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Organic reactions in micro-organized media: Why and how?

Marie-Françoise Ruasse[a],* Iva B. Blagoeva[b], Renata Ciri[a] Luis Garcia-Rio[c], José R. Leis[c], Antonio Marques[a], Juan Mejuto[c] and Eric Monnier[a].

[a]*Institut de Topologie et de Dynamique des Systèmes de l'Université Paris 7-Denis Diderot, 1, rue Guy de la Brosse, 75005 Paris, France.*
[b]*Institute of Organic Chemistry, Bulgarian Academy of Sciences, u.l. Acad. G. Bontchev, bl.9, Sofia 1113, Bulgaria.*
[c]*Departamento de Quimica Fisica, Universidad de Santiago de Compostela, E-15706 Santiago de Compostela, Spain.*

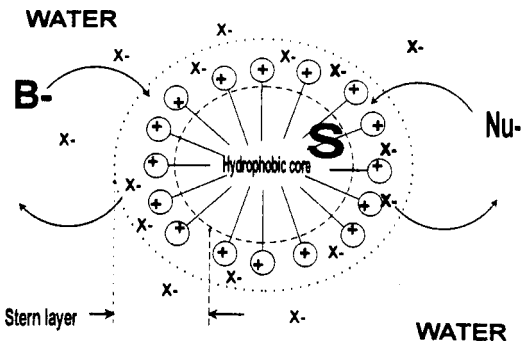
Abstract: Organic reactivity in microorganized media is illustrated by results on micellar catalysis in micelles and on the properties of water in reverse micelles. With cationic micelles, interesting catalytic effects on reactions between hydrophobic and hydrophilic reagents are obtained when the hydrophilic partner, and only it, goes into the Stern layer by shifting the counter-ions of the surfactant. Results on nucleophilic substitution of a lipophilic phosphoric triester, PNDPP, by an oximate, MeCO-C(Me)=NO$^-$, in the presence of various cationic surfactants, cetyltrimethylammonium salts, CTAX, with X$^-$ = Br$^-$, Cl$^-$ and AcO$^-$, and of various buffers, glycine or carbonate, exemplify how the ion exchanges at the micellar interface control the interfacial nucleophile concentration and the reactivity. In anionic AOT-reverse micelles, alkene bromination, a water-promoted reaction between two lipophilic reagents, is taken as a probe for the chemical properties of the sodium-bound water of these microaggregates. Kinetic data show that the electrophilicity of water, i.e. its hydrogen-bond donor ability, is increased by a factor of up to 65 as compared to bulk water. Within the bound-water phase a gradient of counter-ion concentration is observed since the electrophilicity increase depends on the probe location, close to the interfacial layer or to the micellar core. Product data give evidence for a change in the nucleophilic reactivity of this unusual water. These results are discussed in terms of new routes for biomimetic chemistry.

INTRODUCTION

The publication in 1975 of the famous book[1] of Fendler and Fendler on "Catalysis in Micellar and Macromolecular Systems" focused attention on the many interests of organized media for performing highly selective and very fast reactions. In particular, the possibility of obtaining catalytic effects close to those observed with enzymes was suggested as an exciting challenge. About twenty years later, much work has been devoted to micellar catalysis of organic reactions but, in most cases, the results are not as excellent as expected.[2] Nevertheless, although the initial challenge seems to be beyond reach, less ambitious but still enthusiastic objectives emerge from our present knowledge. In this paper, we present results on nucleophilic substitutions in micelles and on alkene bromination in reverse micelles which show that significant and interesting micellar effects can be obtained in organic chemistry by applying simple but efficient rules.

I. OPTIMIZATION OF MICELLAR EFFECTS ON NUCLEOPHILIC SUBSTITUTIONS

Most of the presently available data on micellar catalysis deal with nucleophilic substitutions on aliphatic substrates.[2,3] These reactions can take advantage of micellar media for solubility reasons since the substrates, generally esters, are highly hydrophobic whereas the nucleophiles, mostly organic anions, are hydrophilic. Micelles, which are molecular assemblies of amphiphilic surfactants in water, are considered as convenient reaction media, insofar as the substrate dissolves in the apolar core of the micelles and the nucleophile in the water phase (Scheme 1).



Scheme 1

The reaction between the two reagents can occur when they meet at the interface (Stern layer). Catalytic effects are expected if the rate in the micellar interface is significantly larger than that in the water phase. Since the rates of bimolecular reactions depend on the rate constants and also on the reagent concentrations, micellar catalysis, eq. 1,

$$\text{Catalytic effect} = \frac{k_m[S]_m[Nu]_m}{k_w[S]_w[Nu]_w} \qquad (1)$$

can arise either because of high micellar rate constants, k_m, or because of high reagent concentrations, $[Nu]_m$ and $[S]_m$. Most of the spectacular results have been observed by attempting to obtain high k_m-values. For example, Menger's system[4] or Tonellato's metallomicelles[5] involve surfactants to which the nucleophiles are covalently bound so that large k_m-values are obtained by associating micellar and intramolecular catalysis. In contrast, when usual or commercially available surfactants are used, the micellar rate constants are not markedly higher than those in water.[3] The frequently smaller than unity k_m/k_w ratios are considered as the result of a medium effect, the Stern layer of a micelle where the reaction occurs being less polar than water. In these cases, a significant catalytic effect can be expected from high reagent concentrations at the micellar interface (Scheme 1). The purpose of this paper is to show how micellar reagent concentrations can be controlled by the counter-ion surfactant and the reaction conditions.

NUCLEOPHILIC-COUNTER-ION EXCHANGE

High concentrations of anionic nucleophiles in the Stern layer of a cationic micelle implies that the surfactant counter-ion is readily transfered to the aqueous phase since the reaction must occur at this interface and since the micellar surface cannot be oversaturated by anions. In other words, it is necessary that eq.2 can be shifted to the right,[6] which is possible only when X^-, the counter-ion, is weakly bound to the surfactant head group. In earlier work on micellar effects, various scales of CTA^+ affinity of inorganic

$$CTA^+, X^-_m + Nu^-_w \rightleftharpoons CTA^+, Nu^-_m + X^-_w \qquad (2)$$

anions have been proposed.[6,7] From the inspection of one of the most known of these scales (Figure 1A), it appears that Br^-, the very popular bromide ion since CTABr is commercially available and cheap, is rather strongly bound to micelles and is, therefore, not convenient for high catalytic effects. The other commercially available surfactant, CTACl, seems a priori more appropriate since Cl^- would be about 10 times less strongly bound than Br^-. According to this scale, the most convenient counter-ions are the hydroxyl and fluoride ions. Nevertheless, their preparation, their purification and their use are not straightforward[8] since they are readily exchangeable with a nucleophile but also with any impurity. Therefore, cetyltrimethylammonium acetate which can be readily obtained is a priori a good compromise between the opposite constraints involved in the surfactant synthesis and its reactivity.

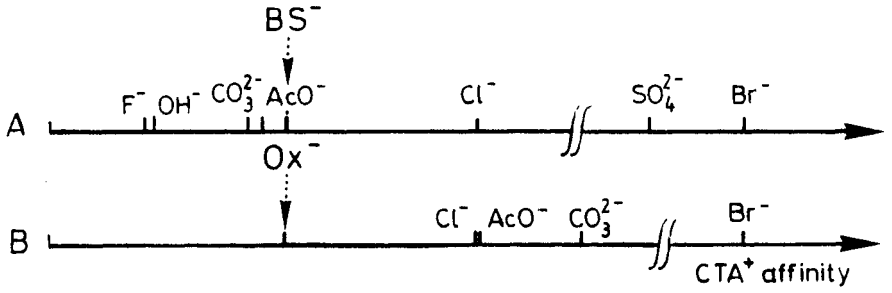


Fig.1. Relative affinities of various anions for cetyltrimethylammonium (CTA^+) micelles. A: from spectroscopic measurements, ref.7a ; B: from reactivity data, this work.

In Figure 2, are shown the results[9] obtained for the nucleophilic substitution of p-nitrophenyl-diphenyl phosphate, a highly hydrophobic ester strongly bound to CTA^+-micelles (PNDPP-CTA^+ association constant = $K_S = 10^4$), by the anion of butadione oxime ($pK_a = 9.3$) . The kinetic counter-ion effect is quite significant since the overall micellar effect, k_{max}/k_w, is approximately doubled on going from bromide to acetate and chloride (Table I). Surprisingly, the difference between acetate and chloride does not agree with Sepulveda's affinity scale. The fact that the experimental lines of Fig.2 for the two surfactants are not parallel can be interpreted in terms of differences in the β-values for the two micellar systems (vide supra).

Fig. 2. Counter-ion effect on the k_{obs}-[CTAX] profile for the PNDPP- butadione oximate reaction at 25°C and pH 9.8 (buffer: 0.1M glycine; [Ox] = 10^{-3}M). The X^--dependence of the rate maximum is attributed to changes in the oximate concentration at the micellar interface, i.e. to different X^--oximate exchange constants, since the micellar rate contant is X^- -independent.

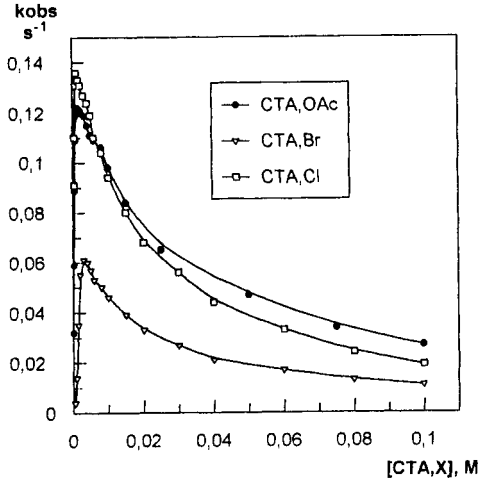


TABLE 1. Kinetic Micellar Effect, k_{max}/k_w, in the presence of CTAX surfactants on PNDPP - butadioneoximate reaction at pH 9.8 (carbonate or glycine buffer) and at 25°C. k_{max}, pseudofirst order rate constant ([Ox] = 10^{-3}M) at the maximum of the k_{obs}-[CTAX] profiles; k_w, pseudo first order rate constant ([Ox] = 10^{-3}M) in the absence of surfactant. The rate is multiplied by 7 on going from the least to the most efficient catalytic system.

	Carbonate	Glycine
CTA^+, Br^-	80	240
CTA^+, OAc^-	-	510
CTA^+, Cl^-	195	550

THE ROLE OF THE BUFFER

Substitutions by anionic nucleophiles imply the use of a buffer in order to control the ionization of the reagent. Therefore, in addition to the nucleophile-counter-ion exchange (eq.2), the exchange between the counter-ion and the anionic component of the buffer, B^-, must be taken into account, all the more that

$$CTA^+, X^-_m + B^-_w \rightleftharpoons CTA^+, B^-_m + X^-_w \qquad (3)$$

buffers are generally used at concentrations markedly higher than that of the nucleophile. In Figure 3, the micellar effects obtained[9] in the presence of carbonate and glycine buffers are compared. The buffer control of the rate is important since on going from carbonate to glycine, the rate maximum increases by a factor of about 3. This result is readily understood in terms of a competition between equilibria 2 and 3. The counter chloride ion is exchanged almost totally by carbonate which, in disagreement with Sepulveda's scale, is strongly CTA^+- bound, so that the nucleophile is hardly included in the Stern layer. This assumption of a carbonate-chloride exchange is confirmed by the marked pH decrease of the buffer solution by addition of CTACl (Figure 4). The pH profile of Figure 4 can be quantitatively interpreted in terms of a decrease of the basic component of the buffer in the water phase. In contrast, the exchange between chloride and hydrophilic glycine does not seem to occur since no pH change is observed (Figure 4).

Fig. 3. Buffer effect on the k_{obs} -[CTACl] profile for the PNDPP - butadione oximate CTACl reaction at 25°C and pH 9.8. The oximate-chloride exchange is partially inhibited by the carbonate-chloride exchange at the micellar interface.

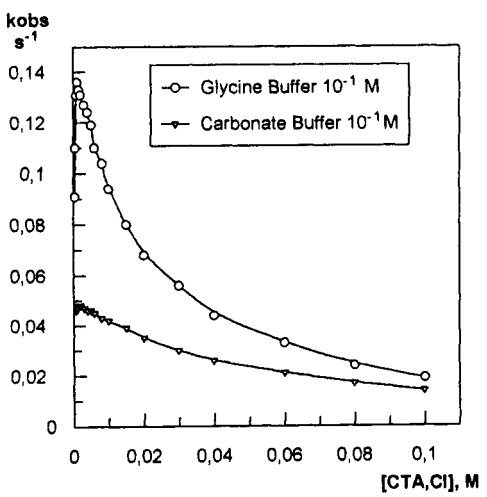
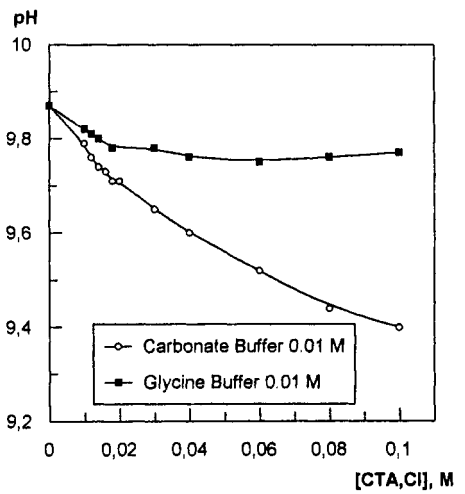


Fig. 4. pH-dependence of buffer solutions on CTACl concentration. The marked pH-decrease observed for carbonate shows a significant decrease in the concentration of the basic component of the buffer in the water phase due to the carbonate association at the micellar interface as a result of its exchange with the surfactant counterions.



QUANTITATIVE ANALYSIS

The results presented in Table I show that it is possible to obtain significant micellar effects on nucleophilic substitutions with currently available cationic surfactants by applying simple rules based on ion exchanges at micellar interfaces. In particular, a reasonable choice of the counter-ions and buffers can provide quite interesting catalytic effects.

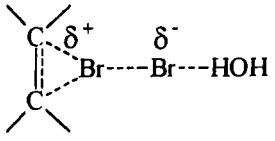
On one hand, an a priori choice depends on the availability of constants for the exchange between counter-ions and added organic ions. The well-known pH change[10,11] of buffer solutions in the presence of

surfactants can be used in this view. For example, the $K_{Cl^-}^{CO_3^{2-}}$ exchange constant can be calculated from data of Figure 4.

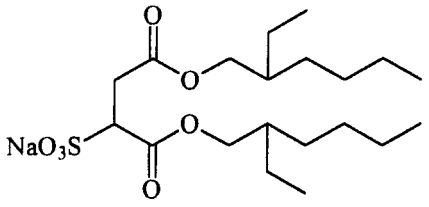
On the other hand, quantitative approach to micellar concentrations and rate constants uses the pseudophase-ion-exchange model.[11] The application of this model requires the knowledge of two characteristics of the surfactant, its cmc and β, the micellar charge. It is obvious that the values of interest are not those of the initially used surfactant but those of that actually involved in the reaction. Since cmc and β are highly dependent on the counter ion and on the ionic strength of the water phase,[12] these parameters must be obtained independently. Methods, readily available in an organic laboratory, such as fluorimetry and pHmetry, are applied in this view.

II. ALKENE BROMINATION AND WATER REACTIVITY IN REVERSE MICELLES

In contrast to micelles, very few organic reactions have been investigated in reverse micelles.[13] Nevertheless, reverse micelles[14] which are water microdroplets dispersed in an apolar solvent can be useful reaction media for water-promoted reactions between hydrophobic reagents. Alkene bromination is an example of this class of reactions since bromine is not readily soluble in water ($K^{tr}_{Br_2}$, coefficient of bromine partition between water and alkane, = 9 x 10^{-3}) and since most of the unsaturated compounds are lipophilic. Moreover, electrophilic bromination which involves the ionization of bromine-alkene charge transfer complex is extremely slow in apolar solvents such as hydrocarbons but extremely fast in aqueous media in which the formation of the bromonium ion is strongly assisted by electrophilic solvation of the leaving bromide ion.[15]



bromination transition state



AOT

Macroscopically homogeneous AOT-isooctane-water solutions[16] are particularly convenient microorganized systems for this reaction. AOT, sodium bis-(2-ethylhexyl)-sulfosuccinate, is a commercially available anionic surfactant with a variable packing parameter because its two branched aliphatic chains can adopt different conformations and, therefore, different volumes and lengths. Consequently, its flexible negative curvature allows for obtaining reverse micelles, or water pools, of variable size without the addition of a cosurfactant. Moreover, the water aggregates formed with this surfactant are spherical and monodisperse and their radii are controlled by w, the $[H_2O]/[AOT]$ ratio.[16] It is commonly agreed[17] that three kinds of water are involved in these aggregates, depending on w, i.e. on their size (Figure 5). At very small w ($w < 4$), or for very small microdroplets, water is almost exclusively interstitial water molecules directly solvating the sulfonate head groups and some of their counter-ions (region 1 in Figure 5). At larger w-values, the water molecules interact strongly with the sodium counter-ions.

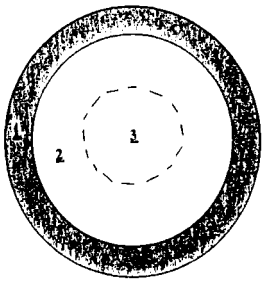
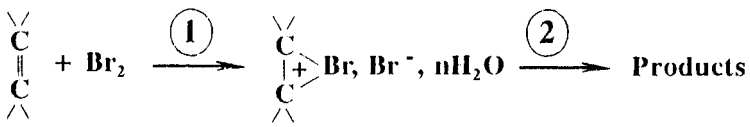


Fig.5. Schematic picture of a reverse micelle (water microdroplet dispersed in isooctane) and its several aqueous regions. Region 1: interfacial layer consisting of the sulfonate head groups and some of their sodium counter-ions. Water is "Interstitial Water" strongly bound to the head groups. 1 is the only region at very small w (w < 4). Region 2: aqueous microphase containing most of the counter-ions. Water is "Bound Water" interacting with the sodium ions, i.e. the water molecules are involved in the solvation sphere of Na^+. 2 exists at w greater than 4. Region 3: water core. The water molecules interact weakly with the surfactant ions and are bulk-like, or network-like, organized. 3 exists at large w (w > 13-16).

At high w-values, or for very large microdroplets, a water core exists in which the interactions with the sodium cations are almost negligible. The limiting value beyond which region 3 appears is not well-established ; it seems to be between 11 and 16, depending on the authors and the investigated water property. It is presently obvious from much physicochemical work that the properties of bound-water in region 2 differ widely from those of bulk water. For example, encased water in this region is more viscous, less polar, has a smaller dielectric constant, a smaller activity, a lower melting point than network-organized bulk water.[17] Nevertheless, these physicochemical results do not tell much about the chemical properties at work in an organic reaction. For instance in bromination (Scheme 2), water acts[15] as an electrophile, i.e. a hydrogen-bond donor, in the ionization step (step 1) and as a nucleophile, i.e. an electron donor, in the product-forming step (step 2). The bromination results reported here have been obtained with the view to obtaining data on these properties of water encased in reverse micelles.



Scheme 2

In Figure 6, are shown the products obtained from trans-β-methylstyrene and 1-octene bromination in AOT-isooctane solutions containing various amounts of water.[18] Since bromination does occur and, in particular, since the bromonium-bromide ion-pair is necessarily formed, and since bromohydrins are obtained, the encased water retains, at least partly, its electrophilicity and its nucleophilicity. Nevertheless, the two alkenes behave quite differently as regards their water -dependence of the bromohydrin formation, probably because of their differences in lipophilicity.

Since the transfer of the alkene from isooctane to water is necessarily one of the limiting factor of their reaction in reverse micelles, we investigated the kinetics of the bromination of alkenes with various transfer coefficients[19] (Table II) as a function of the micellar medium composition determined by w ($[H_2O]/[AOT]$) and z ([IO]/[AOT] ; IO = isooctane). In Table II, are shown the rate constants of the reaction of these alkenes in bulk water. The kinetic results in reverse micelles exhibit a marked rate decrease as compared to bulk water (Fig. 7). As expected, the experimental second-order rate constants increase with the water concentration of the reaction medium. In the investigated w-range (w < 20), fairly linear relationships between these rate constants and the water concentration are obtained when the water activity coefficient,[22] significantly smaller than unity at small w (w < 10), is taken into account. An example of these relationships is shown in Figure 7. Their slopes (s in Table II), i.e. the experimental rate dependence on the water content, vary markedly with the alkene but without any trend parallel to the lipophilicities on the water content, vary markedly with the alkene but without any parallelelism with their lipophilicities

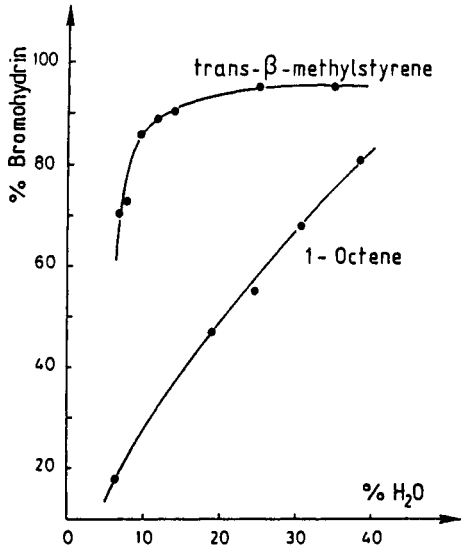


Fig.6. Bromohydrin yield of bromination in reverse micelles of two alkenes of different lipophilicities as a function of the water amount in the micellar solution. % bromohydrin is the bromohydrin percentage in the total products ; the other product is dibromide. Since bromohydrins are obtained, reverse-micelle water behaves as a nucleophile.

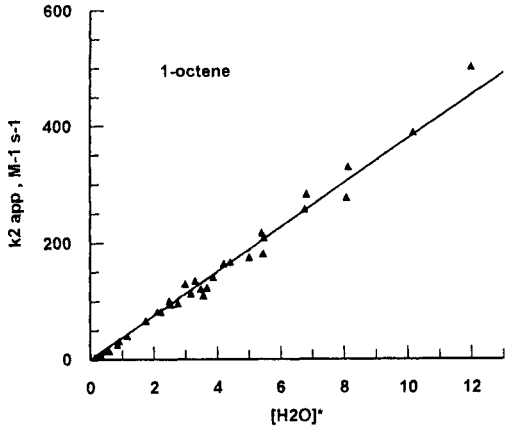


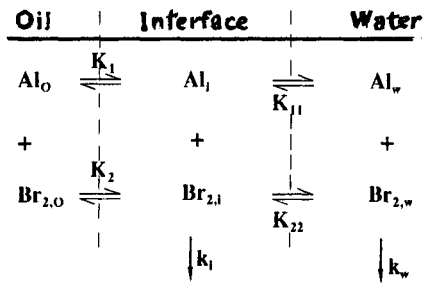
Fig.7. Dependence of $k_{2,app}$,the experimental rate constant of 1-octene bromination in AOT-reverse micelles, on the water concentration in the micellar solution. $[H_2O]^*$ is the water concentration corrected by its activity coefficient which is markedly smaller than unity at low water content, ref. 22. Bromination is strongly inhibited in micelles ($k_2 = 1.2 \times 10^8$ M^{-1} s^{-1} in bulk water). The rate constant sensitivity to the water concentration, $k_{2,app} = s\,[H_2O]^*$, is given by s (see Table II).

TABLE 2. Alkene bromination in AOT-Reverse Micelles. Comparison of the Rate Constants in the Micellar Water Phase and in Bulk Water.

Alkene[a]	K_{al}^{tr} [b]	log $(k_w)_{H_2O}$ [c]	s, $M^{-2}s^{-1}$ [f]	$(k_w)_{RM}$, s^{-1} [g]	$(k_w)_{RM}/(k_w)_{H_2O}$, M
CMP	8×10^{-3}	6.5 [d]	6	3.1×10^6	0.5
β-MS	1.9×10^{-4}	9.0[e]	125	2.1×10^9	2
1-Oct	1.6×10^{-5}	8.1[d]	40	4.9×10^9	45
DPE	1.8×10^{-6}	10.2[e]	320	9.5×10^{11}	65

[a]CMP : 2-chloromethylpropene ; β-MS: trans-β-methylstyrene ; 1-Oct ; 1-Octene ; DPE: 1,1-diphenylethylene. [b] Coefficients of alkene partition between isooctane and water, ref.19. [c] k_w in M^{-1} s^{-1} ; bromination rate constants in bulk water containing 0.1M NaBr. [d] Experimentally measured, ref.20. [e] Extrapolated from mY relationships, ref.21. [f] Sensitivity of the experimental rate constants to the water content of the micellar solution (slope of the linear relationships, $k_{2,app} = s[H_2O]^*$; see Fig.7). [g] Bromination rate constants in the water phase of reverse micelles, calculated from the pseudophase model, eq.4 and Fig.9.

expressed by their transfer coefficients. This is not surprising since the experimental rate constants, $k_{2,app}$, are not usual rate coefficients, related to a well-defined reaction, because of the inhomogeneity of the reaction medium. In order to analyze the experimental rate data in usual terms of organic reactivity, it is necessary to obtain rate constants and reagent concentrations for the reactions in the several microphases of the micellar medum. For this purpose, we set up a kinetic pseudophase model[23] (Scheme 3) assuming, as for direct micelles, that the experimental rate is the sum of the rates of the reactions in the three micellar



Scheme 3

pseudophases, water, interface and isooctane (oil). Equation 4 which relates the experimental rate constant, $k_{2,app}$, to the medium composition ([AOT], z and w), to the rate constants, k_i, and k_w, of the reactions at the interface and in the water phase, and to the coefficients of the reagent transfers between the several microphases, is obtained from this Scheme.

$$k_{2,app}[AOT] = \frac{K_1K_2k_i + K_1^{tr}K_2^{tr}k_w w}{z^2 + (K_2 + K_1)z} \qquad (4)$$

According to eq.4, quadratic and linear relationships between the term $1/k_{2,app}$ [AOT] and z at constant w and between $k_{2,app}$ [AOT] and w at constant z, respectively, are expected and observed, (Figures 8 and 9).

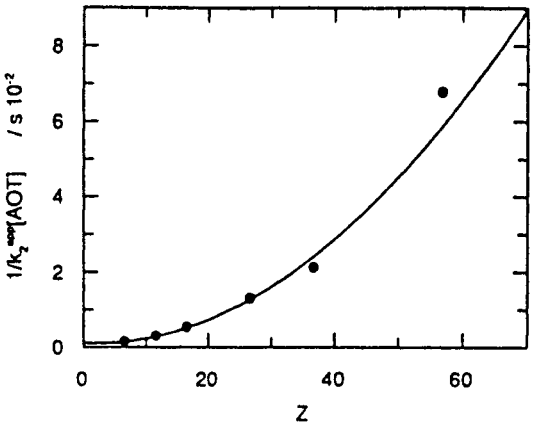


Fig. 8. Dependence of $k_{2,app}$, the experimental rate constant of 1,1-diphenylethylene bromination in AOT-reverse micelles, on z = [IO]/[AOT] at w = 11. The close line calculated from eq.4 fits the experimental data (closed circles).

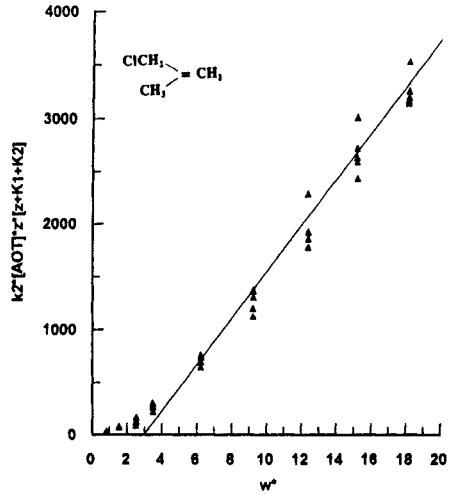
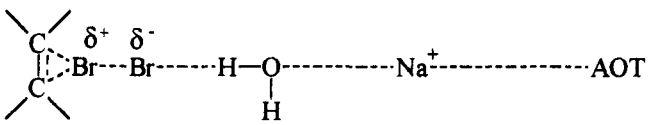


Fig. 9. Dependence of $k_{2,app}$, the experimental rate constant of 2-chloromethylpropene bromination in AOT-reverse micelles, on w* = $[H_2O]^*/[AOT]$ with $[H_2O]$ corrected with the water activity coefficients in micellar solutions, ref. 22. The y-axis values are calculated from the z-dependence of $k_{2,app}$ (Fig. 8). According to the pseudophase model, eq. 4, $(k_w)_{RM}$ is obtained from the slope of the straight line (see text).

After the calculation of the z-term (denominator of eq.4) for the reaction of each alkene from the plots of Figure 8, k_w-values for the bromination in the bound-water phase (region 2) of reverse micelles, $(k_w)_{RM}$ in Table 2, are obtained from the slopes of Figure 9.

The comparison of these data with those obtained in bulk water, $(k_w)_{RM}/(k_w)_{H_2O}$, leads to very surprising results since bromination rate constants in the bound-water phase of reverse micelles are either in the same range as those in network-organized water or markedly greater. Since the driving force of bromination is

the electrophilic solvation of the leaving bromide, it is obvious that the electrophilicity of the water molecules involved in the reactions of the various olefinic substrates varies with the alkene lipophilicity. In other words, the alkenes, depending on their lipophilicity, react with bromine, at different places of the micellar water phase, where the water electrophilicity is markedly different. 1,1-diphenylethylene which cannot go very deep within the micellar core because of its very high hydrophobocity, uses for its reaction with bromine water molecules close to the interfacial region the electrophilicity of which is markedly greater than that of bulk water. In contrast, chloromethylpropene which is not very hydrophobic reacts probably close to the micellar core where the water molecules, hardly perturb by sodium ion interactions, resemble network-organized water. This interpretation in terms of a water-electrophilicity gradient within the reverse micelles is fairly well supported by the following observations. i) The $(k_w)_{RM}/(k_w)_{H_2O}$ rate ratios of Table II parallel the alkene lipophilicities expressed by their isooctane-water transfer coefficients, K^{tr}_{al}. The observed trend is unambiguously related to a change in the rate constants and not in alkene concentrations in the aqueous phase, the effect of which is taken into account in the pseudophase model by the several transfer coefficients. ii) The kinetic solvent effect in bromination is directly related to changes in solvent electrophilicity involved in the solvation of forming bromide ions.[15] iii) The water electrophilicity in reverse micelles depends on the sodium ion concentration in the bound-water phase. It has been previously shown that water molecules in the solvation sphere of cations are more acidic, i.e. more hydrogen-bond donor or more electrophilic, than network-organized water.[24] In the bound-water phase there is necessarily a gradient in the sodium ion concentrations, and therefore, a gradient in the water electrophilicity, from very high close to the sulfonate head group layer to bulk-like in the region of micellar core.



Bromination rates seem to be a very sensitive probe, at a molecular level, of the chemical reactivity of the water molecules within reverse micelles. To the best of our knowledge, these results are the first experimental evidence for the gradient of counter-ion concentration in the bound-water region. More work is in progress to explore quantitatively this original proposal.

CONCLUDING REMARKS

- Organic reactivity in the water pools of reverse micelles is profoundly altered as compared to that in bulk water. Therefore, not only the physicochemical but also the chemical properties of this solvent are markedly modified when it is encased in micellar aggregates. Kinetic data on bromination, and also on comparable solvolytic reactions,[25] exhibit clearly that the water electrophilicity, i.e. its hydrogen-bond donor ability, is markedly increased, up to a factor of 65 in the case of 1,1-diphenylethylene reaction. The water nucleophilicity seems also to be modified, as shown at least qualitatively, by the bromination product analysis (Figure 6). The finding that the reactivity of water which is presently viewed as a unique and universal reagent depends on its environment,opens the way to an original field of organic chemistry since our results suggest that water-sensitive reactions could be controlled by the design of specific micellar aggregates.

- Presently there is much interest *in using water, instead of organic solvents*, for performing organic reactions.[26] The claimed reason for this is the evidence that water is a cheap and non-polluting solvent. There is also an underlying background insofar as water is the solvent of every life process. Nevertheless, biochemical reactions and, in particular, enzyme-catalyzed reactions proceed in an aqueous environment

the water molecules of which are not network-organized as they are in bulk water. Therefore, reverse micelles which are viewed in biochemistry as reasonable models of enzyme water pockets[27] should also be of interest in organic chemistry not only for solving difficult solubility problems but also for obtaining unsuspected reactivities and selectivities.

- Twenty years after Fendler's challenge on biomimetic media, it seems that organic chemistry has not gained very much from microoganized media, except from some spectacular experiments with specifically designed reaction systems. With usual micelles, interesting catalytic effects on reactions between hydrophilic and hydrophobic reagents can be expected if the hydrophilic reagent can be forced into the Stern layer but much work on ion-exchanges is still to be done before this condition can be readily achieved. In contrast, the markedly different reactivity of bound water of reverse micelles renews the initial challenge in exciting terms of biomimetic organic chemistry.

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