Solvation and Steric Effects on Electrophilic Reactivity of Ethylenic Compounds. Part 4. Bromination of Oct-1-ene in Anionic Microemulsions

Marie-Françoise Ruasse,[*,a] **Iva B. Blagoeva,**[b] **Sophie Krys**[a]
and Maria-Angela Sebastian-Gambaro[a]
[a] *Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7, associé au CNRS, 1, rue Guy de la Brosse, 75005 Paris, France*
[b] *Institute of Organic Chemistry, Academy of Sciences, ul. Bonchev 9, Sofia 1113, Bulgaria*

The kinetics and product distribution of the bromination of oct-1-ene in anionic sodium dodecylsulfate (SDS)–butanol–hexane–water and sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–isooctane–water microemulsions are reported. Dibromide and solvent-incorporated products are formed. In both kinds of microemulsion, the dibromide yield decreases smoothly from 100% to 10% as the water content of the reaction medium increases from 0% to 65%, whereas in pure water or butanol it is greater than 80%. The regioselectivity of the water- or butanol-incoporated products is 70:30 Markownikoff:anti-Markownikoff, a ratio identical with that found in pure methanol, butanol or water. Kinetic bromide-ion effects on the reaction in a water-rich (75%) SDS microemulsion, show that bromination occurs in the interfacial oil–water region, and not in one of the two microphases, the only brominating agent being molecular bromine and not the tribromide ion. The overall bromination rate constant in this SDS microemulsion ($k = 1.6 \times 10^4$ dm^3 mol^{-1} s^{-1}) is smaller than that in pure water (2.3×10^7 dm^3 mol^{-1} s^{-1}) and in SDS micelles (2×10^5 dm^3 mol^{-1} s^{-1}), in the same range as that in a 80–20 methanol–water mixture, and greater than that in butanol (2×10^2 dm^3 mol^{-1} s^{-1}). These results are discussed in terms of the particular characteristics (ionization and dissociating abilities, aquation and water properties) of the microemulsion interfaces.

In the search for new reaction media in which the selectivity of chemical reactions can be controlled, we have investigated the chemoselectivity of alkene bromination in microemulsions.

Despite much work on the mechanism of bromination,[1] it is still difficult to understand the selectivity of product formation and, in particular, its chemoselectivity[2] when several nucleophiles compete in the trapping of the bromonium ion. This is because kinetic data on the last, product-forming step are at present inaccessible. Moreover, the microenvironment (solvent, ion-pairing, *etc*) of the bromonium ion, as it is formed in the ionization step and as it reacts with the nucleophiles, is beyond experimental investigation, even if various assumptions have been suggested.[2,3] Nowadays, the complexity of the bromination products precludes the use of this basic reaction for synthetic purposes. For example, bromohydrins, which are useful synthetic intermediates, are not readily obtained by the bromination of lipophilic alkenes.

Microemulsions,[4] which can be viewed as micelles swollen either by a hydrocarbon solvent or by water, have sometimes been used as reaction media, in particular to facilitate the reaction between lipophilic and hydrophilic reagents. In these cases, it is assumed that the reaction occurs at the interface between the two microphases (oil and water) of the microemulsion. These interfaces, the Stern and Gouy–Chapman layers, consisting of the polar head groups of the surfactant, their counter-ions and their solvation water molecules, are highly polar aqueous media. In view of their particular properties, the chemoselectivity of alkene bromination in these macroscopically homogeneous but microscopically heterogeneous media should differ markedly from that observed in the usual homogeneous protic solvents if bromination occurs in the interfacial zone of the microemulsion. Previously reported data on electrophilic additions in micellar media show that this assumption is reasonable.[5-9]

In this paper, we report results on the bromination of oct-1-ene which have been obtained in anionic microemulsions using either sodium dodecylsulfate, SDS, or sodium bis-(2-ethylhexyl)sulfosuccinate, AOT, as the surfactant. We show, in particular, that the solvent-incorporated products can be the major bromination adducts whereas in pure water the dibromide is largely favoured.

Several studies of alkene bromination in various organized media have already been reported.[5-7,9] All have been carried out in micellar solutions, *i.e.*, in media where the oil phase consists only of the hydrophobic tails of the surfactants. Our choice of microemulsions involving hydrocarbon solvents implies (*i*) better solubility of the lipophilic alkenes so that usable reactant concentrations resemble those for preparative experiments, and (*ii*) the possibility of widely varying the microaggregate structures and, therefore, of variations in induced selectivities.[10] Our results have been obtained in anionic microemulsions. This is in contrast with other reports on bromination in cationic micelles.[9] Whereas in the latter case tribromide is the brominating species, anionic surfactants could favour bromination by molecular bromine, a reaction whose mechanism is well established compared with that of tribromide addition.[11]

Results

Microemulsion Composition.—Oct-1-ene was brominated in several microemulsions of varying composition and structure. It is well known that a macroscopically homogeneous solution is obtained by adding a hydrocarbon solvent to an aqueous solution of SDS, in the presence of a co-surfactant only.[12] The phase diagram of the SDS–*n*-butanol–water–hexane system is shown in Fig. 1. Compositions of the quaternary microemulsions at M1–M9 where bromination products have been investigated are given in Table 1.

The water-rich M1 and M2 consist of oil-in-water microdroplets, analogous to direct micelles. In contrast, the water-poor M4 medium involves water-in-oil microdroplets and, therefore, resembles inverted micelles. In the intermediate region, M3, the lamellar organization of the system can be

Table 1 Composition[a] of anionic microemulsions used as bromination media at 25 °C

	Sf:Co–Sf[b]	% Sf	% Co–Sf	% H_2O	% Oil
M1	SDS[c]–BuOH (1:1)	9.4	9.4	76.5	4.7[d]
M2	SDS[c]–BuOH (1:1)	13.7	13.7	65.0	7.5[d]
M3	SDS[c]–BuOH (1:1)	19.5	19.5	30.5	30.5[d]
M4	SDS[c]–BuOH (1:1)	7.5	7.5	15.0	70.0[d]
M5	SDS[c]–BuOH (1:2)	9.2	18.4	65.0	7.5[d]
M6	SDS[c]–BuOH (1:2)	13.0	26.0	30.5	30.5[d]
M7	AOT[e]	13.3	—	6.0	80.7[f]
M8	AOT[e]	42.0	—	18.7	39.3[f]
M9	AOT[e]	55.1	—	24.5	20.4[f]

[a] % by weight. [b] Sf = surfactant, Co–Sf = co-surfactant. [c] Sodium dodecylsulfate. [d] Hexane:oct-1-ene = 20:1 (w/w). [e] Sodium bis(2-ethylhexyl)sulfosuccinate. $W = [H_2O]/[AOT] = 11.0$. [f] Isooctane:oct-1-ene = 20:1 (w/w).

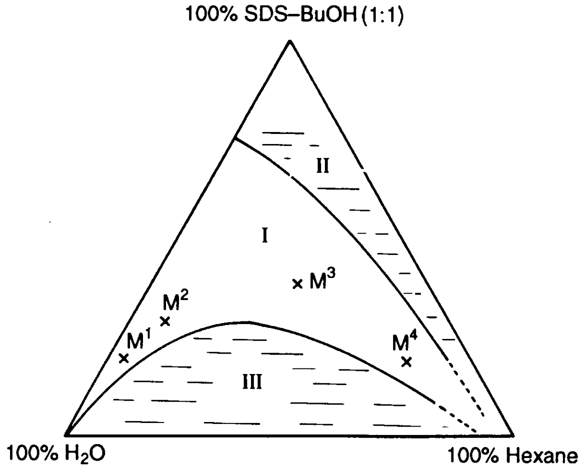

Fig. 1 Phase diagram of the quaternary SDS–*n*-butanol–hexane–water system at 25 °C: I, transparent region; II and III, polyphase regions; M1, M2, M3 and M4, microemulsions used as bromination media

viewed as a sponge where oil and water channels intermingle.[4c] Bromination experiments were also carried out in the ternary AOT–water–isooctane system where it is not necessary to add a co-surfactant to obtain a transparent solution. According to the phase diagram of the AOT solutions,[13] only water-poor media consisting of swollen inverted micelles can be obtained.

Bromination Products.—In the bromination experiments, the hexane:oct-1-ene or isooctane:oct-1-ene ratio was fixed at 20:1 (w/w) so that the phase diagram is not significantly altered by the presence of the alkene. Concentrated solutions of bromine in carbon tetrachloride were slowly added to octene-containing microemulsions, in slight excess (*ca.* 5%) with respect to the alkene, at 25 °C. For the microemulsions of Table 1, the reaction media remained transparent throughout bromine addition.

After work-up with $BaCl_2$ in order to eliminate most of the surfactant, the bromination products, extracted from the reaction mixture with methylene chloride, were analysed by GC. They consisted of dibromide (DB), bromohydrins (BH) and bromobutyl ethers (BuOB) derived from oct-1-ene according to eqn. 1, where R = H or Bu, in the ratios shown in Table 2.

$$nC_6H_{12}CH{=}CH_2 + Br_2 \longrightarrow nC_6H_{12}CHBr\text{–}CH_2Br + nC_6H_{12}CH(OR)\text{–}CH_2Br + nC_6H_{12}CHBr\text{–}CH_2OR \quad (1)$$

Both Markownikoff (M) and anti-Markownikoff (AM) adducts were systematically obtained in a ratio (70% M:30% AM) which did not depend markedly on the external nucleophile (H_2O or *n*-butanol) or on the reaction medium. No bromoethylenic compound which could arise from an addition–elimination mechanism was obtained under the reaction or work-up conditions. No bromosulfate esters derived from the reaction of the bromonium ion with the anionic head groups, analogous to those found in the bromination of unsaturated fatty acids in SDS micelles,[7] were observed either.

Table 2 Product[a] composition[b] of oct-1-ene bromination in microemulsions[c] at 25 °C

	% H_2O	% (H_2O + BuOH)[d]	% DB[e]	% BH[e]	% BuOB[e]
M1	76.5	85.9	9.5	76	15
M2	65.0	78.7	7.5	61	31.5
M3	30.5	50.0	23	50	27
M4	15.0	22.5	43	41	16
M5	65.0	83.4	10	68	22
M6	30.5	56.5	13	64	23
M7	6.0	—	82	18	—
M8	18.7	—	53	47	—
M9	24.5	—	45	55	—
f	100.0	—	91	5	—
g	2	98.0	81	—	19

[a] Yield with respect to oct-1-ene: ≥98%. [b] Average of 4–6 runs; reproducibility: ±3%. [c] Composition given in Table 1. [d] Water and *n*-butanol content (w/w) of the reaction medium. [e] DB, 1,2-dibromooctane; BH, bromohydrins (1-Br-2-OH-octane:1-OH-2-Br-octane, 70:30); BuOB, bromobutyl ether (1-Br-2-OBu-octane:1-OBu-2-Br-octane, 70:30). [f] Pure water; [oct-1-ene] = 10^{-4} mol dm^{-3}. [g] 2% aqueous BuOH (v/v).

In preliminary experiments carried out in the SDS–*n*-butanol systems the dibromodibutylacetal of *n*-butyraldehyde was obtained in amounts increasing with the bromine excess. This bromoacetal is also observed when bromine is added to SDS microemulsions which do not contain oct-1-ene. This latter product probably arises from bromine oxidation of butanol, followed by acetalization and bromination, a process the rate of which is only slightly slower than oct-1-ene bromination.[14] In the AOT experiments, isooctane bromination products were also observed when bromine was added in amounts much larger than stoichiometric with respect to oct-1-ene. These products were not identified but their retention times were determined in experiments where bromine was added to AOT–isooctane microemulsions in the absence of oct-1-ene.

The composition of the products from the bromination of oct-1-ene in pure water and *n*-butanol is also shown in Table 2. Although the experiments in pure water were carried out at very low reagent concentrations (about 10^{-4} mol dm^{-3}), since oct-1-ene and bromine are weakly hydrophilic, it is not certain that fully homogeneous conditions were obtained.

Kinetics.—Kinetic data on oct-1-ene bromination in the water-rich microemulsion, M1, were obtained under second-order conditions by following the bromine uptake spectrophotometrically, as previously described.[15] Bromine concentrations, about twice those of oct-1-ene, were varied by a factor of 10. Good second-order plots were obtained to at least 90% reaction. Therefore, the reaction was unambiguously first order in bromine and in oct-1-ene. Measurement of the kinetics was also attempted in microemulsions M3 and M4 with lower water content. In these media, the kinetic signals did not follow a clean rate law, so it was impossible to obtain a rate constant. It is probable that the partitioning of the reagents between the several microphases of these viscous media is not fast relative to bromination.

In M1, most of the bromination products are solvent-

Table 3 Experimental rate constants[a] of oct-1-ene bromination at 25 °C in microemulsion M1 with added NaBr

$[Br^-]$/mol dm^{-3} [b]	$k/10^3$ dm^3 mol^{-1} s^{-1}	$\varepsilon/10^4$ dm^3 mol^{-1} cm^{-1} [c]
0.2	7.1	2.4
0.1	9.8	1.4
0.05	11.8	1.2
0	16.1[d]	—

[a] ±5%. [b] Sodium bromide concentration in the water phase. [c] Molar extinction coefficient of bromine in M1 containing NaBr at λ = 270 nm; reproducibility ±6%. [d] Extrapolated from eqn. (5).

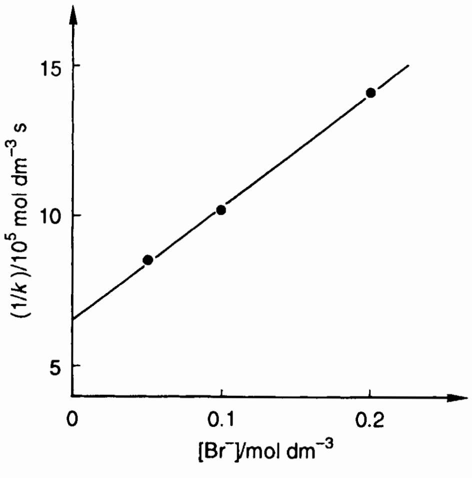

Fig. 2 Kinetic bromide ion effects on oct-1-ene bromination in microemulsion M1 at 25 °C. Application of eqn. (5) corresponding to the addition of free bromine only.

incorporated products so that bromide and, therefore, tribromide anion [eqn. (2)] are generated during the reaction. Since tribromide is a brominating agent, potentially competing

$$Br_2 + Br^- \rightleftharpoons Br_3^- \qquad (2)$$

with molecular bromine, we adopted the same method as that used with usual protic solvents which consists of adding an excess of bromide ion in order to maintain the $[Br_2]:[Br_3^-]$ ratio constant throughout the reaction.[16] Therefore, kinetic experiments were carried out in the M1 microemulsion made up with water containing 0.05, 0.1 and 0.2 mol dm^{-3} sodium bromide instead of pure water. Consequently, the phase diagram of Fig. 1 no longer holds. The experimental rate data for oct-1-ene bromination are shown in Table 3.

The oct-1-ene bromination rate in SDS micelles was too large to be measured accurately by the spectrokinetic method. It can only be estimated that the rate constant in this medium is in the 10^5 dm^3 mol^{-1} s^{-1} range. This constant has, therefore, been calculated from previous data on the bromination of stilbene in pure water[17] ($k = 5.4 \times 10^3$ dm^3 mol^{-1} s^{-1}), assuming that stilbene and oct-1-ene are equally sensitive[17] to medium effects. This calculation gives a reasonable k-value of about 2×10^5 dm^3 mol^{-1} s^{-1} for oct-1-ene bromination in SDS micelles.

The rate constant of oct-1-ene bromination in 2% aqueous n-butanol (v/v) was measured under pseudo-first-order conditions by the usual spectroscopic procedure.[15] The rate constant for free bromine addition, obtained by extrapolation of bromide-ion effects to $[Br^-] = 0$ according to eqn. (3), is $(2.0 \pm 0.1) \times 10^2$ dm^3 mol^{-1} s^{-1}.

Apparent Bromine–Tribromide Equilibrium Constant.—The constant, K_{app}, of equilibrium (2) is necessary to obtain the rate constant for free bromine addition from the experimental data of Table 3 by applying the Bartlett equation,[16,18] eqn. (3). This equation expresses the fact that free bromine and tribromide ion can add to the double bond *via* two different reactions with

$$k_{obs}(1 + K_{app}[Br^-]) = k_{Br_2} + K_{app}k_{Br_3^-}[Br^-] \qquad (3)$$

rate constants k_{Br_2} and $k_{Br_3^-}$. In anionic microemulsions, this equation simplifies to eqn. (4), assuming (*vide infra*) that

$$k_{obs}(1 + K_{app}[Br^-]) = k_{Br_2} \qquad (4)$$

tribromide does not significantly react with oct-1-ene in microemulsions. From eqn. (4), written in the form of eqn. (5), a linear

$$\frac{1}{k_{obs}} = \frac{1}{k_{Br_2}} + \frac{K_{app}}{k_{Br_2}}[Br^-] \qquad (5)$$

relationship between $1/k_{obs}$ and $[Br^-]$ is expected. As shown in Fig. 2, eqn. (5) describes the experimental data fairly well. From the intercept and slope of the plot of Fig. 2, values of k_{Br_2} and K_{app} are calculated.

$$k_{Br_2} = (1.5 \pm 0.07) \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$K_{app} = 6 \pm 2 \text{ dm}^3 \text{ mol}^{-1}$$

Since the K_{app}-value obtained from kinetic bromide ion effects is very imprecise, this value was also measured spectrophotometrically (λ = 270 nm) using eqn. (6), where ε_{Br_2}, $\varepsilon_{Br_3^-}$ and ε are the free bromine, tribromide and experi-

$$\frac{1}{\varepsilon_{Br_3^-} - \varepsilon} = \frac{K_{app}}{\varepsilon_{Br_3^-} - \varepsilon_{Br_2}}[Br^-] + \frac{1}{\varepsilon_{Br_3^-} - \varepsilon_{Br_2}} \qquad (6)$$

mental extinction coefficients, respectively. With $\varepsilon_{Br_3^-}$ (λ = 270 nm) = 4×10^4 dm^3 mol^{-1} cm^{-1}, previously measured in water,[19] a fairly linear relationship is observed when $1/(\varepsilon_{Br_3^-} - \varepsilon)$ is plotted against $[Br^-]$. From this plot, a K_{app}-value of 5 ± 1.5, in satisfactory agreement with that measured from kinetic data, is observed.

The insignificant contribution of the last term of eqn. (3), related to the tribromide ion addition, is confirmed by the fact that using this K_{app}-value, the term $k_{obs}(1 + K_{app}[Br^-])$ does not vary with the bromide concentration. The unlikelihood of there being a tribromide contribution in the M1 microemulsion is also confirmed by the following observation. In pure water, analogous kinetic bromide-ion effects on the reaction of related alkenes[20] are not correctly described by eqn. (5) but only by eqn. (3) in its complete form (the $1/k_{obs} - [Br^-]$ plot is markedly curved). It is also reasonable to exclude the significant participation of butyl hypobromite, a potential brominating agent which could arise from bromine oxidation of butanol [eqn. (7)]. On the one hand, it has been shown that methyl

$$Br_2 + ROH \rightleftharpoons ROBr + Br^- + H^+ \qquad (7)$$

hypobromite is not involved in bromination in methanol.[18] On the other hand, kinetic experiments were carried out in the presence of an excess of bromide ion and of 5×10^{-4} mol dm^{-3} perchloric acid, so that eqn. (7) should be strongly shifted towards free bromine.

Discussion

Reactant and Reaction Microenvironment.—Micelles or microemulsions are generally used as reaction media to make the reaction between hydrophilic and lipophilic reagents

Table 4 Rate constants for free bromine addition to oct-1-ene in homogeneous and microheterogeneous media at 25 °C

	k/dm^3 mol^{-1} s^{-1}
H_2O[a]	2.3×10^7
SDS micelles[b]	2×10^5
M65[c]	1.7×10^5
µE M1[b,d]	1.6×10^4
M80[c]	1.5×10^4
n-BuOH[b]	2×10^2
CTAB micelles[e]	6.9
Hexane[f]	$\approx 10^{-2}$

[a] Ref. 20. [b] This work. [c] M65 and M80: 65–35 and 80–20 (v/v) methanol–water mixtures; calculated from data in ref. 28. [d] µE, microemulsion. [e] Ref. 9(*c*). [f] In dm^6 mol^{-2} s^{-1}; extrapolated from data in ref. 23.

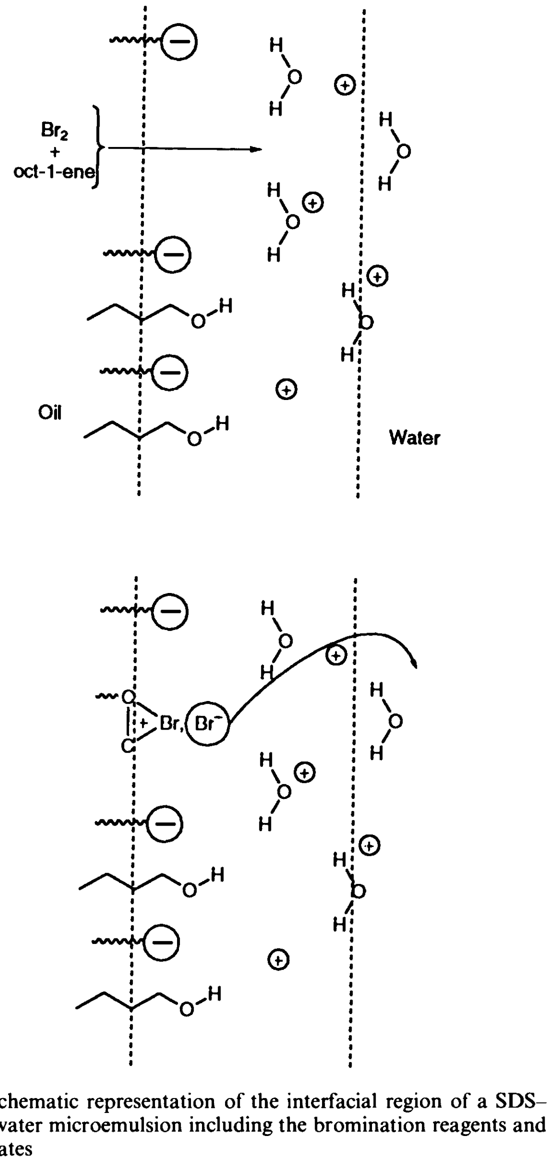

Fig. 3 Schematic representation of the interfacial region of a SDS–butanol–water microemulsion including the bromination reagents and intermediates

possible.[21] In these cases, it is obvious that the reaction occurs at the oil–water interface. For bromination, the situation is different since both reagents are lipophilic. Owing to its lipophilicity, oct-1-ene is located in the oil microphase. Bromine, the hexane–water transfer coefficient[22] of which is about 60, is mainly in the oil phase but also partly in water. Both reagents can, therefore, react in the oil phase. However, bromination is extremely slow in hydrocarbons because of the absence of any external stabilization of the bromonium–bromide ion pair; the rate constant in these media[23] can be estimated to be in the range 10^{-2} dm^6 mol^{-2} s^{-1} (Table 4). In contrast, in water[20] the reaction is very fast; at high dilution (10^{-6}–10^{-7} mol dm^{-3}) the measured rate constant is 2.3×10^7 dm^3 mol^{-1} s^{-1}. At the interface of anionic microemulsions where the bromonium ion experiences an ionic microenvironment which can stabilize it, bromination should occur much faster than in hydrocarbon. Since the reaction is first order in bromine, the reaction does not occur in the oil phase but in a microphase where water is included and assists the bromide-ion departure.[24] Moreover, as illustrated in Fig. 3, unfavourable interactions between the anionic head groups and bromide ions could assist the dissociation of the bromonium–bromide ion-pair. However, these expected effects can play a role only if the alkene and bromine meet at the interface. In view of previous results on alkene bromination[7,9] in micellar solutions, it is reasonable to assume that this latter condition is fulfilled.

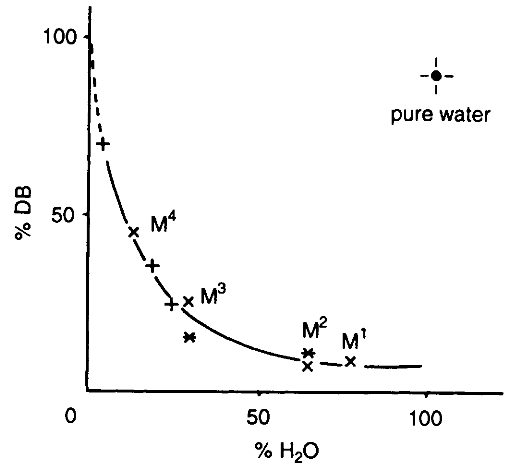

Fig. 4 Decrease in the dibromide (DB) yield with increasing water content (w/w) of the reaction medium. The compositions of microemulsions are given in Table 1. ●, pure water; +, AOT, M7–M9; ×, SDS–BuOH (1:1), M1–M4; *, SDS–BuOH (1:2), M5, M6.

Molecular free bromine and not tribromide is the brominating reagent in the water-rich microemulsion. That eqn. (5) describes the kinetic bromide-ion effect satisfactorily supports this conclusion. This result agrees with previous measurements of $^{81}Br^-$ relaxation times which show that bromide ions do not interact with SDS head groups in micellar solutions.[9b] Consequently, tribromide ions arising from the reaction of bromide with free bromine are probably located in the water rather than at the interface where alkene bromination occurs. In contrast, free bromine resides partly at the interface. From a rough two-phase model, eqn. (8), which assumes that free bromine partitions between the oily and aqueous phases, an apparent bromine–tribromide equilibrium constant of 10

$$\mathrm{Br}_{2,\mathrm{oil}} \overset{K_1}{\rightleftharpoons} \mathrm{Br}_{2,\mathrm{w}} \underset{+\mathrm{Br}^-}{\overset{K_\mathrm{w}}{\rightleftharpoons}} \mathrm{Br}_3{}^-{}_{,\mathrm{w}} \qquad (8)$$

can be calculated $\{K_{app} = K_w/(1 + K_1\,[\mathrm{oil}]/[H_2O])$ with $K_w = 16$, $K_1 = 60$ and $[\mathrm{oil}]/[H_2O] = 10^{-2}\}$. This is greater than the experimental value of 5. The failure of the two-phase model, which suggests that the amount of free bromine involved in eqn. (2) is smaller than expected, implies that the interface plays a significant role in the free bromine partition, *i.e.*, this species resides partly in this region.

Chemoselectivity and Bromonium–Bromide Ion-pair Dissociation.

—The data of Table 2 show that the chemoselectivity depends markedly on the water content of the microemulsions.

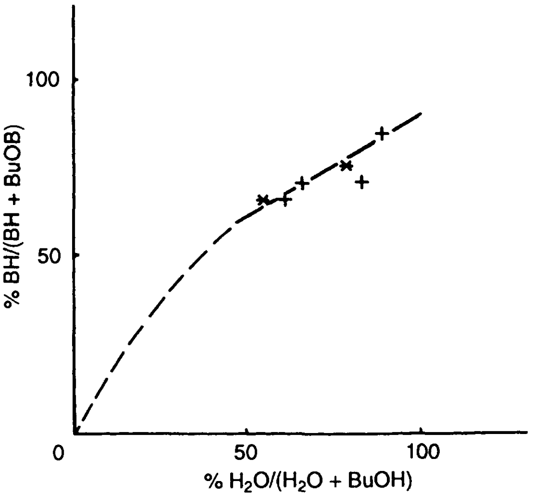

Fig. 5 Competition between water and *n*-butanol reaction with *n*-hexylbromonium ion in SDS microemulsions M1–M6: BH, bromohydrin; BuOB, bromobutyl ether

The more water-rich the medium, the less dibromide is obtained. As seen in Fig. 4, the dibromide yield decreases smoothly as the water content increases, but even at very high water content, about 10% of dibromide is still formed. These results are very different from those obtained in pure water or butanol in which dibromide is the major bromination adduct (>90% and 80%, respectively). In agreement with the above conclusion from kinetic data, the product data also indicate that as bromination occurs neither in water nor in the oil phase it must, therefore, occur at the oil–water interface.

In the absence of external bromide ions at the interface, the observed dibromide arises only from the internal rearrangement of the bromonium–bromide ion pair whereas the solvent-incorporated adducts result from the nucleophilic trapping of the dissociated ion-pair.[3] Therefore, the increase in the bromohydrin and bromobutyl ether yield as the water content increases must be associated with an increase in the ion-pair dissociation and in the bromonium ion stability. This can arise from an extra stabilization of the cationic intermediate by the anionic and aqueous microenvironment in which it is formed. The fact that some residual dibromide exists at high water content probably shows that the external stabilization of the bromonium ion competes with that provided by the bromide ion. In contrast, oct-1-ene bromination in CTAB micelles, the water content of which is very close to 100%, leads to 88% dibromide and 12% bromohydrins only.[9c] The large dibromide yield, which is very high compared with that in water-rich microemulsions, is not surprising since the brominating agent in the cationic micelles is the tribromide ion and since the so-called tribromide addition is mainly bromide-assisted free-bromine reaction[11] which, obviously, leads to dibromide. It is also noteworthy that the nucleophilic selectivity of mercurinium ions with respect to water and alcohols is markedly different when alkene mercuration is carried out in SDS-micellar solutions.[8b]

Since the relationship shown in Fig. 4 corresponds to data obtained in microemulsions of very different composition (AOT or SDS) or structure (micelle-like, lamellar, or inverted-micelle-like), it is probable that the chemoselectivity results are related to the specific properties of the interface, the nature of which does not vary much on going from M1 to M9 (identical polar head groups and counter-ions), rather than to the structural features of the molecular organization of the microemulsions. This result is in contrast with recent observations[6] which show that a change in the shape of micellar aggregates induces a marked change in the rate of *trans*-stilbene bromination when this reaction is carried out in concentrated aqueous SDS solutions. The major difference between these previous experiments and those described here is that microemulsions involve a persistent oily microphase whereas in the absence of added hydrocarbon this phase consists only of the surfactant tails. The lifetimes of the aggregates and the residence time of the lipophilic reagents are, therefore, totally different in the two organized media.

The *chemoselectivity in pure water* where the bromohydrins are minor products (<10%) is surprising in view of previous data on the bromination products of short-chain monosubstituted alkenes in methanol in which bromomethoxy adducts are obtained almost exclusively.[2] This large difference cannot arise from differences in the nucleophilicities of water and methanol whose *N*-values on the Bentley–Schleyer scale[25] are similar. The absence of solvent-incorporated products in oct-1-ene bromination suggests that water is excluded in the micro-environment of the reaction. Owing to their high lipophilicities, it is possible that oct-1-ene microaggregates in which bromine can be incorporated, are formed. Therefore, the relevant bromination mechanism in the concentration range (10^{-4} mol dm^{-3}) where the products have been analysed would not be solvent- but bromine-assisted ionization of the charge-transfer bromine–alkene complex leading to a bromonium–tribromide ion-pair,[24] and not to a bromonium–bromide ion pair, which collapses by internal rearrangement into dibromide and bromine.

Chemoselectivity and Nucleophilicites of Water and Butanol.— In SDS microemulsions, the competition between the two external nucleophiles, water and butanol, in the attack of the bromonium ion is illustrated in Fig. 5 where the bromohydrin: bromobutyl ether ratio has been plotted against the total water: protic solvent ratio of the reaction media. Whatever the water content, the bromohydrin yield (Table 2) is systematically greater than that of butyl ether, by a factor of 2 at least. This can arise either because the local water concentration is higher than that of butanol or because the local water molecules are more nucleophilic towards the bromonium ion than are butanol molecules. It is difficult to estimate the water concentration at the oil–water interface, all the more because several kinds of water molecules, different in their bonding (interstitial or ion-solvating water), are present.[26] In contrast, it is generally believed that, in a microemulsion where SDS–BuOH is 1:1, most of the butanol is located in this region. This common assumption[27] is supported by the fact that reactions carried out in media where SDS:BuOH is 1:2 lead to bromohydrin:butyl ether ratios which do not differ markedly from those obtained in microemulsions with 1:1 SDS:BuOH of similar water content. Consequently, in the water-poor medium, it is highly probable that the interfacial water content is smaller than that of butanol. On the Bentley–Schleyer nucleophilicity scale,[25] butanol is slightly more nucleophilic than bulk water. If this scale applies in bromination and since the butanol concentration at M4 is probably greater than that of water, butanol attack of the bromonium ion should be favoured over that of water. It is, therefore, surprising that even for M4, the water-poor microemulsion, the bromohydrin yield is much greater than that of butyl ether. This result leads to the conclusion that interfacial water molecules behave differently from those in bulk water and, in particular that their nucleophilicity is significantly increased.

The *regioselectivity* of bromohydrin or butyl ether formation (70:30 M:AM) and its invariance with the microemulsion composition is another significant result. In this respect, it is interesting to note that the same regioselectivity has been found for oct-1-ene bromination in methanol.[2] Regioselectivity is related to the difference of the charges on the two carbon atoms of the bromonium ion. Therefore, the absence of medium-dependence of this selectivity supports previous interpretations of various kinetic data which established that the charge distribution in ionic bromination intermediates depends on only the substituents and not on the solvent.[1b]

In Table 4 are collected kinetic data for oct-1-ene bromination in the various components of the microemulsions. Bromination in the M1 microemulsion is much slower than in bulk water and significantly faster than in pure butanol and in hexane. The overall rate in M1 is in the same range as that observed in the 20:80 (v/v) water–methanol mixture. However, this comparison is not meaningful since the exact local reagent concentrations and, therefore, rate constants at the microemulsion interface are unknown. Interfacial rates are generally obtained from pseudo-phase ion-exchange models[29] from which the overall rate variation is expressed as a function of the microemulsion composition. These kinetic models cannot be applied to oct-1-ene bromination in SDS-containing media since clean second-order kinetics are not observed in non-water rich mixtures.

The data of Table 4 show that the reactivity of oct-1-ene is markedly medium-dependent. The rate decrease observed on going from water to organized media is expected since it is generally agreed that interfacial regions are less polar than water.[21] The fact that the rate in SDS micelles is significantly greater than in the analogous microemulsion is also in agreement with previous findings and results probably from interfacial concentrations being smaller in oil-containing media.[30] The rate difference between anionic and cationic micelles is particularly large ($k_-/k_+ = 3 \times 10^5$) as compared with those currently observed[21] ($k_-/k_+ =$ *ca.* 10) and cannot arise only from changes in ionic interactions. This result can be rationalized, at least in part, in terms of differences between the rates of free bromine and tribromide additions, the latter being, in pure water, about 20 times lower than that of free bromine for monosubstituted linear alkenes.[20]

In conclusion, both kinetic and product data suggest that in SDS and AOT microemulsions, the reaction between free bromine and oct-1-ene occurs at the oil–water interface and that tribromide ion, located mainly in the aqueous microphase, does not react with the alkene. The chemoselectivity of product formation depends greatly on the water content of the microemulsion. As this content increases, the yield in dibromide decreases to a limiting value of about 10%. The competition between the two neutral nucleophiles present at the interface, *n*-butanol and water molecules solvating the anionic head groups, always favours water, even at high butanol concentration.

These preliminary results focus attention on two properties of the ionic microemulsion interfaces, high dissociating power and the special behaviour of water molecules. These properties, if they are of general validity and if they can be quantitatively evaluated, could be useful in the control of the selectivity of various reactions going through ionic intermediates. Although there has been much work on the structure and dynamics of these ternary and quaternary microheterogeneous media,[31] data relevant to reactivity control at their interfaces are still rare. Bromination can be used as a model, complementary to others currently studied,[32] to obtain more information on the binding of reactive species at an anionic interface. More work is in progress to understand quantitatively how and why the overall water content controls the selectivity of cation–nucleophile reactions.

Experimental

Materials.—Sodium dodecylsulfate (SDS, 99%; Janssen) was recrystallized from methanol before use. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT, 99%; Sigma) was dried for two days under vacuum at room temperature and used without further purification. Oct-1-ene, whose purity was checked by GC, was supplied by Aldrich. Bromine was analytical grade from Carlo Erba. *n*-Hexane, methylene chloride and carbon tetrachloride were analytical grade from Prolabo; *n*-butanol and isooctane were HPLC grade from Aldrich. All these solvents were used as supplied. Water was doubly distilled. Sodium bromide for kinetic experiments was *suprapur* from Merck. The other salts used in the work-up of the reaction mixtures were analytical grade from Prolabo.

Product Analysis.—SDS microemulsions were prepared by adding the calculated volume of water to SDS (5 g) and *n*-butanol (5 or 10 g) dissolved in the required volume of a hexane–oct-1-ene (20:1 w/w) mixture so that the final composition was that shown in Table 1 (M1–M6). Analogously, the volume of water required to obtain M7–M9 microemulsions was added to a given mass of AOT (*ca.* 5 g) dissolved in a calculated volume of the isooctane–oct-1-ene (20:1, w/w) mixture. This order of mixing the components was adopted to obtain well-defined compositions; the stability of the resulting homogeneous media does not depend on this order.

An aliquot (20 cm^3) of a given microemulsion was transferred to a 50 cm^3 cell thermostatted at 25 °C and stirred. A precise volume (*ca.* 1 cm^3) of a concentrated bromine solution (9 mol dm^{-3}) in carbon tetrachloride, calculated to give a 5% excess of bromine with respect to oct-1-ene, was then added slowly and dropwise so that the pale yellow colour disappeared between each drop. At the end of bromine addition, the reaction mixture was still homogeneous and stirring was maintained for 15 min. Methylene chloride (10 cm^3), sodium chloride (5 g) and barium chloride (approximately fourfold excess with respect to SDS or AOT) were then added. The slurry was vigorously stirred overnight. The precipitate was filtered off and washed three times with methylene chloride (10 cm^3). After separation of the organic and aqueous phases, the organic phase was dried with magnesium sulfate and concentrated under vacuum. The residual mixture (*ca.* 5 cm^3) was centrifuged to eliminate remaining colloidal surfactant particles and analysed by capillary GC (CPSil 5, 25 m, 12 μm). The several bromination products were identified by comparison of retention times with those of authentic samples prepared independently. The detector response was calibrated using tetradecane as an internal reference.

In some experiments, tetradecane was added to the microemulsion at the same concentration as oct-1-ene before bromine addition, in order to measure the yield of bromoadducts. This yield was always higher than 98%.

Kinetics.—The kinetic procedure has already been described.[15] The water-rich SDS microemulsion M1 was prepared in the absence of oct-1-ene and with water containing 0.05, 0.1 or 0.2 mol dm^{-3} NaBr and 5×10^{-4} mol dm^{-3} $HClO_4$. An aliquot (2 cm^3) of this microemulsion was transferred to a UV spectrophotometer cell, stirred and thermostatted at 25 °C. A few drops of a concentrated solution of bromine in methanol were added, so that the absorbance at 270 nm was about 0.2–1.2 ($5 \times 10^{-5} < [Br_2]/\text{mol dm}^{-3} < 5 \times 10^{-4}$). A weighed amount of a concentrated solution of oct-1-ene in methanol was then added with a microsyringe and the disappearance of bromine was monitored ($[\text{1-Oct}] = [Br_2]/2$). The kinetic signal was analysed as usual in terms of a second-order rate equation. The rate constants given in Table 3 are average values of 6–10 runs with a reproducibility of about 5%.

ε-Values of bromine at 270 nm were measured in independent experiments by titration with the highly reactive tetramethylethylene at 25 °C.

The rate constants for oct-1-ene bromination in 2% aqueous butanol (v/v) at 25 °C were measured by the standard procedure, using LiBr instead of NaBr. The experimental rate constants were 17.1, 18.4 and 24.6 dm^3 mol^{-1} s^{-1} with 0.2, 0.1 and 0.05 mol dm^{-3} LiBr, respectively. The reproductibility of 4–6 runs was better than 2%.

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