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ORTHO EFFECTS IV. RATES OF ALKALINE HYDROLYSIS OF ETHYL BENZOATES IN AQUEOUS DIMETHYL SULFOXIDES

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In our last paper (1) it was reported that in the alkaline hydrolysis of substituted ethyl benzoates the change of the solvent from 85 %(wt.) aqueous ethanol to 3 %(wt.) aqueous ethanol caused 50 times increase in the rate of the unsubstituted compound and decrease to a half in the Hammett ρ value, while the ortho effects, estimated as log $(k_{\underline{ortho}}/k_{\underline{para}})$, remained essentialy constant in the two solvents. These results are in good agreement with our earlier expectation (1,2), and therefore extention of this work to include another typical solvent systems seemed necessary.

Dimethyl sulfoxide is a typical dipolar aprotic solvent (3,4) and seemed paticularly attractive since, according to the recent communication (5), alkaline hydrolysis of ethyl benzoate exhibits a significant rate increase in aqueous dimethyl sulfoxide relative to aqueous ethanol. Thus, such a notable medium effect would give a more discriminating results as to the constancy of the ortho effects in this reaction.

Recently, Roberts (6) examined rates of saponification of ethyl esters of various aliphatic carboxylic acids and discussed solvent effects on the basis of the following equation (7).

$$\log k = \log k_o + \rho^* \sigma^* + \delta E_s$$

His results show that although the steric reaction constant δ is essentially equal in 85 % aq. ethanol (0.99) and 85 % aq. dimethyl sulfoxide (0.96) in favor of our views, the polar reaction constant ρ^* in the former solvent (2.09) are much larger than that in the latter solvent (1.25) which are at variance with the related data in this laboratory (8). It seems also of interest to further delineate the specific role of dimethyl sulfoxide as a solvent in a more discriminating way.

These situations prompted us to measure the rates of alkaline hydrolysis of o-, m- and p- variously substituted ethyl benzoates in some water-dimethyl sulfoxide mixed solvents and to examine effects of these solvents on the rate of the unsubstituted compound, the Hammett ρ value and the ortho effects systematically.

Table I presents kinetic data of this work. In Figure 1 these results are shown graphically together with the data in 3 % and 85 % aqueous ethanol, each line representing regression lines of the Hammett plots and the ortho effects, $\log(k_{\underline{ortho}}/k_{\underline{para}})$, being shown as the lengths of vertical lines. Fig. 2 shows changes of the rate of the unsubstituted compounds and of the ρ values with the change of the solvent compositions in the two solvent systems, aqueous ethanol and aqueous dimethyl sulfoxide.

The following facts are readily apparent from these results. i) The ortho effects are almost constant in spite of the large variations in both the rates of the unsubstituted compound and the ρ

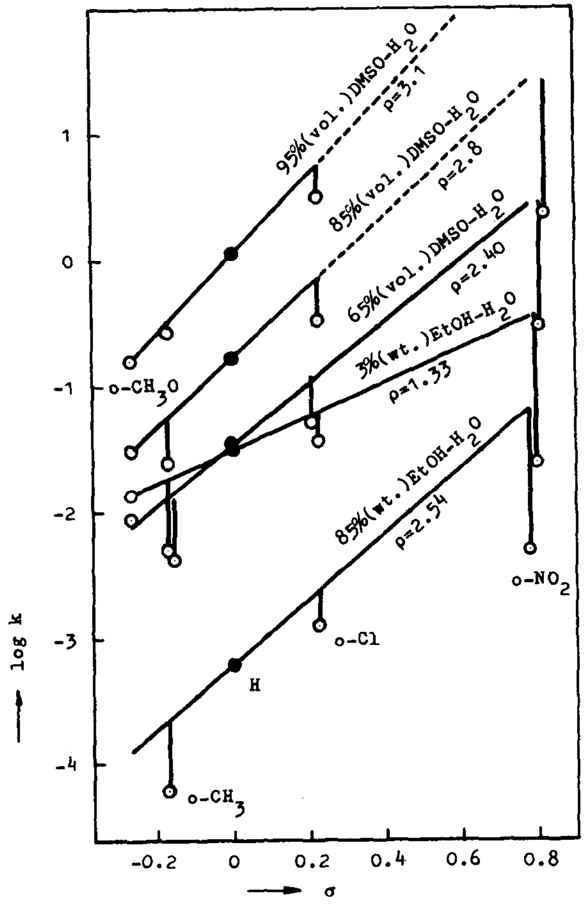

FIG. 1

Rates of Alkaline Hydrolysis of Substituted Ethyl Benzoates in Various Solvents at 25°, Showing That The Ortho Effects Are Essentially Constant in These Solvents.

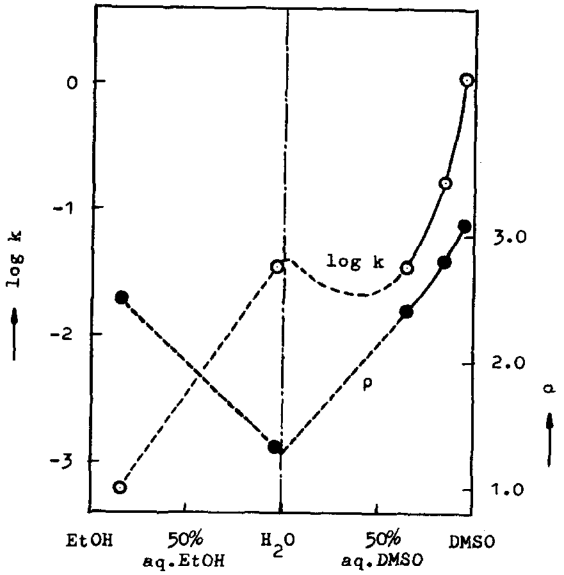

FIG. 2

Comparison of the Solvent Effects in aq. Ethanol and in aq. Dimethyl Sulfoxide on Both Rates and ρ Values for the Alkaline Hydrolysis of Ethyl Benzoates at 25°.

values in these solvents. ii) The rates of the unsubstituted compound decrease in aqueous ethanol and increase in aqueous dimethyl sulfoxide with the decrease in the water content of the solvents, while the ρ values rise similarly in the two solvent systems with the decrease in the amounts of water.

The striking acceleration of the hydrolysis in aqueous dimethyl sulfoxide is probably due to a diminishment in hydroxide ion solvation (3,9), as a result of the competition between this anion and a large amounts of dimethyl sulfoxide for water molecules.

Considering that the ρ value shows almost the same change in both aqueous ethanol and aqueous dimethyl sulfoxide (see Fig. 2) and any contribution of hydroxide ion to the reaction rates (e.g., desolvation) is not involved in these ρ values, changes in the ρ value would be ascribable to the predominance of the influence of solvent polarity on the transition state of the reaction. Diminution of solvent polarity lowers the reaction rate and the desolvation raises it, and therefore the two effects would compete in aqueous dimethyl sulfoxide. This situation can be seen in Fig. 2.

It must be noted here that although the ortho effects remain almost constant with the change of solvents, if the amount of water becomes very low in aqueous dimethyl sulfoxide, the ortho effect for $\underline{o}$-methyl, $\log(k_{\underline{o}\text{-CH}_3}/k_{\underline{p}\text{-CH}_3})$, becomes very small; it is -0.56 in both 3 % and 85 % aqueous ethanol but -0.08 in 95 % aqueous dimethyl sulfoxide. This is probably due to the concurrence of another kind of desolvation, which should be distinguished from the desolvation that is significant even in aqueous dimethyl sulfoxide containing large amounts of water. In favor of this view, similar results can be observed in the alkaline hydrolysis of ethyl $\underline{o}$-isopropyl benzoate

(8) and ethyl pivalate (8), too. These results will be presented in detail in our next paper, together with the other related data.

TABLE I

Rates of Alkaline Hydrolysis of Substituted Ethyl Benzoates in Aqueous* Dimethyl Sulfoxides at 25°C

Substituents	k**(l.mole^{-1}sec.$^{-1}$) x 10^2		
	65% DMSO	85% DMSO	95% DMSO
H	3.45	16.6	115
(H)***	(55.5)	(267)	(1840)
(H)****	(1.15)	(5.52)	(38.0)
p-OCH_3	0.875	2.71	19.2
p-CH_3	1.75	6.16	46.9
p-Cl	16.3	76.5	668
p-NO_2	273	2570*****	—
o-OCH_3	1.07	2.78	19.9
o-CH_3	0.579	2.89	35.8
o-Cl	6.70	35.8	381
o-NO_2	29.5	239	—

* vol.%. ** accurate within ± 5 %. *** relative rates based on the value in 85 % (wt.) aq. EtOH. **** relative rates based on the value in 3 % (wt.) aq. EtOH. ***** estimated from the Hammett plot.

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