

ALKALINE HYDROLYSIS OF AROMATIC DICARBOXYLIC ESTERS IN AQUEOUS DMSO

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As part of a study of the effects of dipolar aprotic-protic solvent mixtures on the rates of hydrolysis of dicarboxylic esters, we have investigated the alkaline hydrolysis of isomeric benzenedicarboxylic esters. In view of the fact that DMSO-water mixtures provide a system with peculiar properties,¹ results obtained in these solvent mixtures are presented in this communication.

TABLE 1
SOLVENT EFFECTS ON THE RATE OF HYDROLYSIS OF DIETHYL PHTHALATE AT 40°
 k_1 and k_2 in l. mol⁻¹ s⁻¹

Solvent Ratio (v/v)	10^2k_1	10^2k_2	k_1/k_2	Solvent Ratio (v/v)	10^2k_1	10^2k_2	k_1/k_2
DMSO-H ₂ O 60 : 40	8.82	0.901	9.79	EtOH-H ₂ O 60 : 40	0.604	0.12	5.03
DMSO-H ₂ O 70 : 30	16.6	1.79	9.26	EtOH-H ₂ O 70 : 30	0.545	0.121	4.51
DMSO-H ₂ O 80 : 20	42.8	5.00	8.55	EtOH-H ₂ O 80 : 20	0.421	0.11	3.84
Dioxan-H ₂ O ^a 60 : 40	2.39	0.475	5.14	Acetone-H ₂ O ^a 60 : 40	2.01	0.410	5.00

^a From Anantakrishnan, S. V., and Radhakrishnamurthy, P. S., *Proc. Indian Acad. Sci.*, 1962, **56**, 249.

TABLE 2
COMPARISON OF REACTIVITIES OF AROMATIC DIESTERS IN 60%
DMSO AT 35°
 k_1 and k_2 in l. mol⁻¹ s⁻¹

Ester	10^2k_1	10^2k_2	k_1/k_2
Diethyl phthalate	6.62	0.664	9.96
Diethyl isophthalate	74.5	4.21	17.2
Diethyl terephthalate	125.0	6.51	19.2

Tables 1 and 2 present the kinetic data of this work. The rate constants for both the steps were evaluated by the method of Frost and Schwemer² from the same kinetic run. The results of the present investigation can be summarized as follows:

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¹ Parker, A. J., *Chem. Rev.*, 1969, **69**, 1.

² Frost, A. A., and Schwemer, W. C., *J. Am. chem. Soc.*, 1952, **74**, 1268.

(1) The rates of hydrolysis are much larger in aqueous DMSO than in aqueous ethanol.

(2) The rate constants increase with decreasing percentage of water in DMSO-water mixtures while the reverse is true in all other solvent systems, viz. ethanol-water, dioxan-water, or acetone-water mixtures.

(3) The k_1/k_2 ratios are much larger in aqueous DMSO when compared to ethanol-water, dioxan-water, or acetone-water mixtures.

Similar results have been reported by us on the alkaline hydrolysis of diethyl succinate.³ The increased rates of both the steps in solvents containing increased percentages of DMSO can be attributed to the presence of poorly solvated hydroxide ion and to an increased transition state solvation. While the first step involves an ion and a dipole, the second step is between the OH^- ion and the half-ester anion. The repulsion between a poorly solvated hydroxide ion and half-ester anion will be much greater in DMSO-water mixtures leading to a considerable diminution in the value of k_2 and thereby results a large k_1/k_2 ratio in these solvent mixtures. The effect of increasing percentages of DMSO on k_1/k_2 , though surprising, is to be attributed to the differential effect of the aprotic solvent on the reaction rates of both the steps.

It is also interesting to note that under the conditions of the saponification presently used the k_1 values for diethyl phthalate are almost the same as the rate constant for the saponification of ethyl benzoate (k_2 for ethyl benzoate is $6.7 \times 10^{-2} \text{ l. mol}^{-1} \text{ s}^{-1}$ in 60% DMSO at 35°).⁴ The rate equivalence can be traced to the cumulative electronic and steric effects of the proximate ethoxycarbonyl group.

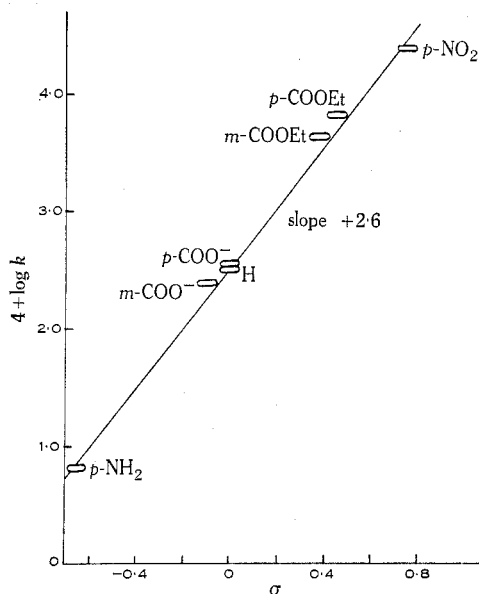


Fig. 1.—Plot of σ against $\log k$ (60% DMSO at 25°).
 k values for H, $p\text{-NO}_2$, and $p\text{-NH}_2$ from ref. 4;
 σ values from ref. 5.

The variations in k_1 and k_2 between the isophthalate and terephthalate esters are essentially due to polar influences through the atom chains in the molecule. This is justified by the excellent correlation (correlation coefficient 0.9972) between

³ Venkatasubramanian, N., and Venkoba Rao, G., *Tetrahedron Lett.*, 1967, **52**, 5275.

⁴ Tommila, E., and Palenius, I., *Acta chem. scand.*, 1963, **17**, 1980.

$\log k$ values and the Hammett σ values of the substituents (Fig. 1). The least-square slope of the line, the Hammett ρ , is $+2.6$ which is nearly the same as the ρ values reported for the alkaline hydrolysis of ethyl benzoates.⁵

TABLE 3
COMPARISON OF REACTIVITIES (80% DMSO AT 40°)
 k_1 and k_2 in l. mol.⁻¹ s⁻¹

Ester	$10^2 k_1$	$10^2 k_2$	k_1/k_2
Diethyl phthalate	42.8	5.0	8.55
Dicyclohexyl phthalate	4.22	0.515	8.19

The effect of variation of the alcohol moiety on the reaction rates has been investigated with dicyclohexyl phthalate. The observed retardation in rates of both the steps in the case of dicyclohexyl phthalate (Table 3) is to be traced to the operation of the steric effects. Similar findings have been reported by Jones and Thomas in the hydrolysis of alkyl acetates.⁶

Experimental

DMSO was purified by the method of Tommila,⁷ while 100% ethanol was prepared by the method of Vogel.⁸ The esters were of the extra pure variety (Fluka, B.D.H.) and were further purified.

The rate studies were made by titrimetric methods using a screened indicator composed of neutral red and methylene blue. The reactions were carried out in the presence of 0.02M KCl to minimize the possibility of any medium changes due to changes in the ionic strength as the diacid anion is produced.

Acknowledgment

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⁵ Hine, J., "Physical Organic Chemistry." (McGraw-Hill: New York 1962.)

⁶ Jones, R. W. A., and Thomas, J. D. R., *J. chem. Soc. (B)*, 1966, 661.

⁷ Tommila, E., and Murto, M. L., *Acta chem. scand.*, 1963, **17**, 1947.

⁸ Vogel, A. I., "A Textbook of Practical Organic Chemistry." (Longmans: London 1959.)