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Reverse Micellar Aggregates: Effect on Ketone Reduction. 1. Substrate Role

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The reduction of three aromatic ketones, acetophenone (AF), 4-methoxyacetophenone (MAF), and 3-chloroacetophenone (CAF), by $NaBH_4$ was followed by UV−vis spectroscopy in reverse micellar systems of water/AOT/isooctane at 25.0 °C (AOT is sodium 1,4-bis-2-ethylhexylsulfosuccinate). The first-order rate constants, k_{obs}, increase with the concentration of surfactant due to the substrate incorporation at the reverse micelle interface, where the reaction occurs. For all the ketones the reactivity is lower at the micellar interface than in water, probably reflecting the low affinity of the anionic interface for BH_4^-. Kinetic profiles upon water addition show maxima in k_{obs} at $W_0 \approx 5$ probably reflecting a strong interaction between water and the ionic headgroup of AOT; at $W_0 < 5$ by increasing W_0 BH_4^- is repelled from the anionic interface once the water pool forms. The order of reactivity was CAF ≫ AF > MAF. Application of a kinetic model based on the pseudophase formalism, which considers distribution of the ketones between the continuous medium and the interface, and assumes that reaction take place only at the interface, gives values of the rate constants at the interface of the reverse micellar system. At $W_0 = 5$, we conclude that $NaBH_4$ is wholly at the interface, and at $W_0 = 10$ and 15, where there are free water molecules, the partitioning between the interface and the water pool has to be considered. The results were used to estimate the ketone and borohydride distribution constants between the different pseudophases as well as the second-order reaction rate constant at the micellar interface.

Introduction

Chemical reactivity in reverse micellar systems is an interesting object of study because these media are macroscopically homogeneous and isotropic but are heterogeneous on the molecular scale. These systems contain aqueous microdroplets entrapped in a film of surfactants and dispersed in a low-polarity bulk solvent. In this way, and depending on the water content, three pseudophases are present in reverse micellar systems, water, interface, and organic ones that allow compartmentalization of solubilized species at the microscopic level.[1−9] The physical characteristics of water microdroplets differ from those of bulk water, mainly in regard to mobility, polarity, and properties affected by its high ionic strength and by the electronic influence of the charged surfactant headgroups.[5,6,10−13]

In principle, reverse micellar systems can affect reaction rates by two main processes;[14] they can increase or diminish the energy of the transition state of the reaction, thus affecting the rate constants. This is what is called the medium effect, and it takes into account all the properties of the interface such as micropolarity, microviscosity, ionic strength, charge density, etc. The other effect is that they can change the reactant location which is called the solubilization effect. In the case of bimolecular reactions, solubilization of the reactants in the interfacial region can significantly accelerate reactions due to a "concentration" effect, while reactions of segregated reactants may be retarded. When both reactants

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are in the water droplet or at the interface, they are concentrated as in a nanoreactor, and since its size is easily varied, it is relatively easy to assess the properties of the micellar system.[15,16] Also, reverse micellar systems are of interest as a reaction medium because they are powerful models of biological systems.[17–19]

In water, micelles influence regioselectivity and stereoselectivity[20–22] of the reduction of ketones with borohydride; i.e., in chiral reverse micellar systems[23] prochiral ketones are reduced to optically active alcohols. A systematic study[24] of the reaction in cetyltrimethylammonium bromide (CTAB) and cetyltrimethylammonium chloride (CTAC) in water shows that there are, for a series of aromatic ketones, decreases (20−50 fold) in second-order reaction rate constants in the micellar pseudophase, relative to those in water. Due to the lack of kinetic studies in reverse micellar systems we have investigated this reaction kinetically in isooctane/AOT/water reverse micellar system.

We report below data on the kinetics of reduction by $NaBH_4$ of three aromatic ketones, acetophenone (AF), 4-methoxyacetophenone (MAF), and 3-chloroacetophenone (CAF), in isooctane/AOT/water reverse micelles to investigate how the reverse micellar system and the ketones structure influence the reaction rate. The results show that the reaction is faster at low water content and decreases with the amount of dissolved water depending on the nature of the ketones.

Experimental Section

General Methods. UV−vis spectra were recorded on a spectrophotometer equipped with a multiple cell holder thermostated at 25.0 ± 0.1 °C. Control experiments of ketones reduction by $NaBH_4$ (under reverse micelle conditions) showed that the ketone disappears and the correspondent alcohol is the only formed product (by GC analysis). Moreover, in the absence of $NaBH_4$, no reaction occurred and there were no changes in the UV−vis spectra.

Materials. Acetophenone, (AF; 99%), 4-methoxyacetophenone (MAF; 98%), 3-chloroacetophenone (CAF; 99%), and 2,2,4-trimethylpentane (isooctane HPLC grade; 99.7%) from Aldrich were used without further purification. Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) from Sigma (>99%) was dried under reduced pressure and was kept under vacuum over P_2O_5 until it was used. $NaBH_4$ (98%) from Acros Organics was used as received. Water was distilled three times.

Procedures. A 0.5 M stock solution of surfactant was prepared by dissolving the necessary amount of surfactant in isooctane. To obtain optically clear solutions they were shaken in a sonicating bath. The appropriate amount of stock solution, to obtain a given concentration of surfactant, was transferred into the cell, and the water was added with a calibrated microsyringe. The amount of water present in the system is expressed as the molar ratio between water and the surfactant (W_0 = $[H_2O]/[\text{surfactant}]$). $NaBH_4$ was dissolved in water in a concentration of 0.1 M before being added to the microemulsion and stored in a refrigerator prior to use. NaOH = 0.1 M was present in the water solution in order to stabilize the ion BH_4^-.[25–29] $NaBH_4$ is not soluble in isooctane, so ionic concentrations in the reverse micelles are referred to that of water, i.e., $[NaBH_4]_W = 0.1$ M. When the surfactant concentration is changed at a determined value of W_0, total amounts of water and $NaBH_4$ differ in every case, but the ratio is always the same.

The concentration of hydride species was assumed to be four times that of the analytical concentration[30,31] due to the presence in the BH_4^- ion of four identical hydrogen atoms.

Kinetics. Reactions were followed spectrophotometrically by monitoring the decrease of the absorbance of the ketones at the following wavelengths and ketones analytical concentrations: MAF, 263, 270, and 277 nm; $[\text{MAF}] = 5 \times 10^{-5}$ M; CAF, 278, 289, and 297 nm; $[\text{CAF}] = 3 \times 10^{-4}$ M; AF, 271, 278, and 286 nm; $[\text{AF}] = 3 \times 10^{-4}$ M at 25.0 ± 0.1 °C. As blank was used a solution of surfactant of identical concentration and W_0. To start the reaction, the appropriate amount of ketone stock solution in isooctane was added (20−30 μL) to a thermostated cell containing $NaBH_4$ in the reverse micellar system. When $[NaBH_4]$ is changed, the method is similar to that described above, but with a 0.15 M stock solution of $NaBH_4$. Dilution of this stock solution to the desired $[NaBH_4]$ is made before adding it to the reverse micellar system.

In every case, first-order plots were obtained with the addition of excess $NaBH_4$. The kinetic data fit the first-order integrated equation in a satisfactory way ($r > 0.999$ for almost $10t_{1/2}$). When the reaction was too slow, the rate constant was calculated from the initial rates. The standard deviation of the kinetic data, using different samples, was less than 5%.

Determination of the Binding Constant of Ketones (K_{ket}) to AOT Reverse Micellar System. The absorbances of isooctane solutions of each ketone at a fixed wavelength (shown above) were recorded and averaged in the presence of different AOT concentrations (0−0.4 M) at W_0 = 5, 10, and 15, obtained by diluting the stock AOT solution (AOT 0.4 M, CAF or AF 3×10^{-4} M, MAF 5×10^{-5} M) with the isooctane−ketone solution. The spectra were run at 25.0 °C, the blank being a solution of surfactant of identical concentration and W_0. Values of K_{ket} were calculated with a least-squares fit to eq 1[32]

$$A^{\lambda} = \frac{(\epsilon^{\text{f}} + \epsilon^{\text{b}}[\text{AOT}]K_{\text{ket}})[\text{ketone}]_{\text{T}}}{(1 + K_{\text{ket}}[\text{AOT}])} \qquad (1)$$

where A^{λ} is the absorbance at different AOT concentration, ϵ^{f} and ϵ^{b} are the molar extinction coefficients for the ketones in isooctane and at the interface of the reverse micelles respec-

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TABLE 1. Kinetic Parameters and Distribution Constants for the Reaction of Ketones with $NaBH_4$ in Water/AOT/Isooctane Reverse Micellar Systems at 25.0 °C

	k_b/M^{-1} $min^{-1\,a}$			water (k_w)/M^{-1} min^{-1}	K_{ket}/M^{-1}		
ketones	$W_0 = 5$	$W_0 = 10$	$W_0 = 15$		$W_0 = 5$	$W_0 = 10$	$W_0 = 15$
MAF	$0.020^{b} \pm 0.005$	$0.017^{c} \pm 0.005$	$0.0083^{c} \pm 0.0005$		$1.0^{b} \pm 0.1$	$1.1^{c} \pm 0.1$	$1.5^{c} \pm 0.1$
	$0.018^{d} \pm 0.005$	$0.015^{e} \pm 0.005$	$0.0088^{e} \pm 0.0005$	0.27 ± 0.02	1.1^{f}	1.0^{f}	1.4^{f}
	(13.5)	(15.8)	(32.5)		0.9^{g}	1.1^{g}	1.6^{g}
CAF	$0.21^{b} \pm 0.04$	$0.16^{c} \pm 0.04$	$0.15^{c} \pm 0.04$		$2.2^{b} \pm 0.1$	$2.1^{c} \pm 0.1$	$2.0^{c} \pm 0.1$
	$0.28^{d} \pm 0.05$	$0.17^{e} \pm 0.05$	$0.14^{e} \pm 0.05$	3.46 ± 0.02	2.5^{f}	2.0^{f}	1.9^{f}
	(16.4)	(21.2)	(22.4)		2.3^{g}	1.9^{g}	2.1^{g}
AF	$0.057^{b} \pm 0.005$	$0.022^{c} \pm 0.005$	$0.019^{c} \pm 0.005$		$0.9^{b} \pm 0.1$	$0.7^{c} \pm 0.1$	$0.8^{c} \pm 0.1$
	$0.055^{d} \pm 0.005$	$0.020^{e} \pm 0.005$	$0.018^{e} \pm 0.005$	1.14 ± 0.02	0.8^{f}	0.8^{f}	0.7^{f}
	(18.2)	(47.3)	(54.7)		0.9^{g}	0.9^{g}	0.7^{g}

[a] In parentheses (k_w/k_b). [b] From Figure 1A–C fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [c] From Figure 1A–C fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [d] From Figure 2A–C fitted by eq 8 (k_b was obtained by correction with eq 10; see text). [e] From Figure 2A–C fitted by eq 9 (k_b was obtained by correction with eq 10; see text). [f] From eq 1. The errors here are not included and are higher than the one which comes from the fitting due to the reason expressed in the Experimental Section. They are estimated to be around 50%. [g] From eq 2. The errors here are not included and are higher than that which comes from the fitting due to the reasons expressed in the Experimental Section. They are estimated to be around 50%. $K_{BH} = 0.7 \pm 0.1$ from eq 9 for $W_0 = 10$ and 15. Parameter values calculated using 0.995 confidence level in nonlinear regression.

tively, [AOT] is the surfactant concentration, and $[\text{ketone}]_T$ is the total ketone concentration referred to total solution volume. It should be borne in mind that precise spectroscopic estimation of the constants is ruled out by the impossibility of having all the ketone at the interface, and therefore, the value of ϵ^b can only be estimated. The spectroscopic estimation of K_{ket} was therefore based on an analysis of the spectroscopic data using a fitting procedure with the ϵ^b as an adjustable parameter.

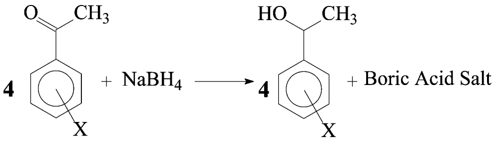
K_{ket} was also determined by using Ketelaar's equation[33–35] (2)

$$\frac{1}{A^{\lambda\text{isoo}} - A^{\lambda}} = \frac{1}{(\epsilon^f - \epsilon^b)[\text{ketone}]_T} + \frac{1}{(\epsilon^f - \epsilon^b)[\text{ketone}]_T K_{ket}} \frac{1}{[\text{AOT}]} \quad (2)$$

where $A^{\lambda\text{isoo}}$ is the absorbance in isooctane and the other terms are defined above. Plotting the left-hand side term of eq 2 vs 1/[AOT] gives the value of K_{ket} from the slopes and intercepts.

Results

The reactions of the ketones with $NaBH_4$ in water and in isooctane/AOT/water reverse micellar system yield the corresponding alcohols (see below) as previously reported in homogeneous media[36,37] and in normal micelles.[24]



X = H; Cl; OMe.

To elucidate how microheterogeneous media affect the reduction reaction several variables were investigated as follows.

Reaction in Water. Kinetic results were obtained in water at $[OH^-] = 0.1$ M by varying $[NaBH_4]_W$ between 0.01 and 0.15 M for AF, MAF, and CAF and are shown in Table 1, where the first-order rate constants, k_{obs} follow the sequence CAF > AF > MAF.

Reaction in the Water/AOT/Isooctane Reverse Micellar System. (1) Effects of AOT Concentration. Kinetics were studied at constant W_0, $[NaBH_4]_W$, and $[NaOH]_W$ and varying AOT concentrations between 0 and 0.4 M. Figure 1A–C show the kinetic results at $W_0 = 5$, 10, and 15 for CAF, AF, and MAF, respectively, where k_{obs} increases on increasing AOT concentrations over the whole range. These results show that the saturation of the ketones at the micellar interface is not reached in the surfactant concentrations range used, although for CAF the kinetic profiles show a more pronounced downward curvature. Moreover, data in Figure 1 A–C show that, for all the ketones, k_{obs} diminishes with increasing water content (W_0).

(2) Effect of $NaBH_4$ Concentration. To study the effect of $NaBH_4$ concentration, the reaction was carried out with 0.3 M of AOT at $W_0 = 5$, 10, and 15. Figure 2A–C shows the results where k_{obs} increase linearly with $[NaBH_4]_W$. Reactions are faster at low water content as was observed by varying [AOT].

(3) Effect of W_0. The effects of changing W_0 on k_{obs} keeping AOT and $(NaBH_4)_w$ concentrations constant are shown in Figure 3A–C for CAF, AF, and MAF, respectively. The value of k_{obs} increases with W_0 up to ~5 and then decreases until W_0 ~10 and then remains practically constant.

Discussion

In water, CAF is the most and MAF the least reactive ketone. These results are, as expected, because, the *m*-chlorine atom in CAF exerts a substrate inductive effect; consequently, it is the most reactive ketone. The reactions were carried out at [NaOH] = 0.1 M. Comparing values of the rate constants with the one obtained in more diluted aqueous NaOH ([NaOH] = 0.1 M versus [NaOH] = 0.0163 M),[24] a small acceleration of the reaction rate is observed probably due to the ionic strength of the media.

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In regard to the reaction environment the $NaBH_4$ is insoluble in isooctane, the ketones are poorly soluble in water,[24] and the anion BH_4^- has the same charge of the AOT interface reverse micelles. Considering all these aspects, reaction can only occur at the interface of the aggregates, with the surfactant providing a new region where the reactants can be in contact as previously found with other kinds of reactants and reactions in reverse micelles.[6-9,15,38,39] For these reasons, in the kinetic model we considered for BH_4^- only the equilibrium partitioning between the water and the reverse micellar interface and for the ketones only the partitioning between the organic phase and the reverse micellar interface.

Moreover, up to $W_0 < 8-10$, all the water is bound to Na^+ and at the ionic headgroup of the surfactant, and only above this value free water exists.[1,3-5,11] A quantitative model may be written based on the pseudophase treatment. It was considered that at $W_0 < 10$, only two pseudophases were present, the interface and the bulk organic solvent and all the BH_4^- resides at the interface (under this conditions no water pool is present), while the ketones are distributed between two environments. At $W_0 \geq 10$, the pseudophase model was extended to include three pseudophases (water pool, isooctane, and AOT), each of which is considered as being uniformly distributed in the total volume of the reverse micellar sistem.[6] In this way, we consider the distribution of the ketones between the organic pseudophase and the interface, and the distribution of $NaBH_4$ between the interface and the water pool where it will be repelled from an anionic interface.

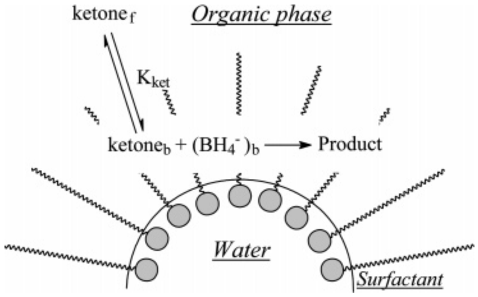
In this model, the distribution of the reactants among the pseudophases can be described by the partition constant, with solute concentrations in the micelles expressed as a function of the occupation number $n = [\text{solute}]_b/[\text{AOT}]$. In this sense, one avoids having to explicitly define the molar reaction volume of the interface,[5,6,10] and the concentration in square brackets refer to the analytical bulk concentration in moles per liter of total solution volume[5]

$$K_{\text{ket}} = \frac{n_{\text{ket}}{}^{b}}{[\text{ketone}]_f} \tag{3}$$

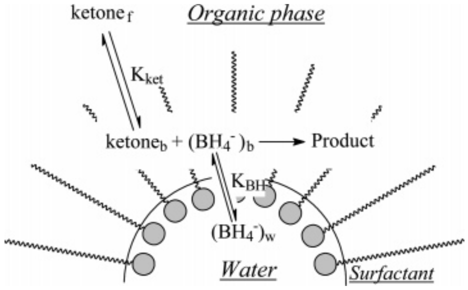
$$K_{\text{BH}} = \frac{n_{\text{NaBH}_4}{}^{b}}{n_{\text{NaBH}_4}{}^{w}} \tag{4}$$

where K_{ket} and K_{BH} are the distribution constants of the ketones and $NaBH_4$ between the organic phase and the interface and between the interface and the water pool, respectively. $n^b{}_{\text{ket}}$, $n^b{}_{\text{NaBH}_4}$, and $n^w{}_{\text{NaBH}_4}$ are the occupation numbers of the ketones and the $NaBH_4$ defined above, respectively. Sub- and superscripts f, b, and w indicate the organic phase, the micellar pseudophase, and the water pool, respectively. These equation applies at a fixed value of W_0 and when $[\text{substrates}]_T \ll [\text{AOT}]$. The occupation number is defined according to the place where the substrate is located inside the aggregate, and in the case of the ketone there is only the occupation number relative to the ketone at the interface ($n_{\text{ket}}{}^b = [\text{ketone}]_b/[\text{AOT}]$); on the other hand, $NaBH_4$ is wholly in the aggregate (reverse micelle surface and water pool, depending on the water content W_0); therefore, there are two occupation numbers relative to $NaBH_4$, the one relative to $NaBH_4$ at the surface ($n_{\text{NaBH}_4}{}^b = [\text{NaBH}_4]_b/[\text{AOT}]$) and the one relative to $NaBH_4$ in the water pool ($n_{\text{NaBH}_4}{}^w = [\text{NaBH}_4]_w/[\text{AOT}]$).[5]

SCHEME 1



SCHEME 2



At $W_0 < 10$ the mechanism summarized in Scheme 1 can be proposed[6,39] (curvature and relative size are arbitrary and drawn only for illustration purposes), and at $W \geq 10$ the mechanism shown in Scheme 2[6-8] can be proposed (curvature and relative size are arbitrary and drawn only for illustration purposes).

The rate of the reaction can be expressed by eq 5 at $W_0 < 10$ and by eq 6 at $W_0 \geq 10$

$$\frac{d[P]}{dt} = k'_b[\text{ketone}_b][\text{NaBH}_4]_T \tag{5}$$

$$\frac{d[P]}{dt} = k'_b[\text{ketone}_b][\text{NaBH}_4]_b \tag{6}$$

where [P] is the concentration of the obtained product and k'_b is the bimolecular interfacial rate constant. The concentrations in square brackets refer to the total volume of reverse micelles.

If $[\text{NaBH}_4]_T \gg [\text{ketone}]_T$, the reaction has a first-order kinetic form. Then with eqs 3–6, and the mass balance for the ketones and $NaBH_4$, we obtain the final expression for the rate (eq 7) and k_{obs} (eq 8 for $W_0 < 10$ and eq

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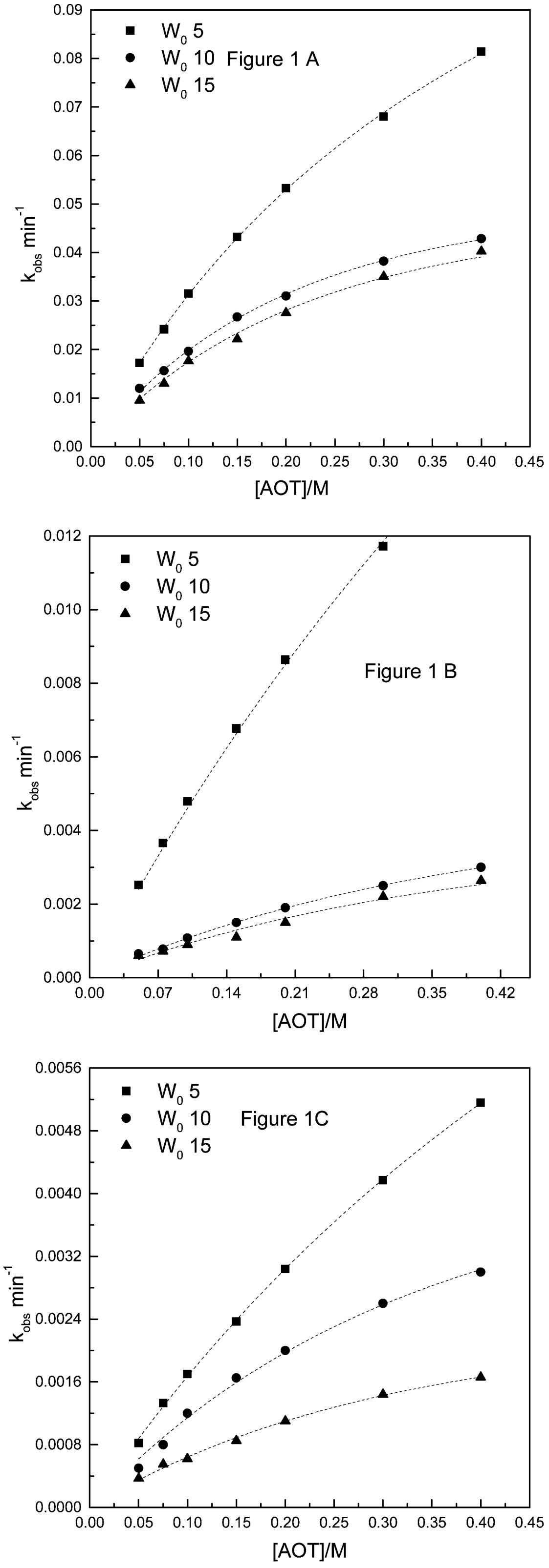

FIGURE 1. Dependence of k_{obs} on the AOT concentration for the reaction between ketones and $NaBH_4$ in water/AOT/isooctane reverse micellar system at different W_0: (A) [CAF] = 3 × 10^{-4} M; (B) [AF] = 3 × 10^{-4} M; (C) [MAF] = 5 × 10^{-5} M. In all cases, $[NaBH_4]_{waterpool}$ = 0.1 M. The dotted line shows the fitting by eq 8 (A) and eq 9 (B and C).

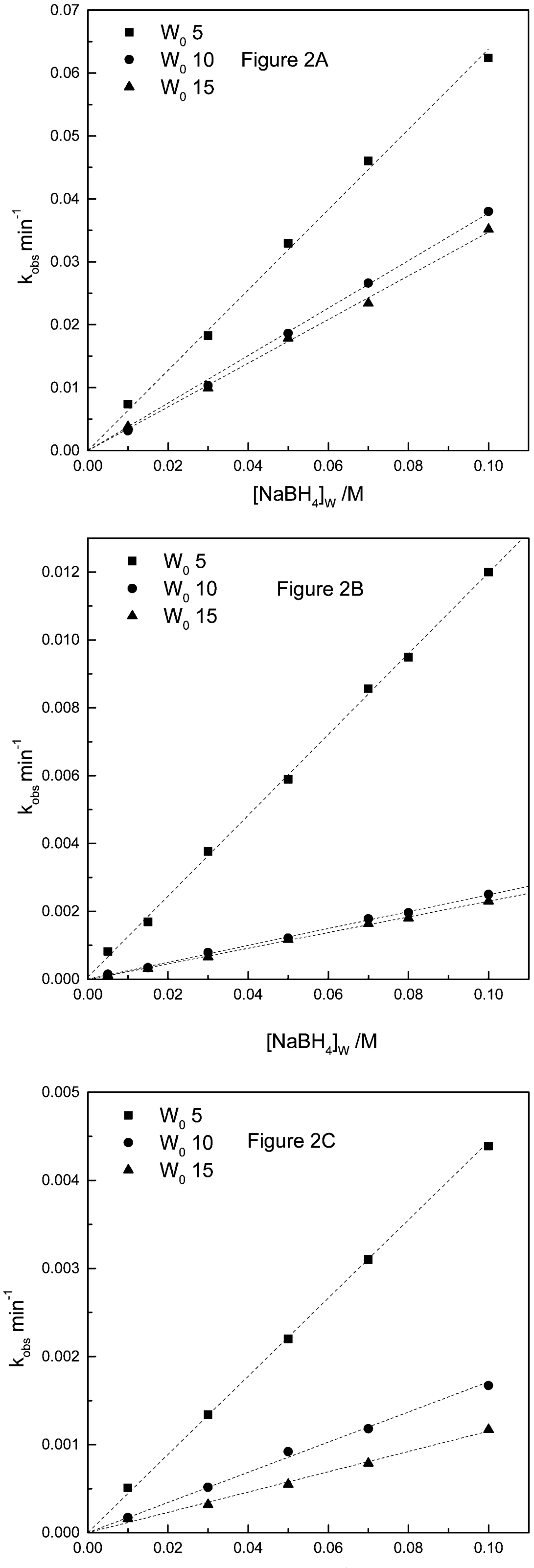

FIGURE 2. Variation of k_{obs} on the $NaBH_4$ concentration for the reaction between ketones and $NaBH_4$ in water/AOT/isooctane reverse micellar system at different W_0: (A) [CAF] = 3 × 10^{-4} M; (B) [AF] = 3 × 10^{-4} M; (C) [MAF] = 5 × 10^{-5} M. In all cases, [AOT] = 0.3 M. The dotted line shows the fitting by eq 8 (A) and eq 9 (B and C).

9 for $W_0 \ge 10$). Note that eq 9 reduces to eq 8 when K_{BH} is $\gg 1$, i.e., for $W_0 < 10$. with

$$\frac{d[P]}{dt} = k_{obs}[\text{ketone}]_T \tag{7}$$

$$k_{obs} = \frac{(4k'_b K_{ket}[\text{NaBH}_4]_T[\text{AOT}])}{(1 + K_{ket}[\text{AOT}])} \tag{8}$$

$$k_{obs} = \frac{(4k'_b K_{ket} K_{BH}[\text{NaBH}_4]_T[\text{AOT}])}{(1 + K_{ket}[\text{AOT}])(1 + K_{BH})} \tag{9}$$

To obtain the micellar second-order rate constants k_b for absolute comparison of reactivity in different media, the molar reaction volume at the interface, should be known. This can be taken from the molar volume of AOT in the reverse micellar system, which can be taken as 0.38.[6−8,40]

In this way, a conventional second-order rate constant (with conventional units $M^{-1}s^{-1}$) is given by[6,24]

$$k_b = k'_b \bar{v}$$

where $\bar{v}$ is the surfactant molar volume.

The increase of k_{obs} with increasing AOT concentrations (Figure 1A−C) at all W_0's could be due to the gradual transfer of the ketones from organic pseudophase into the reverse micellar surface; however, there is no interfacial saturation, reflecting the low values of the distribution constants. By fitting the experimental data with eq 8 (Figure 1A) and eq 9 (Figure 1B,C), the K_{ket} and k_b values are obtained and the results are in Table 1. The K_{BH} value is shown in the footnote of Table 1 and was only determined by fitting the experimental results with eq 9; i.e., it was not experimentally measured as the ketones distribution constants. Values of K_{ket} obtained by UV spectroscopy are in very good agreement with the kinetic values (Table 1). For all the ketones studied, k_b is lower at W_0 15 than at 5 as can be seen from Figure 1 A−C.

CAF is the most and MAF the least reactive in the micellar interface, as in water. This behavior reflects the electron-withdrawing and -donating properties of the aromatic substituents.[41] The ketones are less reactive in the micellar interface than in water, showing that this region at $W_0 = 5$ is less favorable for the reaction, probably reflecting the low BH_4^- affinity for the anionic interface. It must be noted that, at $W_0 = 5$, where all the $NaBH_4$ is located at the interface, reactivity of all the ketones, relative to those in water (k_b/k_w), are practically the same independent from the ketones' structure, but at higher water content, when BH_4^- is repelled from the interface, the rate constants are much lower in the aggregate than in water. It must be pointed that the properties of the interface vary much more at low water content than at a higher one.[5]

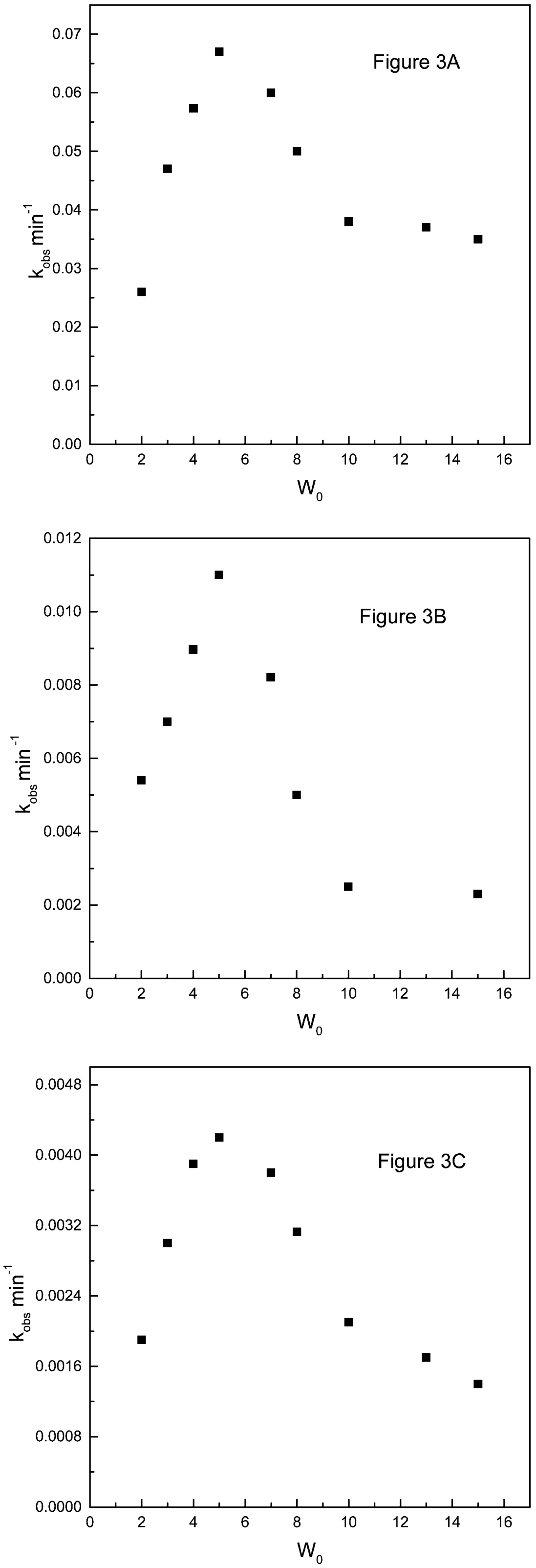

FIGURE 3. Variation of k_{obs} with respect to W_0 for the reaction between ketones and $NaBH_4$ in water/AOT/isooctane reverse micellar system: (A) [CAF] = 3×10^{-4} M; (B) [AF] = 3×10^{-4} M; (C) [MAF] = 5×10^{-5} M. In all cases, [AOT] = 0.3 M.

The partition constants for the ketones are quite small accordingly with the large affinity of the reactants for the organic pseudophase. These constants are practically independent of the water content, showing that the binding is to the interface and not to the water pool. The

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[40] Lang, J.; Jada, A.; Malliaris, A. *J. Phys. Chem.* **1988**, *92*, 1946.
[41] Stewart, R.; Teo, K. C. *Can. J. Chem.* **1980**, *58,* 2491.

m-Cl derivative has the largest distribution constant even for other kinds of reaction carried out in AOT reverse micellar systems, such as aromatic nucleophilic substitution of dinitrobenzene halides by aliphatic amines.[9] It seems that chlorine substituents, in their structure, increase the affinity for the AOT interface in reverse micelles.

Analyzing the distribution constant of NaBH at $W_0 =$ 10 and 15, the low value obtained suggests that the incorporation of $NaBH_4$ into the interface of AOT reverse micellar system is not favored due to electrostatic repulsion. Therefore, the ion largely resides in the water pool of the aggregate.

Equations 8 and 9 also show that, if [AOT] and W_0 are fixed, there should be a linear relationship between k_{obs} and $[NaBH_4]$, and by the introduction of the values of K_{ket} and K_{BH} the values of k_b could be recalculated for each system at $W_0 = 5$, 10, and 15 by fitting the new set of experimental data with these equations (Figure 2). The results are reported in Table 1. As shown, good estimates of k_b, within experimental error, are obtained by two independent methods.

In all the systems studied, the kinetic profile upon addition of water is quite peculiar and difficult to explain (Figure 3). At $W_0 > 5$, the kinetic profiles show that the reaction rate decreases with the water content until $W_0 = 10$, and then it remains practically constant. For $W_0 < 5$, the reaction rate increases with W_0. Our interpretation of those data is that up to $W_0 = 5$, water is solvating the AOT polar headgroup, making less relevant Na^+ BH_4^- ion pairing and leaving the ketones and BH_4^- more reactive. At $W_0 > 5$, the reactants are being solvated and rates decrease. At $W_0 \sim 10$, the water pool is formed and BH_4^- is repelled from the anionic interfacial reaction region. At $W_0 > 10$, $[BH_4^-]$ at the interface is practically constant as is the reaction rate. These results suggest that the reaction is taking place at the interface of the aggregate and not in the water pool because, as can be seen from Table 1, for all the ketones the reaction is faster in water.

Among the three ketones studied, acetophenone has shown the lowest value of K_{ket}. This is the one which is located more in the oil-side of the interface, far away from the $NaBH_4$. Maybe this is the explanation for the bigger difference found between the reaction rate in water and in the reverse micellar system for this ketone (see Table 1).

The highest value of $W_0 = 15$ is much lower than that of ca. 70 that can be reached in isooctane/AOT/water reverse micellar systems,[2,4,5] showing that BH_4^- and HO^- are disturbing the reverse micellar system, probably due to the salt concentrations inside the aggregates.[3,4,11]

Conclusions

The mechanism of reaction between different aromatic ketones and $NaBH_4$ was investigated in a water/AOT/isooctane reverse micellar system by UV spectroscopy. Application of a kinetic model based on the pseudophase formalism, which considers distribution of the ketones between the continuous medium and the interface and assumes that reaction takes place only at the interface, has enabled us to obtain values of the rate constants in the interface of the AOT reverse micellar system. At $W_0 = 5$, it was considered that all of the $NaBH_4$ is at the interface. At $W_0 = 10$ and 15, where there are free water molecules, partitioning between the interface and the water pool was also considered. The observed rate constants of reaction (k_{obs}) increase with increasing surfactant concentration for every ketone and at every water content (W_0) as a consequence of incorporating the substrates into the interface of the reverse micellar system, but saturation of the interface is never reached due to the low value of K_{ket}. For all the ketones studied the reactivity is lower at the micellar interface than in water, probably reflecting the low affinity for the anionic interface of BH_4^-.

The kinetic profiles upon water addition show maxima in rates at W_0 ca. 5: a probable explanation of this experimental evidence is that at low W_0 water is strongly interacting with the polar headgroup of the surfactant, leaving the ketones and the $NaBH_4$ (located at the interface) more reactive. Above this threshold, water molecules probably start to interact with the reactants, and once the water pool is formed, BH_4^- is repelled from the anionic interface where the reaction takes place.

These results provide a good model to predict micellar catalysis, in reverse micellar systems, for ketone reduction. Moreover, this study can be extended to control the stereoselectivity because the core of these aggregates, which are similar to the polar parts of enzymes, are the reactive centers of the whole system and can easily create a chiral environment for dissolving asymmetric solutes in their interiors.

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