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ORTHO EFFECTS III. RATES OF ALKALINE HYDROLYSIS OF ETHYL BENZOATES IN WATER

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From the mechanistic standpoint alkaline hydrolysis of substituted benzoates has repeatedly been studied carefully and much rate data in various conditions are now available (1-3). However, all these measurements were carried out in organic solvents containing relatively small amounts of water. In the course of our investigations on the ortho effects (4) it became necessary to know the rates of alkaline hydrolysis of a series of o-, m- and p- substituted ethyl benzoates in water as solvent and we now report these results.

Rates of both disappearance of the esters and formation of the benzoate anions were followed by measuring changes in optical densities of the solution in the range of 220-290 mμ using a UV spectrophotometer. All the reactions were run in a quartz cell of 1 cm in length, thermostatted at 25.0±0.5°. Concentrations of the esters and potassium hydroxide were $\frac{1}{10,000}$ - $\frac{1}{40,000}$ M. and $\frac{1}{200}$ M. respectively. Solubilities of some esters rejected the use of pure water as solvent and actually water containing 3%(wt.) of ethanol was used throughout in this work.

Second order rate constants for the hydrolysis of these esters are summarized in Table I. As is seen in Table I, ethyl benzoate is hydrolyzed much faster in water than in 85%(wt.) aqueous ethanol $k=6.21\times10^{-4}$(1), the factor being as high as about 50. The high ratio is partly due to changes in both nature and effective concentration of hydroxide ion in the two different solvents but partly can be ascribable to the changes in specific as well as gross solvent effects on the transition state of the reaction.

Hammett reaction constant ρ was evaluated to be 1.33 in water, which was almost a half of the value 2.54 (1) in 85%(wt.) aqueous ethanol and by far the lowest among those reported for the alkaline hydrolysis of benzoates in various solvents (1-3). Since ρ values are concerned with relative reactivities of variously ring substituted compounds, any change in the hydroxide ion (both nature and effective concentration) due to change of the solvent is not responsible for the low ρ value in water. A general principle, i.e., the faster, the less selective, may be satisfactory to account for the situation, but the role of the solvent polarity seems to be still more important in view of our recent results (5) that although ethyl benzoate is hydrolyzed in 65%(vol.) aqueous dimethyl sulfoxide as fast as in water, the ρ value in 65% aqueous dimethyl sulfoxide is almost the same as that in 85% aqueous ethanol.

The most notable facts are seen in values for the ortho compounds. In Fig. 1 are given graphical representation of the data in 3% aqueous ethanol together with that in 85% aqueous ethanol (1) for the sake of comparison, each line representing regression lines of the Hammett plots and the ortho effect, estimated as differences in reactivities of ortho and para compounds, $\log(k_{\underline{ortho}}/k_{\underline{para}})$, being shown as the lengths of vertical lines. Fig. 1 shows that the ortho

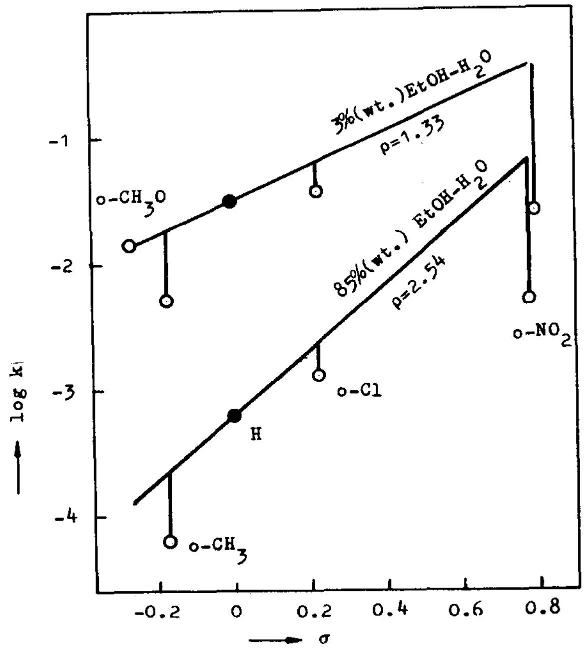

FIG. 1

Rates of Alkaline Hydrolysis of Substituted Ethyl Benzoates in 3% and 85%(wt.) aq. Ethanol (At 25°), Showing That The Ortho Effects Are Essentially Constant in Both Solvents.

effects are almost constant in the two solvents, 3% and 85% aqueous ethanol, in spite of the large differences in both the individual rates and ρ values in these two solvents. Surprisingly, this was also found to be the case with the hydrolysis in 65% aqueous dimethyl sulfoxide. In connection to these observations it seems of interest to note that although change of the solvent from ethanol to water causes enhancement of the acidities and lowering of the ρ value in the ionizations of substituted benzoic acids (6, 7), just like in the alkaline hydrolysis of their ethyl esters, the ortho effects in the ionization are very sensitive to the solvent change (7), while the ortho effects in the hydrolysis are indifferent to the similar solvent change.

In general, ortho effects should be very sensitive to the specific solvent effects, because the gross solvent effects would be mostly cancelled out by taking the difference, log $k_{\underline{ortho}}$ - log $k_{\underline{para}}$, and ortho substituents are situated very close to the reaction center, i.e., the site of specific solvation. As far as the present data is concerned, the hydrolysis of the ethyl benzoates appears to exhibit an exception to this rule. These results are, however, in good conformity with our ealier expectation (4), the reason of which will be clarified in our subsequent papers.

Systematic studies of the effects of solvents on individual rates, Hammett ρ values and ortho effects would be a promising approach to the problem of the solvent effect and are now in progress in this laboratory.

TABLE I

Rates of Alkaline Hydrolysis of Substituted Ethyl Benzoates in 3%(wt.) aq. Ethanol at 25°C.

Substi- tuents	k^*(1.mole^{-1}sec.$^{-1}$) x 10^2		
	Ortho	Meta	Para
H	3.01**	3.01	3.01
NO_2	3.34	31.2	56.5
Br	2.52***	——	6.01
Cl	3.35***	——	5.88
CH_3	0.492	——	1.78
CH_3O	1.62	——	1.58
NH_2	0.100	2.41	——

* accurate within ± 5%

** A valu, 2.65 x 10^{-2} in 4 wt.% aq. ethanol, was observed by titration method (7).

*** less accurate than the others

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