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HYDROLYSIS OF BENZYLIDENE ANILINE IN THE PRESENCE OF CETYL TRIMETHYL AMMONIUMBROMIDE

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FROM investigations carried out by Robinson,[1] Schöpf,[2] Haley and Maitland[3] a.o. it is well-known that many organic reactions of the ionic type occur smoothly under physiological (or cell-possible) conditions in aqueous solution. Nevertheless, up to now this reaction medium has found hardly any practical application, owing to the very low solubility of most organic compounds in water. Several years ago we started a new research project in this field, guided by the idea that adding detergent salts to this medium would increase the solubility of the reactants. Moreover, investigations on emulsion polymerization have clearly indicated that detergent salts could be favourable used to accelerate reactions and increase yields.

We now wish to report a kinetic study of the proton catalysed reaction

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[1] R. Robinson, J. Chem. Soc. **111**, 876 (1917).

[2] C. Schöpf, Angew. Chemie **50**, 779 (1937); Ibid. **50**, 797 (1937).

[3] C. A. C. Haley and P. Maitland, J. Chem. Soc. 3155 (1951).

benzylidene aniline + water $\rightleftharpoons$ benzaldehyde + aniline

in a boric acid - sodium borate buffer at pH 9 and 25 ± 0.1°C. (Benzylidene aniline dissolved in methanol was added to the detergent salt buffer solution, in order to obtain in a reasonable time, a macro-homogeneous reaction medium; the final content of the latter amounted to 0.2% methanol).

The reaction can be followed most conveniently by ultraviolet spectrophotometric methods, which show that the equilibrium is shifted almost completely to the right (99.6%). The overall rate constants of the hydrolysis were determined in the presence of various amounts of the cationic detergent salt cetyl trimethyl ammoniumbromide (CTAB) and in its absence. In all cases the amount of CTAB present in solution exceeded the critical micelle concentration.

Addition of this cationic detergent salt invariably causes a considerable retardation of hydrolysis, much more than can be accounted for by normal salt effects. So far, our results are in complete agreement with those of Duynstee and Grunwald,[4] who recently described the influence of 0.01 M of detergent salts on the alkaline fading of triphenylmethane dyes and sulphonphtalein indicators.

The overall (pseudo first order) rate constants (k^*) of the hydrolysis of benzylidene aniline in the presence of different concentrations of CTAB, as measured by our method, are given in the following table:

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[4] E. F. J. Duynstee and E. Grunwald, J. Amer. Chem. Soc. **81**, 4540 (1959); Ibid. **81**, 4542 (1959).

mol CTAB	$k^{*} \times 10^{3}$ min^{-1}
0.00	56.5
0.01	2.82
0.02	1.53
0.03	0.97
0.04	0.76
0.05	0.62
0.06	0.51
0.07	0.44

From these data it is evident that the overall rate constant is inversely proportional to the molarity of the detergent salt at least between the limits of 0.01 and 0.07. This fact could possibly be explained by the assumption that the number of detergent molecules, associated in a "Hartley micelle" increases proportionally with increasing concentration of the detergent salt until the micelle is filled completely. At the site of the reaction (in or on the micelle) the medium may be influenced by a change in composition of the micelle, and this fact could account for the change in overall reaction rates as shown above.

Our study will be continued and published elsewhere in full detail.

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