

# Microemulsion-promoted changes of reaction mechanisms: solvolysis of substituted benzoyl chlorides

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When the hydrolysis of substituted benzoyl chlorides is carried out in a water/oil (w/o) microemulsion, the point in the substituent  $\sigma^+/\lg k$  plot at which the mechanism changes from associative to dissociative depends on the water content of the microemulsion.

Water-in-oil (w/o) microemulsions<sup>1</sup> can be considered as consisting of three compartments in which small solutes may be located: the aqueous core of the droplets; the continuous non-polar phase; and the intervening micellar interface made up of surfactant molecules with their polar head groups facing the aqueous core.<sup>2</sup> They are extensively used for foods, cleaning products, drug delivery, tertiary oil recovery,<sup>1</sup> and as media for chemical reactions.<sup>3</sup> This latter application derives largely from their ability to catalyse reactions by bringing water-soluble reagents dissolved in the aqueous compartment into contact, at the micellar interface, with water-insoluble organic reagents dissolved in the non-polar compartment; microemulsion catalysis is an alternative to phase-transfer catalysis<sup>4</sup> and other techniques for favouring reaction between water-soluble and water-insoluble compounds. In addition, however, microemulsions can also bring about catalysis simply by concentrating water-soluble reagents in the aqueous droplet core and at the interface, the droplets thus acting as 'microreactors'.<sup>5</sup> Furthermore, reaction rates can be influenced by the altered properties of the water in droplets with very low water contents.<sup>6,7</sup>

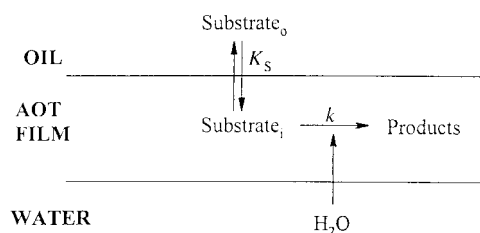
In this work, we found that the altered properties of microemulsion water can affect not only reaction rates, but also the mechanism by which certain reactions take place. The specific class of reactions investigated was the hydrolysis of substituted benzoyl chlorides in water/AOT/isooctane microemulsions [AOT = sodium bis(2-ethylhexyl)sulfosuccinate] with water contents  $W = [\text{H}_2\text{O}]/[\text{AOT}]$  ranging from 2 to 50.

The kinetics of the hydrolysis of benzoyl chlorides in microemulsions can be investigated using our extended pseudo-phase model of the latter.<sup>8</sup> Specifically, since the poor solubility of benzoyl chlorides in water makes it safe to assume that the amount of substrate dissolved in the aqueous compartment is negligible, we applied the model shown in Scheme 1, where  $K_S$  ( $K_S = ([\text{Substrate}]_i Z)/[\text{Substrate}]_o$ ) governs the partition of substrate between the organic phase and the interface, the only region in which the reaction occurs. For the observed rate constant  $k_{\text{obs}}$ , this model affords eqn. (1), in which  $k$  is the

$$k_{\text{obs}} = \frac{kK_S}{K_S + Z} \quad (1)$$

pseudo first-order rate constant for the reaction in the interface and  $Z = [\text{isooctane}]/[\text{AOT}]$  is the ratio of the molar concentrations of the non-polar solvent and the surfactant.

As predicted by eqn. (1), plots of  $1/k_{\text{obs}}$  vs.  $Z$  are linear in all cases studied (errors are always <10–12% for the intercepts and ca. 1–2% for the slopes). Fig. 1 shows these results for some of the benzoyl chlorides used. For each value of  $W$ , the values of  $k$  (errors are always <15%) so obtained were used to construct the corresponding Hammett plot. Fig. 2 shows the results for  $W = 2$  and 50.



Scheme 1

Mechanistically, the solvolysis of benzoyl chlorides can proceed *via* either of two phenomenologically distinct kinds of mechanism: one in which the rate-limiting step includes a transition state with little or no cleavage of the bond binding the leaving group [an associative mechanism, Scheme 2(a)], and one in which it shows well advanced cleavage of the leaving group bond [a dissociative mechanism, Scheme 2(b)].<sup>9,10</sup> A positive  $\rho^+$  value provides evidence for an associative transition state that involves bimolecular attack of water on the acyl chloride with little or no bond-breaking to the leaving group in the rate-limiting step. This corresponds to the initial step of an addition-elimination mechanism, but we do not know if there is an intermediate with a significant lifetime on the reaction path. An 'uncoupled concerted' reaction pathway may occur, in which there is no intermediate, but in which bond formation and bond cleavage are not balanced; *i.e.* bond-making and bond-breaking have not occurred to the same extent at the same time.<sup>9</sup>

The mechanism of a given reaction depends on the nature of the substituent and the solvent in which the reaction takes place.<sup>9</sup> The slope of a Hammett plot for solvolysis of benzoyl chlorides in water changes from negative (indicative of dissociative reactions,  $\rho^+ = -3.09$ ) to positive values (indicative of associative reactions) somewhere between the points corresponding to 3-(trifluoromethyl)benzoyl chloride and 4-ni-

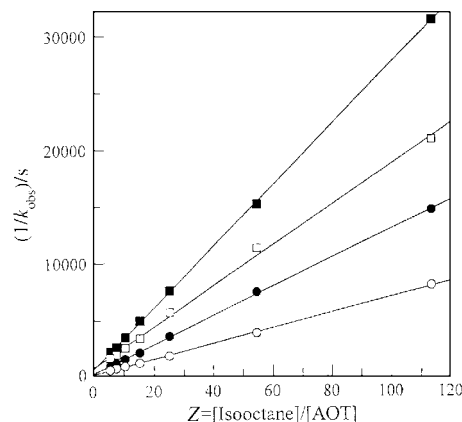
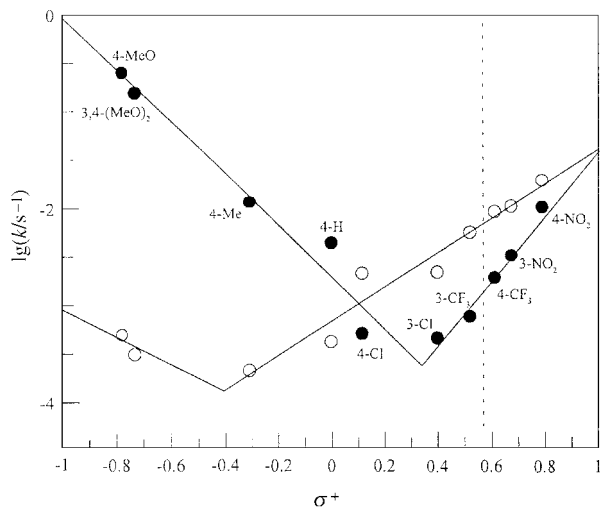
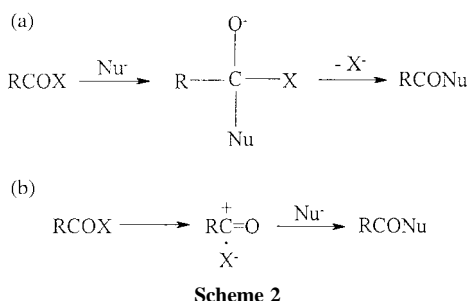


Fig. 1 Plots of  $1/k_{\text{obs}}$  vs.  $Z = [\text{isooctane}]/[\text{AOT}]$  [see eqn. (1)] for the hydrolysis of substituted benzoyl chlorides at 25 °C in AOT/isooctane/water microemulsions with  $W = 18$ . (■) 4-Cl, (□) 4-H, (●) 4-Me, (○) 4-CF<sub>3</sub>.



**Fig. 2** Hammett plots for the hydrolysis of substituted benzoyl chlorides in AOT/isooctane/water microemulsions with different water contents: (●)  $W = 50$  and (○)  $W = 2$  at 25 °C. The dashed line indicates the point at which a similar plot for the reaction in water changes from negative to positive slope (ref. 9).



trobenzoyl chloride, the latter of which reacts faster than the former.<sup>9</sup>

Fig. 2 shows that in microemulsions, as in water, there is indeed a switch from the dissociative to the associative mechanism. For the microemulsion with  $W = 50$  this occurs at  $\sigma^+ \text{ ca. } 0.3$ , between the points for 4-chlorobenzoyl chloride and 3-chlorobenzoyl chloride: for  $\sigma^+ > 0.3$  there is very good Hammett correlation with a slope of  $\rho^+ = 3.5 \pm 0.3$ , whereas the least-squares line through the results for substituents with  $\sigma^+ < 0.3$  has a slope of  $\rho^+ = -2.7 \pm 0.3$ , close to the value of  $-3.0$  observed for reaction in pure water.<sup>9</sup> For the microemulsion with  $W = 2$ , the switch occurs at  $\sigma^+ \text{ ca. } -0.4$ , just below the point for 4-methylbenzoyl chloride, with a Hammett slope of  $\rho^+ = 1.8 \pm 0.2$  for  $\sigma^+ > -0.4$  (the number of substrates with more negative  $\sigma^+$  values was too few for accurate calculation of a Hammett slope for the dissociative branch).

As the water content of the medium falls, so too does the  $\sigma^+$  value at which the mechanism switch occurs (see Fig. 2, in which the value at which the switch occurs in bulk water is shown by a dotted line). This can be attributed to the change in the properties of micelle-borne water.<sup>11,12</sup> The change from a

dissociative to an associative reaction path with increasingly electron-withdrawing substituents occurs much later in water than in AOT/isooctane/water microemulsions with  $W = 50$ . The rate of the associative reaction is independent of the leaving group, while the dissociative reaction is strongly dependent on the nature of the leaving group and on its solvation.<sup>9</sup> For large values of  $W$ , water at the centre of the aqueous micelle core is similar in nature to that of bulk water, but water in or adjacent to the interface is devoted to solvating the surfactant head groups<sup>12</sup> and, hence, has a limited ability to assist the leaving group; in microemulsions with  $W = 2$ , all water is of this latter kind. Consequently, lowering  $W$  favours the associative pathway, with the result that the change in mechanism occurs at lower  $\sigma^+$  values; in the microemulsion with  $W = 2$ , even 4-methylbenzoyl chloride, with its electron-donating substituent, is hydrolysed *via* the associative mechanism.

In conclusion, in this work we found that carrying out the hydrolysis of benzoyl chlorides in microemulsions allows not only the reaction rate but also the reaction mechanism to be controlled by modifying the quantitative composition of the microemulsion. The effect on the mechanism can be attributed to the dependence of the properties of micelle-borne water on the value of  $W = [\text{H}_2\text{O}]/[\text{surfactant}]$ . We envisage that this phenomenon may prove to be of use for investigation of other reaction mechanisms.

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