Tetrahedron. Vol. 26, pp. 5503 to 5505. Pergamon Press 1970. Printed in Great Britain

SOLVENT EFFECTS IN THE HYDROLYSIS OF DIETHYL MALONATE

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(*Received in the UK* 3 *June* 1970; *Accepted for publication* 23 *July* 1970)

Abstract—Kinetic studies of hydrolysis of diethyl malonate in aqueous DMSO, aqueous dioxan, and aqueous acetonitrile are reported. It has been observed for the first time that in up to 25% of DMSO there is a decrease in rate with increase in DMSO, and later the reaction rate increases with increase in the percentage of DMSO. k_1/k_2 ratios decrease with increasing percentage of organic solvent. All these features are discussed.

INTRODUCTION

PARKER[1] has very clearly demonstrated the marked rate enhancing ability of some dipolar aprotic solvents, like dimethyl sulfoxide, upon bimolecular displacement reactions effected with anions. A number of papers on the alkaline hydrolysis of esters in DMSO—water mixtures,[2–4] indicate that on increasing the percentage of DMSO, there is considerable rate enhancement which has been attributed to the diminution of OH ion solvation as a result of the competition between this anion and DMSO molecules for the water molecules and to an increase in the transition state solvation. We have now thoroughly investigated the effect of DMSO on the alkaline hydrolysis of diethyl malonate in varying proportions of DMSO—water mixtures. We find significant results indicating that the statement that dipolar aprotic solvents like DMSO cause rate enhancement is true only beyond a certain mole fraction of DMSO, below which the reaction rate follows the normal solvent effect of decrease in rate with increase in the percentage of organic solvent.

RESULTS AND DISCUSSION

The alkaline hydrolysis of diethyl malonate has been studied in varying proportions of DMSO at a constant ionic strength of 0·02 M. The reaction sequence is as follows:

$$CH_2(COOEt)_2 + 2NaOH \xrightarrow{k_1} CH_2(COOEt)COONa \xrightarrow{k_2} CH_2(COONa)_2 + 2EtOH + NaOH + EtOH$$

Frost–Schwemer[10] treatment has been utilised for the computation of rate constants of the two step hydrolysis of the diester. We plotted the $1/K$ values against the corresponding time ratios, as listed in Frost–Schwemer tables. The resulting straight line was extrapolated to include the experimental ratios for the particular run, and the values of $1/K$ corresponding to the particular time ratios were obtained. Values of k_2 were obtained specifically by hydrolysing the monoester in each case under identical conditions. With these values of k_2 and the estimated $1/K$, which is the ratio of k_1/k_2, k_1 was evaluated. This value agreed with the k_1 calculated, using ordinary second order rate expression, up to the first 25% of the reaction, assuming that there was no incursion of the second step. Similarly, beyond 50% of the reaction, it can be shown through the use of the equation

$$\alpha = \frac{\beta^K}{2(1 - K)} + \frac{(1 - 2K)\beta}{2(1 - K)}$$

that the concentration of the diester is very low when $\alpha = 0·5$, and $1/K$ is beyond 40. Thus, it is evident that only the second step of the reactlon is significant beyond 50% of the reaction. k_2 Values thus obtained after 50% of the reaction are in agreement with the k_2 obtained from a study of the alkaline hydrolysis of the monoester, under identical conditions. The second order rate constants are given below:

TABLE 1. SECOND ORDER RATE CONSTANTS (l moles^{-1}sec^{-1} × 10^2) FOR THE ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN AQUEOUS DIMETHYL SULFOXIDE AT 35°C.

Solvent composition (% vol/vol)	^{N}DMSO	k_1 *Calc*	k_1 *Obs*	k_2	k_1/k_2
100% water	0	344·9	334·6	3·85	86·9
10% aq DMSO	0·02749	122·1	130·0	1·70	76·47
15% aq DMSO	0·04288	100·9	100·4	1·525	65·90
20% aq DMSO	0·05969	79·82	82·8	1·297	63·83
25% aq DMSO	0·07800	71·20	70·11	1·150	60·98
30% aq DMSO	0·09804	90·63	94·03	1·741	54·00
40% aq DMSO	0·1447	136·20	132·20	2·606	50·65
50% aq DMSO	0·2025	208·30	203·60	4·373	46·56
60% aq DMSO	0·2758	275·70	276·50	6·747	40·98

$\underset{Calc}{k_1}$ -values calculated using rate expression.

Plots of log k_1 and k_2 vs ^{N}DMSO are given in the graph (Fig 1), which shows clearly that the reaction rates decrease till a mole fraction of DMSO (0·064) and then increase with increasing mole fraction of DMSO. The behaviour is quite normal like other solvent mixtures till the mole fraction of 0·064 of DMSO, then increasing the proportion of the organic solvent decreases the kinetic rate, as expected for this hydrolytic reaction. Beyond a mole fraction of 0·064 of DMSO, the reactions are accelerated with increase in DMSO, due to the anion desolvation and stabilization of the polarizable transition state by the larger solvation shell of DMSO, whereas for other solvent mixtures there is a general decrease at all mole fractions, with increasing proportions of the organic solvent. The report of a dualistic solvent effect with DMSO is novel and observed for the first time.

The rate constants with solvent mixtures like dioxan-water and acetonitrile-water are given below, for purposes of comparison.

A common feature observed in all the mixtures is the decrease of the k_1/k_2 ratio with increasing proportions of the organic solvent. The obvious reason is decrease of repulsion between the monoester anion and the OH ion with decreasing dielectric constant of the medium, with consequent increase in the kinetic rate of the second step, resulting in decrease in k_1/k_2 ratio. Also, the field effect due to the carboxylate anion on the reaction centre is considerably reduced in a solvent of low polarity.

TABLE 2. SECOND ORDER RATE CONSTANTS (l moles^{-1} sec^{-1} × 10^2) FOR THE ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN AQUEOUS DIOXAN AT 35°C

Solvent (% vol/vol)	^{N}dioxan	k_1 *Calc*	k_1 *Obs*	k_2	k_1/k_2
50% aq dioxan	0·1746	126·9	129·1	1·600	80·69
60% aq dioxan	0·2408	116·6	119·1	2·002	59·53
70% aq dioxan	0·3304	102·3	108·2	2·753	39·30

TABLE 3. SECOND ORDER RATE CONSTANTS (l moles^{-1}sec^{-1} × 10^2) FOR ALKALINE HYDROLYSIS OF DIETHYL MALONATE IN AQUEOUS ACETONITRILE AT 35°C

Solvent (% vol/vol)	^{N}acetonitrile	k_1 *Calc*	k_1 *Obs*	k_2	k_1/k_2
50% aq acetonitrile	0·2557	62·77	66·74	1·262	52·9
60% aq acetonitrile	0·3399	47·80	51·09	1·074	47·56
70% aq acetonitrile	0·4447	40·31	40·66	0·932	43·62

k_1 *Calc* -values calculated from rate expression.

EXPERIMENTAL

Materials. Diethyl malonate was of BDH (AR) grade, and was distilled before use (b.p. 198°). Potassium ethyl malonate was prepared by the method of Nielsen.[5] DMSO was of BDH grade and was used after purification by the method of Roberts (loc. cit.); 1,4-dioxan was purified by the method of Eigenberger;[6] acetonitrile was of BDH (AR) grade and was used without further purification. Sodium carbonate free NaOH, and azeotropic HCl solns required for kinetic studies were prepared using standard procedure. The initial concentration of ester and that of alkali were ·0025 M and ·005 M respectively. The product was the disodium salt. Under these conditions, there was no decarboxylation of the malonic acid, which has been substantiated by Svirbely[7] and Ingold.[8]

Kinetic method. The rate studies in these solvents were made by titrimetric methods, using a screened indicator composed of 0·1% solution of neutral red and methylene blue in absolute alcohol. It was found that in DMSO mixtures the use of HCl is as good as potassium hydrogen phthalate. Roberts (loc. cit.) recently used HCl for alkaline hydrolysis of mono esters in DMSO mixtures. The complication of any acid catalysis with the ester is nil as the acid cleavage is very slow with diethyl malonate.[9] The possibility of carbanion formation is also unlikely as the concentration of alkali is low.

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