

HYDROLYSIS OF BENZYLIDENE ANILINE IN THE PRESENCE OF
CETYL TRIMETHYLAMMONIUM BROMIDE

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In a communication to this journal (1), van Senden and Koningsberger have reported the pronounced retardation of the proton catalysed hydrolysis of benzylidene aniline in the presence of the surfactant, cetyl trimethylammonium bromide (C.T.A.B.). With C.T.A.B. concentrations in the range 0.01-0.07M where virtually all the surfactant is in the micellar form, the rate was reduced by a factor which ranged from 20 at 0.01 M C.T.A.B. to 128 at 0.07M C.T.A.B. These retardations are far greater than can be accounted for by normal salt effects.

It is the aim of this communication to present a possible explanation for the results obtained.

van Senden and Koningsberger propose that reaction may occur 'in or on the micelle', However the probability of hydrolysis inside the micelle is very small, for although it is known that water may penetrate to the α -carbon of the tenside chain, hydrolysis experiments (2) indicate there is little water in the liquid paraffin interior of the micelle. Thus reaction would be expected to occur principally at the micelle-water interface.

It is known that the pH at the surface of a charged micelle is different from the pH in the bulk solution (3,4,5). Hartley and Roe (3) deduced that at 25°C.

$$pH_s = pH_b + \zeta/60$$

where s and b denote the surface and bulk quantities, and ζ is the electrokinetic or zeta potential in millivolts. (Although some workers(2,5) suggest that the potential in the above equation is not

strictly the zeta potential as ordinarily measured, nevertheless the above is thought to be a reasonable approximation).

With the benzylidene aniline at the surface of a cationic micelle (positive ζ) reaction will take place in an environment of higher pH, and hence at a lower rate, since it is a proton catalysed hydrolysis.

Assuming that the rate of hydrolysis is directly proportional to the $[H^+]$, values of pH_s and subsequently ζ (from the Hartley-Roe equation) may be calculated from the kinetic data of van Senden and Koningsberger obtained in a borate buffer at pH_b of 9.0. For 0.01M C.T.A.B. pH_s is found to be 10.3 and ζ +78 mV; for 0.07M C.T.A.B. the corresponding values are 11.1 and +126 mV. This range of ζ values from +78 to +126 mV is very reasonable for C.T.A.B. (4).

The decrease in rate with increasing concentration of C.T.A.B. could arise from an increase in surface charge density (higher ζ - higher pH_s) due to a closer packing of surfactant molecules in the micelle.

This difference in surface and bulk pH may explain (in part at least) the results of numerous studies of reactions at interfaces. King and Mukerjee (6) reported the retardation of alkaline hydrolysis of amyl acetate emulsified in anionic surfactants. Painter and Morgan (7) demonstrated an increase in rate of acid hydrolysis of certain basic polysaccharides in solutions of water soluble polystyrene sulphonic acid. Twitchell (8) has shown that the acid hydrolysis of fats is accelerated in the presence of anionic surfactants. In addition, it has been found (2,9) that the acid hydrolysis of monoalkyl sulphates is faster above the critical micellar concentration than below it. In all these cases the surface is negatively charged, so that acid hydrolysis would be accelerated, and alkaline hydrolysis retarded.

References

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