Pseudophase Model for Reactivity in Reverse Micelles. The Case of the Water-Promoted Reaction between Two Lipophilic Reagents, Bromine and 1-Octene, in AOT Microemulsions

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Received: March 13, 1996[⊗]

Kinetic investigation of 1-octene bromination in AOT–isooctane–water microemulsions $(13 \le w = [H2O]/$ $[AOT] \le 24$ and $6 \le z = [IO]/[AOT] \le 57$) shows that the reaction is first-order in alkene and first-order in bromine, as usually found in protic media. Although both reagents are mainly located in the isooctane phase (K^{tr}, transfer coefficients from isooctane to water, are 1.5×10^{-5} and 8.8×10^{-3} for alkene and bromine, respectively), bromination occurs in an aqueous microenvironment, as illustrated by the high sensitivity of the bromination rate to the water content of the microemulsion. A kinetic pseudophase model describes the rate constant dependence on microemulsion composition satisfactorily by assuming competition between reactions at the interface and in the aqueous phase. Reasonable values for the coefficients of reagent partition between the interface and the two microphases and for the local bromination rate constants are obtained from the kinetic equations derived from the model. In particular, spectroscopically observed AOT-bromine complexation is in agreement with the high bromine concentration at the interface (K_2 , bromine partition coefficient from isooctane to interface, = 6.8). The water-phase bromination rate constant, $k_{\rm w} = 1 \times 10^8$ M^{-1} s⁻¹, is in the same range as that measured in bulk water. The lower limit for the interfacial rate constant, k_{i} , is 10³ M⁻¹ s⁻¹, a value close to that observed in poorly aqueous methanol (MeOH/H₂O = 95/5 v/v). These data are compared with those recently obtained in the same microemulsions for solvolysis, a reaction which, like bromination, is water-promoted but supposed to take place at the interface only. The results are discussed in terms of the chemical properties of the water molecules encased in the microemulsion droplets.

Reverse micelles and w/o microemulsions¹ are more and more frequently used as microreactors² for performing reactions in constrained environments, taking advantage of reagent compartmentalization and of the particular properties of the encased water.3-7 Nevertheless, the extension of these water-poor microorganized media to a wide variety of reactions is still limited by the paucity of relevant reactivity data. For example, numerous organic reactions, the rate constants of which are markedly higher in water than in less polar solvents,^{8,9} would benefit from the hydrophilicity-hydrophobicity balance in microemulsions. But the reactivity changes, resulting from the difference³⁻⁷ in the structure of encased water compared to that in network-organized bulk water, are far from being well-known and still less well-controlled. In this respect, extensive kinetic studies of reaction in reverse micelles and w/o microemulsions are indispensable. However, these investigations can be interpreted in terms of reactivity, only if local reagent concentrations and intrinsic rate constants in the various microphases of these organized media can be obtained from the overall, apparent rate data. Presently, the kinetic models¹⁰ that give access to these intrinsic reactivity constants are still scarce and much less welldocumented than those for reactions in direct micelles.¹¹ A pseudophase model, analogous to that widely used in micellar catalysis and which assumes competition between possible reactions in three microphases (oil, water, and the interface), has recently been proposed.¹² However, its scope is presently limited to reactions occurring a priori in one microphase only.^{12,13} This is, in particular, the situation when the two reagents are hydrophilic so that they can react together only in the water phase¹⁴ or when a hydrophilic substrate reacts with a

hydrophobic reagent so that the reaction must necessarily occur at the interphase.^{12,13} The local reagent concentrations and rate constants are, therefore, readily obtained from a single-phase model since the complete kinetic equation is greatly simplified. More sophisticated reactions need to be investigated to validate this complex kinetic model.

In this paper, we report results on the electrophilic bromination¹⁵ of 1-octene in AOT-isooctane-water microemul $sions^{16}$ (AOT = sodium bis(2-ethylhexyl)sulfosuccinate), which involves reactions in at least two microphases. The two reagents, bromine and the alkene, are highly hydrophobic and are, therefore, mainly located in the oily microphase.¹⁷ However, this reaction needs water to occur,¹⁸ Scheme 1. The ratelimiting ionization of the bromine-alkene charge transfer complex must be electrophilically assisted by water molecules in order to promote the departure of the leaving bromide. The second, product-forming step is the nucleophilic trapping of the bromonium ion either by its counter-bromide ion or by any external nucleophile such as water. Consequently, it is expected that bromination, if it occurs in AOT microemulsions, takes place in an aqueous environment, i.e. at the interface and/or in the water microphase. We show that the reaction does occur in these w/o microemulsions, although the reagent concentrations are very small in the aqueous microphases, and that the pseudophase model describes the kinetic data fairly well when two different reaction phases are taken into account.

Results

Table 1 summarizes the experimental second-order rate constants, $k_{2,app}$, of 1-octene bromination at 25 °C in AOTisooctane-water microemulsions of various compositions. These data were obtained from the 1-octene concentration dependence of the pseudo-first-order rate constants measured by the stopped-flow technique, which ensured the rapid mixing

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[®] Abstract published in Advance ACS Abstracts, June 15, 1996.



2) Product Formation : nucleophilic water

 TABLE 1: Experimental^a and Calculated^b Second-Order

 Rate Constants for 1-Octene Bromination in AOT–

 Isooctane–Water^c Microemulsions of Various Compositions^d

no.	w^d	z^d	$[AOT]^e$	$[H_2O]^e$	$k_{2,\mathrm{app}}^{\mathrm{exp}}$	$k_{2,\mathrm{app}}^{\mathrm{calc}}$
1	13.3	57.8	0.099	1.32	38.8	40.01
2	13.3	27.7	0.19	2.53	80.6	81.45
3	13	18	0.28	3.64	112	116.4
4	13.3	12.1	0.38	5.05	166	170.2
5	13.3	6.68	0.588	7.82	282	279.3
6	15.9	27.7	0.19	3.02	94.9	92.82
7	15.7	18	0.27	4.24	140	138.5
8	16.2	12.2	0.37	5.99	207	199.3
9	15.9	12.1	0.372	5.91	216	198.1
10	15.9	6.76	0.56	8.90	328	328.3
11	19.9	27.7	0.19	3.78	109	110.3
12	19.7	18	0.27	5.32	174	164.9
13	19.9	12.1	0.36	7.16	256	243.3
14	20	6.71	0.54	10.80	388	410.7
15	24	12	0.35	8.40	276	294.9
16	24	6.67	0.52	12.48	502	498.3

^{*a*} $k_{2,app}$ in M⁻¹ s⁻¹ (molar units) measured with a reproducibility on 4–6 runs better than ±2%. ^{*b*} In M⁻¹ s⁻¹, calculated by eq 14. ^{*c*} Water contained 0.1 M NaBr and 10⁻⁴ M HClO₄. ^{*d*} w = [H₂O]/[AOT] and z = [IO]/[AOT]. ^{*e*} In M in the total solution volume.

of the two microemulsions, each containing one of the reagents. Bromine disappearance was monitored spectroscopically at 290 nm (ϵ in the 10⁴ range). Alkene concentrations were in the range of 5 × 10⁻³ to 5 × 10⁻² M in the total volume of the microemulsion, while bromine was about 10⁻⁴ M. The kinetic signals were always rigorously monoexponential; that is, the reaction was clearly first-order in bromine. In particular, there was no induction period on the reaction time scale (0.1–2 s), which would suggest a slow mixing of the initial microemulsions containing either the bromine or the alkene. As expected, reagent exchange between the microdroplets ($k_e = 10^9 \text{ M}^{-1} \text{ s}^{-1}$) was fast compared to the reaction time.¹⁹

The water phase of the microemulsions contained 0.1 M sodium bromide so that the reaction could be monitored at 290 nm, where the tribromide ion, obtained from bromine by the very fast equilibrium (1), absorbs strongly.²⁰ With this proce-

$$Br_2 + Br^- \rightleftharpoons Br_3^-$$
 (1)

dure, high bromination rate constants can be measured using very small bromine concentrations since ϵ_{Br_3} at 290 nm is ca. 10^4 , whereas that of molecular bromine ($\lambda_{max} = 415$ nm) is 10^2 times smaller. It was confirmed that, when bromination was not very fast (entry 1 of Table 1), the rate constants obtained by monitoring bromine consumption at 290 and 415 nm were identical within experimental error. Moreover, perchloric acid (10^{-4} M) was added to the water content of the microemulsion in order to minimize the formation of the nonbrominating hypobromic acid²¹ via the fast equilibrium 2.

$$Br_2 + H_2 O \rightleftharpoons BrOH + H^+ + Br^-$$
(2)

The second-order rate constants were obtained from the pseudo-first-order rate constants measured at several alkene concentrations, with a reproducibility better than $\pm 2\%$. A typical second-order plot is shown in Figure 1. In all the microemulsions, these plots were always rigorously linear



Figure 1. Second-order plots for 1-octene bromination in AOTisooctane-water microemulsions: (\bigcirc) [AOT] = 0.38 M, [IO] = 4.66 M, and [H₂O] = 4.22 M; (\triangle) [AOT] = 0.37 M, [IO] = 4.50 M, and [H₂O] = 5.98 M. For nonzero intercept, see text.

(correlation coefficient, r > 0.99). Therefore, 1-octene bromination is first-order in alkene. The slopes of these plots gave the $k_{2,app}$ values collected in Table 1. It must be mentioned that their intercepts are not zero, as would be expected for usual bimolecular reactions. This comes from the fact that the microemulsions contained bromine-consuming impurities. Therefore, before the addition of the reagents, they were presaturated with bromine. Consequently, a small portion of 1-octene, used for the preparation of the alkene-containing microemulsion at several concentrations, was consumed by the bromine excess before the kinetic run itself.

Bromine-containing microemulsions were not stable over long periods (1-2 h) due to a slow reaction of bromine with the solvent. This reaction led to complex kinetic curves, typical of radical chain reactions²² (incubation period, changes of kinetic order, autocatalytic accelerations, etc.). However, this uncontrolled and slow bromine consumption did not interfere with the much faster 1-octene bromination and did not perturb the monoexponential signals described above. In agreement with this finding, the addition of isoamyl nitrile, a radical scavenger,²³ to the microemulsion did not modify the values of the experimental rate constants.

The microemulsion composition, defined as usual by $w = [H_2O]/[AOT]$ and z = [IO]/[AOT] (IO, isooctane), was varied from w = 13 to 24, while z was between 6 and 57. Since the aim of this work was to confirm experimentally the ability of a pseudophase model to describe quantitatively the reactivity in these media, w = 13 was chosen as the lower limit of the investigated microemulsion range. It is generally agreed that below this value there is no bulk but only bound water.^{7,24} Above w = 24, the corresponding AOT–isooctane–water mixtures were not homogeneous but turbid, due to the reduction of the L2 area in the phase diagram²⁵ of this system by addition of 0.1 M sodium bromide to the water component.

Discussion

1-Octene bromination does not occur in the isooctane microphase since the reaction is first-order in bromine, as observed in any protic solvent.¹⁵ In contrast, second-order in bromine kinetics was observed in nonprotic solvents such as halogenated hydrocarbons.²⁶ This is currently attributed to differences in the reaction mechanisms. In protic solvents, the formation of the bromonium–bromide ion-pair is solvent-



Figure 2. Dependence of the experimental rate constants on water concentration: (+) w = 13.3; (O) w = 15.9; (\times) w = 19.9; (\triangle) w = 24.

assisted, whereas in nonprotic solvents, a second bromine molecule assists bromide ion departure by forming a tribromide ion, markedly more stable than bromide in these media. The absence of reaction in the isooctane phase was expected a priori since the bromination rate constant in apolar hydrocarbons can be estimated to be as small as $10^{-2} \text{ M}^{-2} \text{ s}^{-2}$, from a previously published Kirkwood-Westheimer relationship for solvent effects on bromination rates.²⁶ In fact, in hydrocarbons homolytic bromination by bromine radicals²² is expected to be faster than polar reactions. Nevertheless, the monoexponential kinetic signals observed in AOT microemulsions do not correspond to a radical reaction. The bromination kinetics are, therefore, in agreement with a reaction occurring in an aqueous environment, although the reagent concentrations in the water phase are very small. The coefficients for 1-octene²⁷ and bromine transfers²⁸ from isooctane to water are 1.5×10^{-5} and 8.8×10^{-3} , respectively.

The Role of the Water Content. 1-Octene bromination is strongly inhibited in AOT microemulsions as compared with the same reaction in pure water, where the rate constant²⁹ is $2.3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (or $1.1 \times 10^9 \text{ s}^{-1}$ in the same units as those in microemulsions), or in water containing 0.1 M sodium bromide, $k = 1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ (or $6 \times 10^8 \text{ s}^{-1}$). As shown in Figure 2, there is a sharp increase in the apparent rate constant as the water content increases. Despite the approximate linearity of this plot, since extrapolation of the linear regression between $k_{2,\text{app}}$ and water concentration would lead to a k_w value in pure water ([H₂O] = 55 M) of $2 \times 10^3 \text{ s}^{-1}$, i.e. much smaller than that experimentally observed, the relationship cannot be linear.

Analogous inhibition has already been found in micellar solutions. In micelles of SDS,³⁰ a surfactant with the same polar head group as AOT, the rate constant for 1-octene bromination is $2 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$. The inhibition $(k_{\rm m}/k_{\rm w} = 10^{-2})$ in this medium, where $[\text{H}_2\text{O}] = 55 \text{ M}$, is much smaller than in microemulsions where at the highest water content, $[\text{H}_2\text{O}] = 12.5 \text{ M}$, the inhibition is as large as 10^{-5} . This comparison exhibits clearly the key role of water. A different situation was found in the bromination of unsaturated fatty esters,³¹ for which the inhibition is extremely large, 10^{-8} . In agreement with McClelland's conclusion, this enormous deceleration suggests strongly that bromination of these substrates occurs in a very poorly hydrated region of the micelle. In CTAB solutions³² ($k = 6.9 \text{ M}^{-1} \text{ s}^{-1}$) the inhibition is also very large. However, it





results not only from differences in the hydration of the reaction environment but also from different brominating agents. In CTAB micelles, the brominating agent is not molecular bromine but the poorly electrophilic tribromide ion, due to strong interactions³³ between bromide ions and ammonium head groups at the interface which shift eq 1. In AOT microemulsions, there is evidence that molecular bromine is the main reagent. In agreement with the negligible interactions³³ between bromide and a sulfate head group, a constant for equilibrium 1 of 0.2– 0.4 in the range of investigated *w* values, as compared to 16 in pure water, has been measured spectroscopically.³⁴ It is, therefore, reasonable to conclude that the reactivity data of Table 1 correspond mainly to the reaction of molecular bromine.

The Pseudophase Model for Reaction Kinetics in Microemulsions. The experimental rate coefficients shown in Table 1 are not usual rate constants related to a given elementary reaction and are, therefore, meaningless as regards the reactivitydetermining factors. In agreement with the pseudophase model widely applied to reactions in direct micelles,¹¹ local reagent concentrations¹⁷ and local rate constants are the only parameters relevant to the understanding of reactivity. In microemulsions, a kinetic model implying competition between reactions in three phases, oil, water, and interface, can be constructed^{10,12} with the same assumptions as those used for reactions in micellar media. In particular, it is assumed that the reaction time scale is large with respect to that of the dynamics of the medium,^{16,17,19} so that three different phases can be considered. This hypothesis is reasonable for bromination since the absence of any induction period in the first-order kinetic signals clearly excludes any influence of percolation between the aqueous microdroplets initially containing one of the two reagents. Therefore, Scheme 2, where the subscripts 1, 2, o, i, and w refer to alkene, bomine, oil, interface, and water, respectively, can be assumed. K_i and K_{ii} , with i = 1 or 2, are the transfer coefficients of the reagents from isooctane to interface and from water to interface, respectively, expressed in terms of molar ratios in each phase (eqs 3-6) and k_i , the local rate constants in the o, i, and w phases.

$$K_1 = \frac{[\text{AI}]_i [\text{IO}]}{[\text{AOT}][\text{AI}]_o} \tag{3}$$

$$K_2 = \frac{[\text{Br}_2]_i[\text{IO}]}{[\text{Br}_2]_o[\text{AOT}]} \tag{4}$$

$$K_{11} = \frac{[\mathrm{Al}]_{\mathrm{i}}[\mathrm{H}_2\mathrm{O}]}{[\mathrm{AOT}][\mathrm{Al}]_{\mathrm{w}}}$$
(5)

$$K_{22} = \frac{[Br_2]_i[H_2O]}{[AOT][Br_2]_w}$$
(6)

From Scheme 2, the experimental rate, v_{app} , is the sum of

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the local rates in each phase. Since for bromination, there is no reaction in isooctane, Scheme 2 is expressed by eq 7, where the subscript T refers to the total reagent concentration, as shown in eqs 8 and 9.

$$v_{\rm app} = k_{2,\rm app} [Br_2]_{\rm T} [Al]_{\rm T} = \frac{k_{\rm i}}{[AOT]} [Br_2]_{\rm i} [Al]_{\rm i} + \frac{k_{\rm w}}{[H_2O]} [Br_2]_{\rm w} [Al]_{\rm w}$$
(7)

$$[Br_2]_T = [Br_2]_0 + [Br_2]_i + [Br_2]_w$$
(8)

$$[Al]_{T} = [Al]_{o} + [Al]_{i} + [Al]_{w}$$
 (9)

If the microemulsion composition is defined by $w = [H_2O]/[AOT]$ and z = [IO]/[AOT], the local reagent concentrations expressed in terms of total concentrations are given by eqs 10 and 11.

$$[AI]_{\rm T} = [AI]_{\rm i} \left(1 + \frac{w}{K_{11}} + \frac{z}{K_1} \right) \tag{10}$$

$$[Br_2]_{\rm T} = [Br_2]_{\rm i} \left(1 + \frac{w}{K_{22}} + \frac{z}{K_2} \right) \tag{11}$$

With these definitions, the $k_{2,app}$ dependence on microemulsion composition is given by eq 12, obtained by combining eqs 7–11.

$$k_{2,\text{app}} = \frac{k_{i} + (1/K_{11}K_{22})k_{w}w}{[\text{AOT}]\left(1 + \frac{w}{K_{11}} + \frac{z}{K_{1}}\right)\left(1 + \frac{w}{K_{22}} + \frac{z}{K_{2}}\right)} \quad (12)$$

In eq 12, the w/K_{ii} terms are negligible with respect to z/K_i since the K_{ii} constants are necessarily very large because of the small reagent concentrations in the water phase. Therefore, eq 12 simplifies into eq 13, where K_1/K_{11} and K_2/K_{22} are the experimentally obtained transfer coefficients^{27,28} of alkene and bromine, i.e., K_1^{tr} and K_2^{tr} , from isooctane to water.

$$k_{2,\text{app}} = \frac{K_1 K_2 k_i + K_1^{\text{tr}} K_2^{\text{tr}} k_w w}{[\text{AOT}](K_1 + z)(K_2 + z)}$$
(13)

Another simplification that makes the statistical data analysis easier and that is justified by the following discussion can be made assuming that in the denominator of eq 13 the product K_1K_2 is negligible as compared to the terms in z^2 and z. Finally, eq 14 will be used to analyze the bromination rates.

$$k_{2,\text{app}}[\text{AOT}] = \frac{K_1 K_2 k_i + K_1^{\text{tr}} K_2^{\text{tr}} k_w w}{z^2 + (K_2 + K_1) z}$$
(14)

Interfacial Bromination Only? Equation 14 involves two terms related to the reaction at the interface and in the water phase, respectively, reagent partition between isooctane and the interface being taken into account in the denominator. It can be assumed, firstly, that the reaction takes place essentially at the interface. A priori, this assumption seems reasonable since the reagent concentrations in water are almost negligible because of the very small values of their transfer coefficients. A similar hypothesis has recently been postulated for the hydrolysis of diphenylmethyl chloride in the same microemulsions.¹³ However in the case of bromination, this assumption does not hold. If the reaction in the water phase is negligible, eq 14 reduces to eq 15. Firstly, it is obvious from Figure 2 that $k_{2,app}$ depends

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$$k_{2,\text{app}}[\text{AOT}] = k_{i} \frac{K_{1}K_{2}}{z^{2} + (K_{2} + K_{1})z}$$
 (15)

on the water concentration or on w, since w is related to it. This dependence can be expressed by eq 15 if k_i is w-dependent. Secondly, the $k_{2,app}$ dependence on z is expressed by the ratio in the right-hand-side term of eq 15 and does not depend on w. Therefore, linear relationships should be observed between $k_{2,app}$ -[AOT] values at various w values, the slope of which would be the ratios of k_i values at these w.

$$(k_{2,app}[AOT])_{w=a} = \frac{(k_i)w_a}{(k_i)w_b}(k_{2,app}[AOT])_{w=b}$$
 (16)

Figure 3 shows clearly that relationships 16 are not linear and, therefore, that eq 15 does not apply. In conclusion, bromination must also occur in the water phase.

Partition Coefficients and Local Rate Constants. Since bromination does not occur exclusively at the interface, the kinetics data of Table 1 were analyzed in terms of eq 14, which assumes competition between reactions at the interface and in water. A nonlinear least squares regression procedure gives the results shown in Table 2. The calculated rate constants agreed well with the experimental values of $k_{2,app}$ (Table 1 and Figure 4), and the assumption that 1-octene is brominated in two microemulsion phases appears to be justified. In particular, it is noticeable that the two terms of eq 14 ($k_i K_1 K_2$ and $k_{\rm w} K_1^{\rm tr} K_2^{\rm tr}$) are of similar magnitude. The first striking result of the calculation is that the coefficient of bromine partition, K_2 , between isooctane and the interface is large and very close to 6.8 since K_1 for 1-octene is necessarily much smaller than K_2 (vide supra). The bromine concentration at the interface is, therefore, quite significant. This result is not unexpected. Bromine is a highly polarizable species that would be stabilized in the polar interfacial microenvironment better than in the nonpolar isooctane phase. Accordingly, complexation between bromine and AOT, analogous to that observed for iodine,³⁵ is suggested by preliminary spectroscopic studies.³⁴ Similar complexation between AOT and 1-octene is less probable. Even if the 1-octene preference for the interface were as large as that of bromine, the K_1 value for the alkene could not be greater than 1×10^{-2} , i.e. negligible compared to K_2 for bromine. (This estimation assumes proportionality between the transfer coefficients of the two reagents and the coefficients of their partition between isooctane and the interface.) From these data, it is possible to calculate the bromine partition coefficients (K_2 and K_{22} of Scheme 1) and to estimate those of 1-octene. These results are shown in Table 3.

The lower limit for the interfacial rate constant, k_i , can be estimated from the calculated $k_i K_1 K_2$ term of eq 14. Term k_i is, at least, in the range of 6×10^4 s⁻¹ (or 1×10^3 M⁻¹ s⁻¹). This is a small value compared to that of bromination of the same alkene in bulk water²⁹ ($k = 6 \times 10^8 \text{ s}^{-1}$) but much larger than that found for diphenylmethyl chloride solvolysis¹³ in the same microemulsions, which leveled off at $9 \times 10^{-3} \text{ s}^{-1}$ for high water contents ($w \ge 30$). Nevertheless, this last result is not surprising since it is well-known that alkene bromination is much faster than the solvolytic processes. The interfacial bromination rate constant in the 10³ M⁻¹ s⁻¹ range corresponds³⁶ to that in poorly hydrated bulk methanol (MeOH/H₂O, 95/5, v/v). This is in agreement with an interface polarity significantly smaller than that of bulk water³⁷ but large enough to promote the fast ionization of the bromine-ofefin charge transfer complex.

Finally, k_w , the rate constant in the aqueous core of the microdroplets, is obtained from the coefficient of the *w* term in



Figure 3. Comparison of rate data at various constant w values, eq 16. The curvature in the plots shows that bromination does not occur exclusively at the interface; see text.

TABLE 2: Parameters of the Nonlinear Least Squares Fitting of Eq 14 to the Experimental Data ($\chi^2 = 0.002$)



Figure 4. Agreement between experimental and calculated kinetic data for 1-octene bromination. The straight line is calculated from the pseudophase model, eq 14.

TABLE 3: Partition Coefficients and Local BrominationRate Constants of Scheme 2, Calculated from thePseudophase Model

$K_1^{\mathrm{tr}a}$	$K_2^{\mathrm{tr}b}$	$K_1{}^c$	K_2^d	K_{11}^{e}	$K_{22}^{d,e}$
1.5×10^{-5}	8.8×10^{-3}	$\leq 1 \times 10^{-2}$	6.8	$\geq 7 \times 10^2$	7.7×10^{2}
k _i ^c		$(k_{ m w})_{\mu m E}{}^d$		$(k_{ m w})_{ m H_2O}^f$	
$\geq 6 \times 1$	0^4 s^{-1}	$6 \times 10^9 \mathrm{s}^{-1}$		$6 \times 10^8 \mathrm{s}^{-1}$	

^{*a*} Reference 27. ^{*b*} Reference 28. ^{*c*} Estimated, see text. ^{*d*} Standard error less than 10%. ^{*e*} $K_{ii} = K_i/K_i^{\text{tr}, f}$ Reference 29.

eq 14. The value found from the two-phase calculations, $k_w = 6 \times 10^9 \text{ s}^{-1}$ (or $1 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ in concentration units), is quite consistent with that measured in 0.1 M NaBr water, $k = 1.1 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$. The discrepancy between the two values is probably not significant, in view of the large error (±20%)

on the experimental rate constant in bulk water and the assumptions of the pseudophase model. Nevertheless, the differences in the chemical properties of bulk and microemulsion-encased water, which can be viewed as a reagent in bromination, are frequently mentioned although not yet well-known.^{4,7,24}

Competition between Bromination at the Interface and in the Water Phase. With the rate constants and partition coefficients obtained by application of the pseudophase model, it is now possible to estimate the importance of the competition between the reactions in the two microphases from the relative values of the two terms of eq 14 at various w values. At the highest investigated w (w = 24), the two terms of eq 14 are in a ratio of 4.5; that is, more than 80% of the reaction occurs in the water phase. This may seem surprising since the reagent concentrations in this phase are very small. However, it is still more surprising that at the smallest w (w = 13), the limit between reverse micelles and microemulsions,⁷ about 70% of the reaction still takes place in a water phase. This means that, although the reagent concentration is significant at the interface as shown by the non-negligible K_1 and K_2 values, the rate constant k_i is not large. In fact, the competition is controlled not only the relative concentrations but also by the relative rate constants. In bromination, the rate constant ratio, k_w/k_i , is large, in the range of 10⁵. Consequently, even though the concentrations in the water phase are exceedingly small, the reaction still prefers this phase. Nevertheless, in Figure 4, some scatter for a given w is observed. This probably comes from the neglect of the w/K_{ii} terms in eq 12, which are related to the concentrations in the water phase. This small scatter would, therefore, indicate that these concentrations are not as negligible as deduced from the pseudophase model. In contrast, in the diphenylmethyl chloride solvolysis,¹³ k_w/k_i is much smaller, about 10^2 , so that the competition is controlled to a greater extent by the localization of the reagents within the several microphases.

The differences between the two reactions, bromination and solvolysis, which are both water-promoted and exhibit similar solvent effects in homogeneous media,³⁶ point out the need of a better understanding of water behavior in reverse micelles and w/o microemulsions.

Concluding Remarks

Insofar as reverse micelles and microemulsions are of interest⁵ as microreactors for water-promoted reactions, it is essential to understand the chemical properties of the encased water. In this respect, the numerous spectroscopic investigations^{4,6,7,24} on the nature of bound water, i.e. on the interactions of water molecules and surfactant head groups or their counterions, are of great significance. Nevertheless, the relationship between these interactions and the availability of water as an electrophilic or nucleophilic reagent for performing chemical reactions³⁸ is not clear. The only reactions which have presently been investigated with this aim are acid-base-catalyzed reactions^{4,39} involving protonated water, H_3O^+ , or the hydroxyl anion, OH^- . However, the question of the proton existence in reverse micelles is still open,⁴⁰ because of the difficulties (pH meaning, probe localization, etc.) of the approaches to acid-base equilibria^{7,39} in these media. In this regard, the present results on bromination and those recently published on hydrolytic processes¹³ can open a new way to tackle these problems.

However, measurement of rate data meaningful in terms of microscopic or local reactivity is an obligatory preliminary. Our present results show that the extension of the pseudophase model to w/o microemulsions can be useful to obtain them. More work is in progress to extend this model to the understanding of the reactivity of bound water molecules in these microorganized media.

Experimental Section

Materials. AOT (Sigma) was of the highest purity available and used without further purification after drying in a vacuum desiccator over P_2O_5 for two days. 2,2,4-Trimethylpentane (isooctane, Aldrich) was of spectrophotometric grade. 1-Octene was used as supplied. Bromine and sodium bromide were Suprapur Merck. A stock solution of bromine (1 mL) in 25 mL of CCl₄ was prepared shortly before use under protection from external light.

Typical Preparation of Microemulsion. Microemulsions with a constant z value and variable w values were prepared by addition of the calculated amounts of 0.1 M NaBr solution in distilled water to an isooctane-AOT solution of known molarity. The microemulsion composition was checked by weighing. Usually, 50 mL of AOT solution in isooctane was weighed in a closed vessel and weighed again after addition of the water solution. The microemulsion obtained was pretreated by addition of small amounts of bromine solution in CCl4 in order to eliminate traces of bromine-consuming impurities. The "presaturation" with bromine was controlled by UV at 270 nm. This "mother" microemulsion was further used for the preparation of the series of three different concentrations of alkene used for the determination of k_{2app} . The density was determined by weighing 10 mL of the microemulsion in volumetric flasks, and the concentration of the alkene by weighing a syringe containing $40-120 \ \mu L$ of 1-octene. The final concentrations of 1-octene were in the 10^{-2} M range.

Typical Kinetic Runs. All kinetic runs were performed on a Hi-tech stopped-flow spectrophotometer thermostated at 25.0 \pm 0.1 °C and equipped with a data acquisition system. One syringe of the apparatus contained microemulsion with bromine and the other microemulsion with 1-octene. The reaction was followed by the decrease of absorbance due to Br₃⁻ at 290 nm instead at the maximum of absorbance at 270 nm as better conditions for the work of the photomultiplier could be obtained. Pseudo-first-order rate constants k_{exp} were calculated from the monoexponential kinetic signals by the Marquardt procedure⁴¹ for least squares nonlinear curve fitting.

Acknowledgment. We gratefully acknowledge Professor J. R. Leis and his group for helpful suggestions and stimulating discussion. We are indebted to Professor A. Lattes and Dr. I. Rico-Lattes, whose pioneer work inspired this research. I.B.B. would like to thank CNRS and the University of Paris 7 for the award of a Research Associateship.

References and Notes

(1) The term "reverse micelles" is used here for aggregates in which the water is interfacial only, i.e. in strong interaction with surfactant head groups and counterions. "Microemulsions", sometimes called swollen micelles, refers to aggregates containing a core water phase more or less analogous to bulk water.

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JP960772A