

Promoting Mechanistic Changes: Solvolysis of Benzoyl Halides in Nonionic Microemulsions

P. Campos-Rey, C. Cabaleiro-Lago,* and P. Hervés

Department of Physical Chemistry, Faculty of Chemistry, University of Vigo, 36200 Vigo, Spain

Received: April 29, 2009; Revised Manuscript Received: July 22, 2009

Solvolysis of benzoyl halides has been studied in nonionic isooctane/Brij30/water microemulsions. The reaction takes place only at the microemulsion interface due to the low solubility of benzoyl halides. The variation of the properties (water content and hydration water nucleophilic character) of the microemulsion interface as the amount of water in the system decreases favors mechanistic changes in the solvolytic reaction. The true rate and equilibrium constants at the interface were obtained by means of the formalism of the pseudophase. Rate constant values at the interface change as the water content of the microemulsion is modified. The changes are consistent with a shift of mechanism from dissociative toward associative. The predominance of either dissociative or associative mechanism is dependent on the characteristics of the leaving group. The associative character decreases as the salient group of the benzoyl halides improves. Moreover, the associative pathway is strongly favored in the microemulsion system studied.

Introduction

The solvolytic reactions are well-known processes widely studied in different solvents.^{1–4} The reaction mechanism is highly sensitive to the properties of the reaction media. This makes those substrates suitable as probes for the investigation of complex media properties and the effect of additives on the structure of water.^{2–5} The mechanisms for the reaction of benzoyl halides can be classified according to its dissociative or associative character. The change from a dissociative to an associative pathway is defined by the nature of the substituent as well as by the leaving group. For example, the change of mechanism with increasingly electron-withdrawing substituents occurs much later for benzoyl chlorides than for benzoyl fluorides. The rate of the associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the leaving group.^{1,6} The reactivity in different solvents and solvent mixtures revealing a high sensitivity to the properties of the media has been reported by several groups.^{1,2,7} Moreover, benzoyl chlorides have been studied in different microheterogeneous media, such as micelles,^{8,9} vesicles,¹⁰ and microemulsions.^{11–14} Specifically, studies in both ionic and nonionic microemulsions show interesting aspects since both the rate and the mechanism of the reaction are modified.

Microemulsions are thermodynamically stable, macroscopically homogeneous mixtures of at least three components: a polar liquid, a nonpolar liquid, and a surfactant. At the microscopic level, the surfactant forms a film separating the two immiscible liquid subphases. The different compartments are available for the distribution of small solutes.^{15,16} This compartmentalization of the reactants allows the solubilization of a large variety of compounds of different hydrophobicity, hence overcoming solubility problems in organic and enzymatic reactions.^{17,18} Reactions carried out in microemulsions can be either inhibited, due to the distribution of reactants in different phases, or catalyzed by increasing the reactants local concentration due to the microheterogeneous nature of this media. Both types of behavior have been observed experimentally for

reactions that take place in the polar subphase and/or at the interface.^{19–21}

In a previous study,¹¹ we have shown that the special characteristics of a Brij30 nonionic microemulsion promote the associative pathway for substituted benzoyl chlorides in a higher extent than an ionic AOT microemulsion.^{11,13} In this work, we will analyze the effect of this Isooctane/Brij30/water microemulsion on the solvolysis of benzoyl halides to understand the influence of the system on substrates with different leaving group. Benzoyl fluoride solvolysis has, even in water, a stronger associative character than other benzoyl halides. The associative character of the reaction mechanism is expected to increase due to the favorable conditions for an associative pathway at the microemulsion interface. The obtained results show a strong shift from a partially dissociative pathway to a high associative pathway upon variation of the microemulsion composition which suggests an effective promotion of the associative pathway due to the intrinsic properties of the interfacial water.

Experimental Section

Poly(oxyethylene) dodecyl ether (Brij30), isooctane, benzoyl bromide (BzBr), benzoyl chloride (BzCl), and benzoyl fluoride (BzF) were supplied by Aldrich and used as supplied without further purification.

Kinetic measurements: Microemulsions were prepared by mixing isooctane, water (distilled and deionized), and 2 M Brij30 in isooctane solution in the appropriate proportions. The solvolysis reactions were followed spectrophotometrically by monitoring the decrease in absorbance of the aromatic reactants using a Hewlett-Packard 8453 UV–vis spectrophotometer and a Varian Cary 5000 UV–vis–NIR spectrophotometer, both fitted with thermostatted cell holders (all experiments were performed at 25.0 ± 0.1 °C). The wavelengths used for the kinetic studies fell in the range of 285–290 nm. Concentration for substrates was 1.6×10^{-4} M for the BzCl, 3.8×10^{-4} M for the BzBr, and 1.17×10^{-3} M for the BzF. Kinetic studies for BzBr and BzCl were satisfactorily fitted to the first-order integrated rate equations, while the method of initial rates was used for BzF due to its slow solvolysis. Rate constants were reproducible within 3%.

* Corresponding author. E-mail: celiaci@uvigo.es.

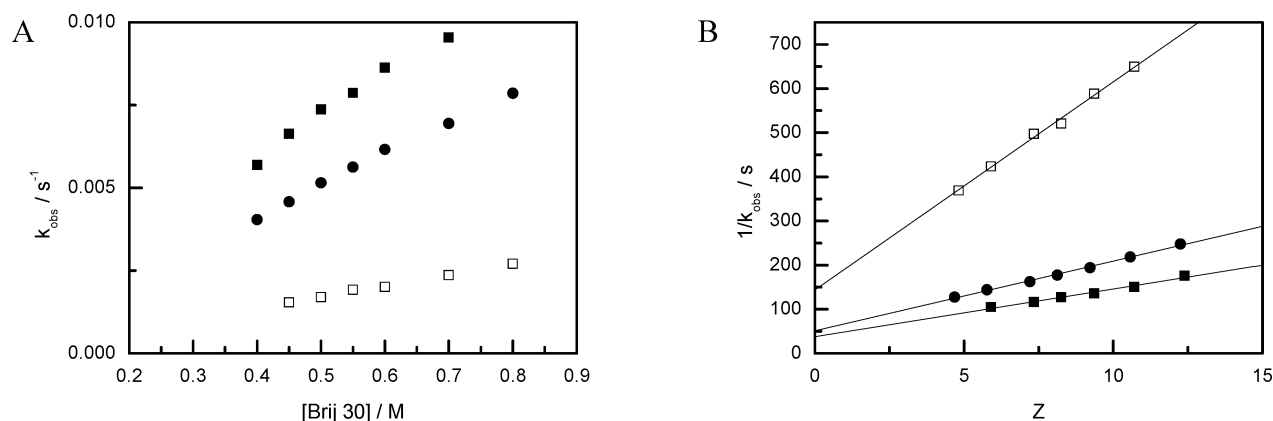
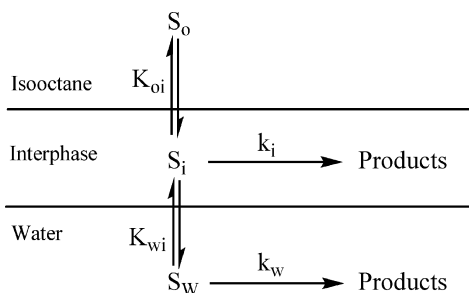


Figure 1. (A) Variation of the observed rate constant for the solvolysis of benzoyl halides with the concentration of Brij30 in microemulsions isooctane/Brij30/water at 25 °C at $W = 5$: (■) k_{obs} for BzBr, (□) $10k_{\text{obs}}$ for BzCl, and (●) 10^3k_{obs} for BzF. (B) Variation of the inverse of the observed rate constant for the solvolysis of benzoyl halides with Z in microemulsions isooctane/Brij30/water at 25 °C at $W = 5$: (■) $1/k_{\text{obs}}$ for BzBr, (□) $1/10k_{\text{obs}}$ for BzCl, and (●) $1/10^3k_{\text{obs}}$ for BzF.

SCHEME 1



Results

The effect of the microemulsion composition on the solvolysis reaction for the benzoyl halides has been analyzed by varying the concentration of Brij30 in the system, keeping the ratio between water and surfactant ($W = [\text{water}]/[\text{Brij30}]$) constant.

Figure 1A shows the observed pseudofirst-order rate constants (k_{obs}) for the solvolysis reaction for the studied benzoyl halides. For all cases, the observed rate constant increases as the concentration of the surfactant increases due to the increase of reactant local concentration at the interface.

For a quantitative analysis of the microemulsion effect on the solvolysis, it is necessary to propose a model which allows the determination of the concentration of reactants in the different regions of the microemulsion as well as the corresponding rate constants. The pseudophase model,^{22,23} originally developed for aqueous micellar systems, has been extended to other colloidal aggregates such as vesicles and microemulsions with satisfactory results.^{24–28} This model considers the microemulsion divided in three regions (water, oil, and interface) between which the reactants are distributed.^{23–25} In the most general scenario, the benzoyl halides can be distributed in the three pseudophases, and consequently the reaction can take place at both the aqueous pseudophase and the interface of the microemulsion (see Scheme 1).

According to the model proposed, the observed rate constant for this system is expressed as

$$k_{\text{obs}} = \frac{k_i K_{oi} K_{wi} + k_w K_{oi} W}{K_{oi} K_{wi} + K_{oi} W + K_{wi} Z} \quad (1)$$

where k_i and k_w are the rate constant for the solvolysis at the interface and in bulk water, respectively, and the distribution

TABLE 1: Influence of W on the Intercept/Slope Ratio for the Solvolysis of Benzoyl Halides in Isooctane/Brij30/Water at 25 °C

W	intercept/slope ratio		
	BzCl	BzBr	BzF
3.0	3.0	3.1	—
4.0	5.2	3.6	—
5.0	3.0	3.5	3.2
6.0	2.2	3.0	—

constants between oil and interface, K_{oi} , and water and interface, K_{wi} , are defined as

$$K_{oi} = \frac{[S]_i}{[S]_o} Z; \quad K_{wi} = \frac{[S]_i}{[S]_w} W \quad (2)$$

where concentrations refer to the total volume of the system and Z and W are defined as the molar ratio $Z = [\text{isooctane}]/[\text{Brij 30}]$ and $W = [\text{water}]/[\text{Brij30}]$.

Equation 1 can be transformed into

$$\frac{1}{k_{\text{obs}}} = \frac{K_{oi} K_{wi} + K_{oi} W}{k_i K_{oi} K_{wi} + k_w K_{oi} W} + \frac{K_{wi}}{k_i K_{oi} K_{wi} + k_w K_{oi} W} Z \quad (3)$$

which predicts a linear dependence between the inverse of the observed rate constant and Z. Figure 1B shows the experimental results for the different benzoyl halides. A clear linear dependence between the inverse of the k_{obs} constant and Z is observed at a constant value of $W = 5$.

From eq 3, the ratio intercept/slope gives the following expression

$$\frac{\text{intercept}}{\text{slope}} = K_{oi} + \frac{K_{oi}}{K_{wi}} W \quad (4)$$

Equation 4 predicts an influence of W in the defined ratio.

However, the results obtained for the different substrates and for different values of W show that the ratio intercept/slope remains fairly constant with W (see Table 1). This fact indicates that the reaction only takes place at the interface of the microemulsion. Similar behavior has been observed previously

SCHEME 2

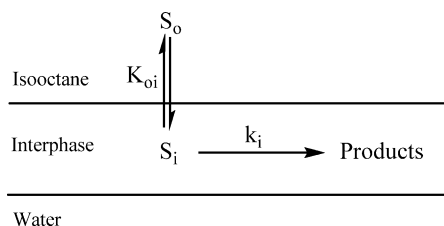


TABLE 2: Influence of W on k_i (s^{-1}) Values for Solvolysis of Benzoyl Halides in Isooctane/Brij 30/Water Microemulsions at 25 °C

W	k_i (s^{-1})		
	BzBr	BzCl	BzF
2	$3.16 \cdot 10^{-2}$	$1.60 \cdot 10^{-3}$	$2.75 \cdot 10^{-5}$
2.5	$2.92 \cdot 10^{-2}$	$1.07 \cdot 10^{-3}$	$2.49 \cdot 10^{-5}$
3	$2.71 \cdot 10^{-2}$	$9.47 \cdot 10^{-4}$	$2.27 \cdot 10^{-5}$
3.5	$2.67 \cdot 10^{-2}$	$7.81 \cdot 10^{-4}$	—
4	$2.64 \cdot 10^{-2}$	$7.49 \cdot 10^{-4}$	$2.08 \cdot 10^{-5}$
5	$2.77 \cdot 10^{-2}$	$7.01 \cdot 10^{-4}$	$2.04 \cdot 10^{-5}$
6	$3.24 \cdot 10^{-2}$	$7.83 \cdot 10^{-4}$	$2.04 \cdot 10^{-5}$
6.5	—	—	$2.08 \cdot 10^{-5}$
7	$3.49 \cdot 10^{-2}$	$8.25 \cdot 10^{-4}$	$2.08 \cdot 10^{-5}$
8	$3.86 \cdot 10^{-2}$	$9.04 \cdot 10^{-4}$	—
water	80.8	1.10	$1.78 \cdot 10^{-3}$

for different substrates (e.g., substituted benzoyl chlorides) in microemulsions.^{11,13}

Taking this result into consideration, the reaction Scheme 1 can be simplified to Scheme 2. Consequently, the observed rate constant can be expressed as

$$k_{\text{obs}} = \frac{k_i K_{oi}}{K_{oi} + Z} \quad (5)$$

Equation 5 can be rewritten to express the observed linearity between the inverse of k_{obs} and Z

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k_i} + \frac{Z}{k_i K_{oi}} \quad (6)$$

On the basis of the simplified model, the ratio between the intercept and slope provides the distribution constant, K_{oi} , for each microemulsion composition (eq 6). Consistent values, in the same order of magnitude, were obtained for all substrates and W values (although some deviations can be observed due to the uncertainty in the determination of the intercept). Taking this into consideration, approximate mean values of the distribution constant between oil and interface for the three substrates were determined: $K_{oi}^{\text{BzBr}} = 3.4$, $K_{oi}^{\text{BzCl}} = 3.0$, $K_{oi}^{\text{BzF}} = 3.2$.

According to the model, once the distribution constants of the substrates are known, it is possible to obtain the true rate constant at the interface of the microemulsion, k_i . These values allow us to study the effect of the water content of the microemulsion (proportional to W) for a constant value of Z . Table 2 shows the results obtained for different values of W for $Z = 7$ using the mean values of the distribution constant (see previous paragraph).

The reaction is inhibited for all substrates when it is performed in the studied microemulsion; i.e., the rate constant at the microemulsion is smaller than the rate constant in water (see Table 2) for all the W values studied. Figure 2 shows that the

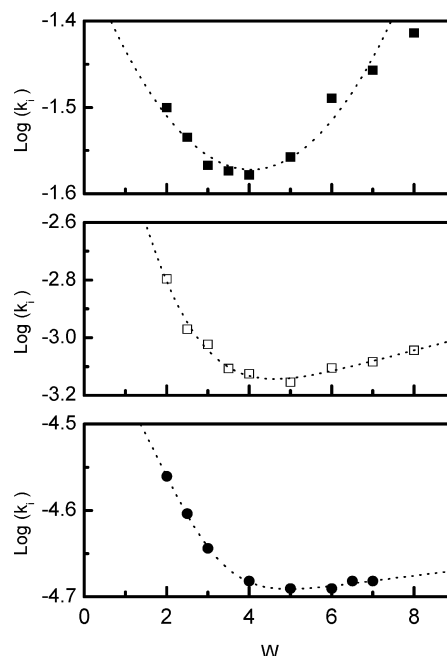
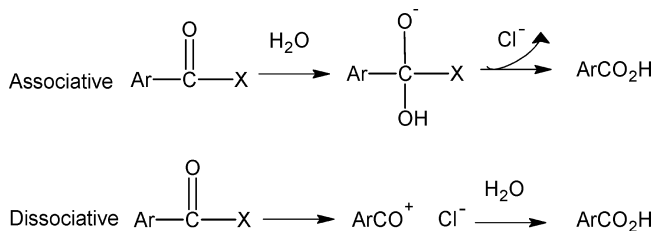


Figure 2. $\text{Log}(k_i)$ vs W for the solvolysis reaction of (■) BzBr, (□) BzCl, and (●) BzF in a nonionic microemulsion at 25 °C. Dashed lines are a guide for the eye.

SCHEME 3



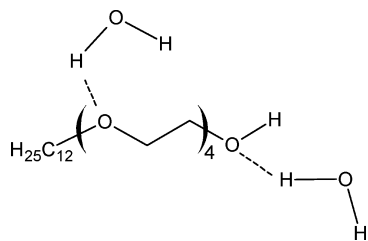
variation of the rate constant with W does not have a monotonous decreasing or increasing trend. Instead a change of trend or leveling off is observed.

Discussion

The solvolysis of benzoyl halides is strongly affected by the media properties as well as by the substituents on the ring and the nature of the leaving group. Different reaction mechanisms have been proposed for alkyl and acyl centers. Some authors propose a weakly defined borderline mechanism.¹ Other studies of a series of benzoyl halides with different substituents in a variety of solvents found, in few cases, the formation of acylium ions by ionization as a rate-determining step,¹ whereas substrates with more electrophilic substituents proceed by an association dissociation mechanism with a rate-determining association step.^{1,7,29} We can classify the mechanism of solvolysis of benzoyl halides into two distinct mechanisms in terms of the characteristics of the transition state: a dissociative mechanism, involving ionization to give an acylium ion of short lifetime, and an associative mechanism that can be either a carbonyl addition–elimination mechanism with the formation of an unstable tetrahedral intermediate or a concerted nucleophilic attack with little or no bond breaking (Scheme 3).

The rate constant at the interface for the studied substrates shows a strong dependence with the water content of the microemulsion and the nature of the leaving group. The effect of the microemulsion and the leaving group can be explained

SCHEME 4



in terms of this balance of mechanism which will result in the final overall kinetic behavior.

Effect of Microemulsion Composition. The influence of microemulsion composition on the reaction rate will depend on the predominant reaction mechanism. The dissociative pathway is strongly affected by the properties of the medium, especially the polarity and the ability to solvate the leaving group. The reaction rate will increase with increasing polarity for a reaction that follows the dissociative pathway. The associative pathway is less polarity dependent but more affected by the nucleophilic character of the nucleophile involved in the reaction, in this case water. A mechanistic change from one mechanism to another can be achieved by changing the properties of the media.

The analysis of the variation of k_i with the water content of the microemulsion reveals that for BzBr, initially, k_i decreases as the water content (proportional to W) decreases (Figure 2). Previous studies with a fluorescence polarity probe, Nile Red, show that the interface of the microemulsion is less polar than water, with a polarity similar to 2-propanol, and that the polar character decreases as W decreases.¹¹ The low polarity and electrophilic character imply a reduced ability to solvate the leaving group at the microemulsion interface which will be reflected in lower solvolysis reaction rates. The following increase of the rate constant when W continues to decrease can not be explained by means of a dissociative mechanism. For that reason, a contribution of an associative channel is assumed.

In general, the rate constant of benzoyl halides always decreases regardless of the reaction mechanism when polarity decreases.³⁰ If the associative mechanism, which is less sensitive to polarity effects, contributes to the overall reaction rate, the observed decrease, with decreasing polarity, will be less sharp (due to the associative contribution to the reaction rate). Nevertheless, the opposite behavior can be achieved in microheterogeneous media^{11,13} and alcohol/water mixtures.³¹

For AOT and Brij microemulsions, the rate constant increases as the polarity decreases when the associative mechanism is present or predominant. For both types of microemulsions, the nucleophilic character of water at the interface is higher than bulk water. For Brij30 microemulsions, NMR data show that the nucleophilic character of the water at the interface increases due to the hydration of the EO groups of the surfactant (see Scheme 4) at low water content.¹¹ The hydration of the headgroup tends to increase the electron density of protons in water molecules and consequently disrupts the hydrogen bond network. This effect is statistically more pronounced at lower W and increases the nucleophilic character of the interfacial water. The progressive increase of nucleophilicity as W decreases would favor the associative pathway, hence, an increase of reaction rate is observed when the water content decreases. Similar effects are observed for AOT microemulsion even though the nucleophilicity of water at the AOT interface is lower than for the Brij30 microemulsion. This difference arises due to compensatory effects between the AOT head groups and the counterions.¹¹ The interactions between the counterions (Na^+)

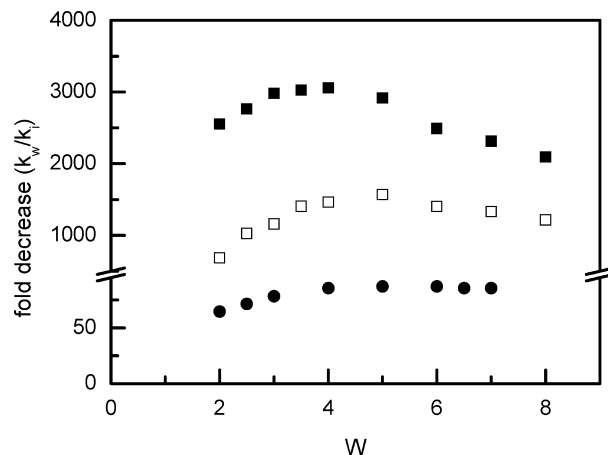


Figure 3. Inhibitory effect (k_w/k_i) for the solvolysis of (■) BzBr, (□) BzCl, and (●) BzF microemulsions isooctane/Brij30/water at 25 °C.

and water molecules reduce the nucleophilic character of water. Due to this compensation effect, the percentage of associative character in the solvolysis of BzBr in the AOT microemulsion is lower than in the Brij30 microemulsion.

Consequently, in the case of benzoyl bromide we can clearly postulate that two reaction pathways, associative and dissociative, contribute to the overall reaction rate. The contribution of each pathway changes as the properties of the media are modified. The dissociative reaction rate is reduced at low W due to the decrease of polarity at the interface and the less efficient solvation of the leaving group. On the other hand, the associative pathway rate increases due to the increase of the nucleophilic character of the interfacial water due to the low hydration of the head groups of the surfactant.

The trend of k_i when changing W varies between the three substrates studied (Figure 2). BzBr shows a clear change in the trend of k_i with different values of W . At lower W , k_i decreases with water content, while over $W = 4$ k_i increases with water content. This change is not so obvious for the other two substrates. The increase of the rate constant when the polarity of the microemulsion increases is much more moderate for BzCl, and no significant increase is observed for BzF. The increase of rate constant with increasing water content for W over 4 indicates that the dissociative pathway becomes a relevant contributor to the overall reaction rate. If a similar contribution of the dissociative mechanism would be in place for the BzCl and BzF substrates, a similar increase should be observed. This is also the case for BzCl but to a much more moderate degree and at higher values of W than for BzBr. The difference on the point of change of trend suggests a different balance of the associative and dissociative pathways in the reaction mechanism for BzBr and BzCl. In the case of BzF, k_i decreases with W and levels off at high W values. The leveling off of k_i could indicate that at high W values a weak contribution of the dissociative pathway starts; however, the experimental results cannot support this hypothesis. Therefore we can assume that the associative channel is predominant for the solvolysis reaction of BzF in the whole W range studied.

Effect of the Leaving Group. Brij30 microemulsion causes, in all studied substrates, a reduction of the reaction rate with respect to the reaction in water due to the lower polarity of the microemulsion interface as discussed above.¹¹ In the case of BzBr, a ~ 2500 -fold decrease in reaction rate is observed when going from bulk water to a microemulsion with $W = 2$. This inhibition increases to ~ 3000 for $W = 4$ and decreases to ~ 2000 for $W = 8$ (Figure 3). This strong inhibition effect can be

consistent with a dissociative mechanism which is strongly affected by the polarity of the media. However, the difference observed between the reaction in water and microemulsion for *p*-methoxybenzoyl chloride is much higher ($\sim 12\,000$). This substrate reacts via a pure dissociative mechanism as shown by the strong inhibition effect when the polarity of the media decreases at the microemulsion interface.¹¹ Taking this into consideration, a pure dissociative pathway can be ruled out.

The extent of inhibition (k_w/k_i) drastically changes from one benzoyl halide to another. The decrease is smaller for BzCl (from ~ 1500 -fold at $W = 5$ to 700 at $W = 2$) and even smaller, and almost constant, for the BzF, ~ 75 (see Figure 3). The fact that the observed inhibition from going from bulk water to microemulsion depends on the leaving group is indicative for the formation of different transition states for each benzoyl halide. The observed smaller effect of the polarity on the reaction rate may indicate a shift toward a more associative mechanism. For a reaction following an associative mechanism the decrease of polarity will reduce the reaction rate but not as drastically as for a reaction following a dissociative pathway. Therefore, a process less affected by the reduction of polarity must have a higher associative character. With this in mind, the results for the investigated benzoyl halides indicate that the reaction mechanism of the solvolysis of benzoyl halides gains associative character as we move along the series BzBr < BzCl < BzF.

However, a comparison with a substrate, *p*-nitrobenzoyl chloride, which undergoes solvolysis purely via an associative mechanism, rules out a pure associative mechanism for the studied substrates. The solvolysis of *p*-nitrobenzoyl chloride is catalyzed in Brij30 nonionic microemulsion.¹¹ The reaction rate is higher than in water due to the extremely favorable conditions of the microemulsion interface for the associative pathway. Similar behavior would be expected if BzF would react through a mechanism with a strong associative character. However, for BzF the reaction is still inhibited in microemulsion although to a much lesser extent than the other two substrates.

The variation on the behavior of the different halides in microemulsion must reside consequently on the nature of the leaving group. The leaving group needed for solvation must have an important role for a reaction following the dissociative mechanism. Due to the small size, F^- will be the most sensitive leaving group, in the investigated series, to small changes in polarity and electrophilic character of the microemulsion (greater necessity for solvation). However, according to experimental results (see Figures 2 and 3), the opposite is observed. The solvolysis of the BzF is less sensitive to the variation of the polarity, indicating that the solvolysis of BzF mainly follows the associative reaction pathway. On the other hand, the solvolysis of BzBr is more sensitive to the variation of the media conditions indicating that its solvolysis reaction presents a higher dissociative character.

A comparison of the reaction rates for the different halides confirms that the solvolysis reaction is taking place via a balance of different reaction mechanisms. Figure 4 shows the variation of the quotients k_{Br}/k_{Cl} , k_{Br}/k_F , and k_{Cl}/k_F with W . Two important facts can be observed. First, the ratios in bulk water ($k_{Br}/k_{Cl} = 73$, $k_{Br}/k_F = 46 \cdot 10^3$, and $k_{Cl}/k_F = 620$) and in microemulsions are different. In all cases, the ratios are smaller in microemulsions than in bulk water. The second important observation is that these relationships do not remain constant as the water content of the microemulsion varies.

The solvolysis of *p*-nitrobenzoyl halide in aqueous solutions does not show any dependence of the rate constant on

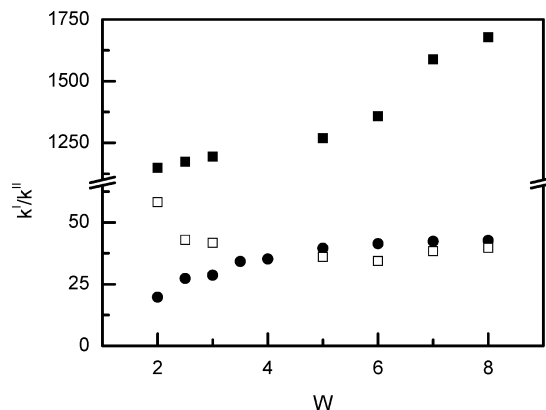


Figure 4. Variation of (■) k_{Br}/k_F , (□) k_{Cl}/k_F , and (●) k_{Br}/k_{Cl} ratios with W for the solvolysis of benzoyl halides in isooctane/Brij30/water microemulsions.

the leaving group. The reason for this is that the main reaction mechanism has an associative character where no bond breaking of the leaving groups occurs in the transition state, hence there is no effect of the leaving ability of the halide ions. In the case of *p*-nitrobenzoyl halides, k_{Cl}/k_F is quite low (1.2) which indicates an associative mechanism.¹ This ratio increases to $k_{Cl}/k_F = 35$ for the reaction of methyl halides in water³² that takes place by means of a S_N2 process. For the solvolysis of 4-(dimethylamino)-benzoyl halide, a value of $k_{Cl}/k_F = 3 \times 10^7$ was observed.¹ This reaction occurs by a dissociative path, in which the electrophilic solvation is the main determining factor in the reaction rate, leading to a more pronounced effect of the leaving group. For the substrates studied in this work, the ratio k_{Cl}/k_F falls in the range 35 to 60 which is much lower than the expected value for a pure dissociative process, larger than that reported for the associative pathway and close to the value for a S_N2 process, indicating a concerted pathway. Besides, the 13-fold decrease when going from water ($k_{Cl}/k_F \cong 620$) to Brij30 microemulsions clearly indicates that the contribution of the dissociative mechanism decreases in the presence of microemulsions.

To explain the variation of the relationships k_{Br}/k_{Cl} , k_{Br}/k_F , and k_{Cl}/k_F with W , it is necessary to recall the different influence that the water polarity and W have on the rates for the associative and dissociative processes. If the reaction took place through a pure associative mechanism, then the BzBr, BzCl, and BzF solvolysis reactions would show the same dependence on W , which means that the quotients k_{Br}/k_{Cl} , k_{Br}/k_F , and k_{Cl}/k_F would remain virtually constant since the associative mechanism is not affected by the solvation of the leaving group. On the other hand, if the reaction takes place by means of a dissociative mechanism, the electrophilic solvation of the leaving group would be the main determining factor in the reaction rate as a result of differences in the electronegativity of the atoms on which the negative charge is located.³³ The necessity for solvation follows the sequence $F^- > Cl^- > Br^-$, and consequently the relationships k_{Br}/k_{Cl} , k_{Br}/k_F , and k_{Cl}/k_F should increase as W decreases.

We can see in Figure 4 the observed experimental behavior. The decrease in the relationships k_{Br}/k_{Cl} and k_{Br}/k_F with the reduction of W is consistent with a shift of mechanism from dissociative to associative, with a higher decrease in the dissociative contribution for the solvolysis of BzBr than for BzCl and BzF as W decreases. The rate of solvolysis through the dissociative pathway of BzBr decreases with W ; however, the relative decrease in the rate of solvolysis of BzCl or BzF is much less pronounced since the mechanism has a less dissocia-

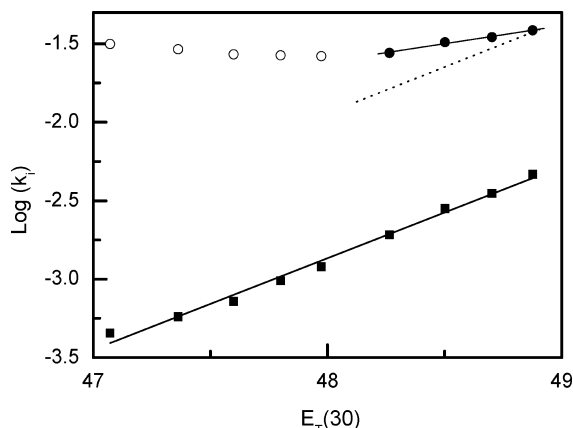


Figure 5. Correlation between $\log(k_i)$ and $E_T(30)$ polarity parameter for (■) *p*-methoxybenzoyl chloride and (●) BzBr. Solid lines indicate linear fit, and dashed line indicates expected slope for a dissociative mechanism.

tive character, which means that k_{Br}/k_{Cl} and k_{Br}/k_F will decrease with W . In contrast, the ratio k_{Cl}/k_F (Figure 4) shows a much lower dependency with W and remains practically constant along the whole W range (certain deviation can be observed for low W values that can come from uncertainties in the rate constant value calculations). A constant k_{Cl}/k_F ratio implies that the mechanism for these two substrates has a high associative character, and it is independent of the nature of the leaving group.

The quotient between the reaction rates for the halides whose reaction mechanism is either mainly associative or dissociative results in a predictable variation of k_{Br}/k_{Cl} , k_{Br}/k_F , and k_{Cl}/k_F with W . When both mechanisms coexist in either of the two halides, the variation of these relationships depends on W and the magnitude of the rate constants. Our experimental results are complex because we discuss reactions that proceed through different mechanisms. Solvolysis of BzBr is predominantly dissociative, whereas for BzCl and BzF the associative pathway is more important; however, in all cases, both associative and dissociative mechanisms coexist in different percentages.

To finally assess the amount of dissociative contribution to the reaction mechanism, the rate constant values were plotted against the polarity of the interface indicated by the empiric polarity parameter $E_T(30)$.³⁴ A fluorescence probe, Nile Red, was used to obtain the values of $E_T(30)$ at different W . In the case of a dissociative mechanism, a good correlation between $\log(k_i)$ and a polarity indicator can be found.^{11,13} On the other hand, deviation of the correlation would be observed for associative reactions. In Figure 5, a good linear correlation for the *p*-methoxybenzoyl chloride, which reacts by means of a dissociative mechanism, is shown.¹¹ In the case of the BzBr, only a linear correlation can be found at high polarity values, i.e., at high microemulsion water content. However, the slope of the correlation greatly differs from the expected for a dissociative reaction which could indicate a lesser sensitivity to the electrophilic character of the interfacial water.¹² The correlation is worse or none for the other two substrates. The deviations of the correlation between $\log(k_i)$ versus E_T are a consequence of the change of solvolysis mechanism from an extreme where the reaction takes place with a high dissociative character to another extreme where the associative mechanism predominates.

Conclusions

The solvolysis reaction of benzoyl halides is affected by nonionic microemulsions. By analyzing the real rate constant at the interface of the microemulsion, we can conclude that the mechanism of solvolysis for those substrates has a contribution from both reaction pathways, associative and dissociative. However, the associative/dissociative character of the reaction changes depending on the nature of the leaving group. In the case of the worst leaving group, fluoride ions, the predominant mechanism is associative and the associative character decreases as the leaving group solvation ability increases. In the case of BzBr, a stronger contribution of the dissociative mechanism can be observed and is evident at high water content values. This kind of nonionic microemulsion offers an excellent system for the study of solvolysis mechanism contributions and shift due to the low polarity at the interface and the enhancing of the nucleophilic character of the water due to the effect of the headgroup of the surfactant.

Acknowledgment. C.C.L. acknowledges the Isidro Parga Pondal Program fellowship (Xunta de Galicia, Spain). This work has been supported by the Spanish Ministerio de Educación y Ciencia (Project CTQ2007-64758).

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JP9039463