Kinetics of the basic hydrolysis of *O*-alkyl *O*-aryl chloromethylphosphonates in the sodium bis(2-ethylhexyl)sulfosuccinate–decane–water reverse micellar system

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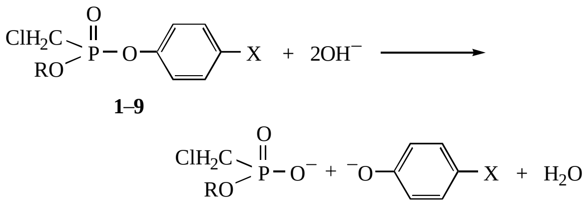
The reactivity of the substrates in the title system is mainly determined by the electronic effect of substituents and slightly influenced by their hydrophobicity.

Reverse micelles and microemulsions are of interest because of their biomimetic properties.[1–6] Previously,[7,8] the influence of the nature of surfactants on the reactivity of phosphorus acid esters in reverse systems has been investigated. The aim of this work is to examine the dependence of the micellar rate effect of the reverse systems on the substrate structure. We studied the basic hydrolysis of *O*-alkyl *O*-aryl chloromethylphosphonates **1**–**9** in the sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–decane–water reverse micellar system (Scheme 1).

Substrates **1**–**9** were prepared according to the published procedure.[9] Commercial AOT (Sigma) and sodium hydroxide were used without further purification. Decane was distilled prior to use. Microemulsions were prepared by mixing AOT, decane and doubly distilled water and shaking vigorously until a transparent solution was obtained; the molar ratios $W = [H_2O]/[AOT]$ and $Z = [decane]/[AOT]$ lied within the ranges 9.8–37.6 and 5–22, respectively. According to the AOT phase diagram,[10] the solutions used were reverse micellar solutions.



1–**9**

1 R = Et, X = NO_2
2 R = Bu, X = NO_2
3 R = n-C_6H_{13}, X = NO_2
4 R = Et, X = Br
5 R = Et, X = H
6 R = X = Et
7 R = Et, X = Bu
8 R = Et, X = n-C_8H_{17}
9 R = Et, X = i-$C_{12}H_{25}$

Scheme 1

Kinetic measurements were performed in freshly prepared transparent solutions containing all the components, to which a substrate was added. The reaction was monitored by the absorption of the leaving group. A Specord M-400 spectrophotometer with temperature-controlled cell holders was employed. All runs were performed at a substrate concentration of 5×10^{-5} mol dm^{-3} with a large excess of sodium hydroxide so that the first-order kinetics was followed. The observed rate constants (k_{obs}) were determined from the equation: $\ln(A_\infty - A) = -k_{obs}t + \text{const}$, where A and A_∞ are the absorbance of micellar solutions at the point t in time and after completion of the reaction, respectively. The k_{obs} values were calculated using the weighted least-squares computing methods from the mean of at least three independent determinations differing by 4%. Experiments were performed at AOT concentrations between 0.2 and 0.8 mol dm^{-3} with the water/AOT mole ratio W ranging from 9.8 to 37.6.

In water with no surfactant added, a minor decrease in the reactivity of **1**–**3** towards the OH$^-$ ion is observed due to an increase in the steric hindrance at the electrophilic phosphorus atom with the alkyl chain length. It is well known that the nature of a leaving group essentially influences nucleophilic substitution reactions. The higher stabilization of the electron-rich atom of the leaving group, the higher the reactivity of the substrate is. Thus, electron-seeking substituents favour the reaction, whereas electron-releasing ones retard it. In the series **1**,**4**–**9**, a high sensitivity towards the substituent X is observed for **1**,**4**–**6** phosphonates. A reduction in the reactivity within this series is due to the weakening of the electron-seeking effect of X, which results in destabilization of the leaving group. In the series **6**–**9**, a smoother decrease in the reactivity is observed because the positive electronic effect increases with the alkyl chain length.[11] Moreover, a steric hindrance at the pentacoordinated phosphorus atom in the S_N2 P transition state can be responsible for this decrease in the reactivity.

Reverse micellar systems are thermodinamically stable fluids composed of water and oil domains separated by a surfactant monolayer, which reduces an unfavourable oil–water contact.[12,13] In accordance with the pseudo-phase approach, nano-sized water droplets, a surfactant monolayer with polar head groups turned into the micellar interior and hydrophobic tails at the exteriors and oil are considered as separated pseudo-phases.[14] In general, the solubilization of reagents and their interaction can occur in all the pseudo-phases. An increase in local reagent concentrations and a change in their microenvironments (micropolarity, solvation, *etc.*) are responsible for the reactivity of the compounds on their transfer to the micellar pseudo-phase.[15] Thus, a source of catalysis or inhibition of reactions in micelles can be elucidated only if local reagent concentrations and intrinsic rate constants for various microphases can be obtained from the

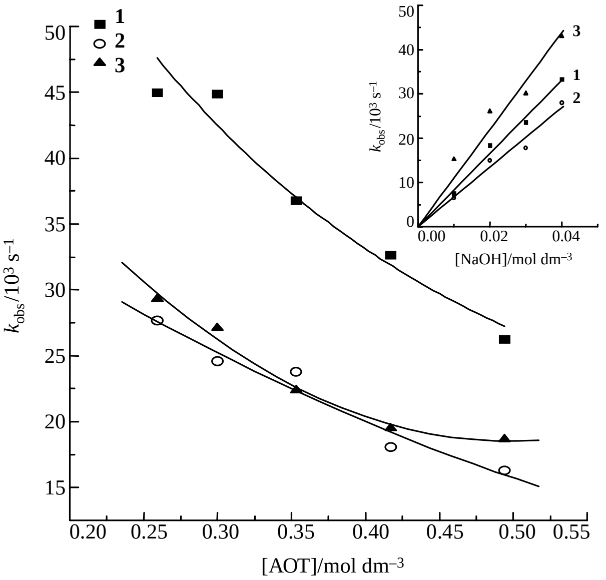


Figure 1 Observed rate constants of the basic hydrolysis of **1**–**3** in the AOT–decane–water micellar system as functions of surfactant concentration (25 °C, W = 15.1, 0.02 M NaOH). Insert: the observed rate constants of the basic hydrolysis in the AOT–decane–water micellar system as functions of NaOH concentration (25 °C, W = 15.1, 0.04 M AOT). The curve numbers in the insert correspond to the substrate numbers in Scheme 1.

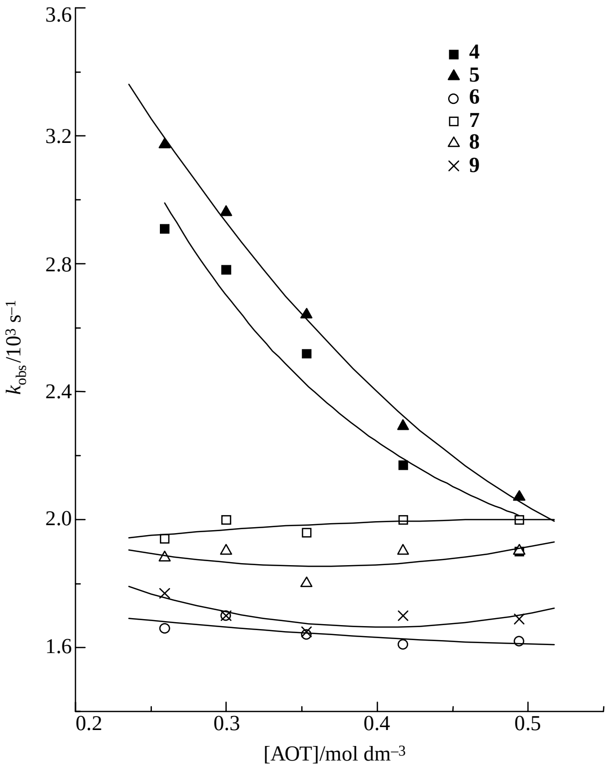


Figure 2 Observed rate constants of the basic hydrolysis of **4**–**9** in the AOT–decane–water micellar system as functions of surfactant concentration (25 °C, $W = 15.1$, 0.02 M NaOH).

overall apparent rate data. Presently, the kinetic models that give access to these intrinsic reactivity constants are still scarce. A pseudo-phase model analogous to that widely used for reactions in direct micelles and which assumes competition between reactions in three microphases (oil, water and the interface) has been proposed.[4] However, it is limited by reactions occurring *a priori* in a microphase. Based on published data,[4,7,8] we assume that the alkaline hydrolysis of phosphonates proceeds in the surface layer, where a balanced hydrophilic–lipophilic environment provides a contact between hydrophobic substrates and a highly hydrophilic nucleophile. For interface reactions when a reactant is distributed between an aqueous pseudo-phase and the surface layer and the other, between an oil pseudo-phase and the surface layer, k_{obs} is expressed as follows:[4,16]

$$k_{obs} = \frac{k_i K_s K_{OH}[OH]_t}{(K_s + Z)(K_{OH} + W)[AOT]}, \qquad (1)$$

where k_i can be expressed in terms of the pseudo-first-order rate constant k'_i and the molar ratio between the nucleophile at the interface and the AOT ($k'_i = k_i[OH]/[AOT]$); K_s and K_{OH} are the partition coefficients of the substrate and the nucleophile, respectively.

The kinetic data for the AOT–decane–water reverse micellar system and substrates **1**–**5** are summarised in Figures 1–3 and Table 1. The kinetics for **6**–**9**, which exhibit constant k_{obs} values at various surfactant concentrations, *a priori* cannot be treated in terms of equation (1). It is likely that in this case the reaction occurs not only in one phase. In particular, the fact that k_{obs} is independent of [AOT] suggests a noticeable contribution made by the reaction in the aqueous phase to the observed rate constant.[5] Whereas in the single-phase model the overall kinetic equation is simplified, it becomes too complex in the case of simultaneous processes occurring in more than one phase. Therefore, we restricted ourselves to the qualitative kinetics for the phosphonates **6**–**9**.

In general, the reactivity changes in the order **1** > **2** ≈ **3** >> **4** ≈ **5** > **6** ≈ **7** ≈ **8** ≈ **9**. In the series **1**–**3**, the reaction was inhibited by a factor of 5, as compared to the case of water. The observed rate constant linearly increases with NaOH concentration and decreases with AOT and water concentrations (Figures 1 and 3). This may result from the dilution of reactants as the volume fraction of the dispersed phase increases. Such a tendency is usually observed in reactions occurring at the surface layer of reverse micelles.[4,7,8] We found previously[7,8] that, as a rule, the basic hydrolysis of phosphonates proceeds at the surface layer of AOT and sodium dodecyl sulfate based reverse micellar systems. Note that a change in the reactivity is observed only on going from **1** to **2**, whereas a further increase in the hydrophobicity of R has no effect on the reaction rate.

Table 1 Kinetic data treated in terms of the pseudo-phase model.

Substrate	K_s	K_{OH}	k_i/s^{-1}	$k^a_{2,i}$ /dm^3 mol^{-1} s^{-1}	$k^b_{2,w}$ /dm^3 mol^{-1} s^{-1}
1	90	1.3	9.0	2.43	4.0
2	45	1.3	6.0	2.22	3.6
3	45	1.5	5.0	1.85	3.0
4	40	6	0.2	0.074	0.55
5	30	1.5	0.65	0.24	0.24

[a]The value of $k_{2,i}$ was calculated using $V = 0.37$ dm^3 mol^{-1}. [b]$k_{2,w} = 0.2$ (for **6**), 0.16 (**7**), 0.12 (**8**) or 0.08 dm^3 mol^{-1} s^{-1} (**9**).

The effect of substituents in the leaving group (substrates **1**,**4**–**9**) is different from that in **1**–**3**. The replacement of an NO_2 group by the less electronegative Br results in a more than 10-fold reduction of k_{obs}, and a further decrease in the electronegativity of X (the replacement of Br by H) produces no effect on the reactivity. An increase in the hydrophobicity of X exerts a noticeable influence on the reactivity only on going from **5** to **6**, whereas a further increase in the alkyl chain length in **6**–**9** has no effect on k_{obs} (Figure 2). Note that in substrates **1**,**4**–**7** the reaction was inhibited, as compared to water, whereas for phosphonates **8** and **9** nearly identical reactivities both in water and in the micellar system were found.

In addition, the tendency of k_{obs} to decrease with surfactant and water concentrations is preserved for substrates **1**, **4** and **5** (X = NO_2, Br, H), whereas k_{obs} is independent of AOT concentration at a constant *W* for **6**–**9** (X = *n*-butyl, *n*-octyl, isododecyl), although it decreases with *W* at a fixed [AOT] (Figures 2 and 3). Apparently, this means that the reaction transferred from the surface layer to another pseudo-phases. This can be explained by the fact that substrates **6**–**9** are amphiphiles and can be involved in the formation of mixed micelles, which can result in changes in the micellar structure and location of the reagents and hence in a transfer of the reaction from the surface layer to another pseudo-phase. The independence of k_{obs} from

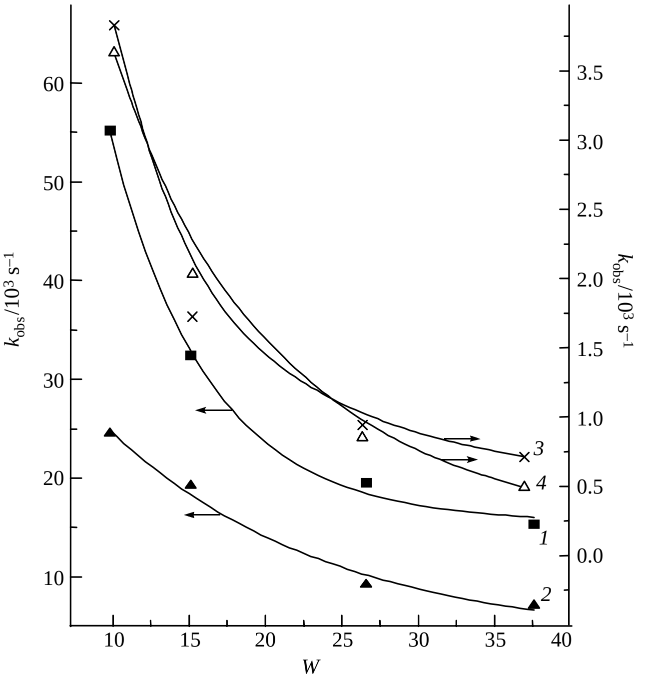


Figure 3 Observed rate constants of the basic hydrolysis of *1*, **1**; *2*, **3**; *3*, **5** and *4*, **7** in the AOT–decane–water micellar system as functions of water content (25 °C, 0.4 M AOT, 0.02 M NaOH).

the surfactant concentration at a constant W can be considered as a kinetic argument supporting that the reaction occurs in the aqueous core of droplets[5] or at the interface and in the water core simultaneously.

Table 1 shows that the substrate structure has a minor effect on the partition coefficients of the reagents between pseudophases with the exception of phosphonate **1**, for which K_s is about twice as large as that for the other compounds. Thus, changes in k_{obs} in the series **1**–**5** are mainly influenced by differences in the reactivity of the substrates in the surface layer, which is characterised by $k_{2,i}$ values. The latter are lower than the corresponding second-order rate constants of the reaction in water ($k_{2,w}$) for all the substrates; because of this, the process was inhibited in the micellar system in comparison with water.

Thus, the basic hydrolysis was inhibited in comparison with water as a result of the effect of reactant microenvironments at the interface. The reactivity in the series **1**–**9** is mainly influenced by the electronic effect of the substituents and is unaffected by the hydrophobicity.

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