of reaction with 1-hexene in heterogeneous conditions in H_2O. The loss of brominating agent is probably due to side reactions with Brij. There is no precipitation in the absence of Br^-, suggesting that complex formation involves Br_3^-. Addition of acid is also necessary for complex formation, although in CTABr a similar orange solid is obtained in addition of Br_2 in the absence of acid.[13] Acid should suppress formation of HOBr.

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