Kinetic Study of the Hydrolisys of Phenyl Perfluorooctanoate in Water: Deaggregation Effect of β-Cyclodextrin

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Abstract: The kinetics of the hydrolysis of phenyl perfluorooctanoate was studied at pH 6.00 and 9.90 in water. The substrate is aggregated under all working reaction conditions, which is indicated from the decrease in the reaction rate when the substrate concentration is raised. The addition of β-cyclodextrin produces the deaggregation of the ester catalyzing the reaction.

Introduction

The hydrolysis of amides derived from long chain perfluoroalkyl acids undergoes aggregation in water at very low concentrations. The addition of β-cyclodextrin breaks such interactions and catalyzes the hydrolysis. [1] To evaluate the effect of the change of the polar head group on the aggregation properties, we studied the hydrolysis of phenyl perfluoroalkyl esters bearing different chain lengths. We present here the results obtained from the kinetics of the hydrolysis reaction of phenyl perfluorooctanate in water, in presence and in absence of β-cyclodextrin.

Experimental

The reactions at pH 6 were followed in a conventional spectrophotometer whereas those at pH>9 were carried out in a stopped flow equipment.

The reaction conditions were: temperature $25.1 \pm 0.1°C$.; ionic strength 0.2 M; cosolvent acetonitrile 3,8%; buffer concentration 0.1 M.

Results and Discussion

We found that the rate constants decrease as the substrate concentration increases which indicates that it is aggregated under all working concentrations. This aggregation phenomenon was also observed in the UV spectrum.

The kinetics of the hydrolysis at pH 6.00 and at concentrations between 8.4 x 10^{-6} and 1.8 x 10^{-5} M corresponded to only one process that fits to a single exponential. On the other hand, at concentrations higher than 2.4 x 10^{-5} M, the change in absorbance with time no longer fits to a single exponential equation. Two processes could be observed at some wavelengths, that is, an initial rise at very short times followed by a decay. The first process became more important compared to the second one as the substrate concentration increased. The former process is attributed to the aggregation of the substrate and the latter arises from its hydrolysis. Similar results were obtained for the reactions measured at pH 9.90.

We also found that small amount of β-cyclodextrin results in a remarkable increase in the rate constant. Such increment reaches a maximum value that remains almost unchangeable with later addition of the host. The absorbance vs. time plot can be fit by a single exponential equation. Besides, in the presence of cyclodextrin, the observed rate constant is independent of substrate concentration and its value is in the order of that expected for the free substrate in solution. These results indicate that the host deaggregates the substrate at very low concentration and suggest the formation of an inclusion complex. The rates of hydrolysis of the free and included substrate are about the same probably because the reacting ester group protrudes outside the cavity

References and Notes

1.   Granados, A.; de Rossi, R.H. *J. Am. Chem. Soc.* **1995,** *117*, 3690.