

Kinetics of the Acid Hydrolysis of Diethoxymethane in Dioxane-Water Mixtures

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The kinetics of the acid hydrolysis of diethoxymethane has been studied in dioxane-water mixtures with hydrochloric, perchloric, and sulphuric acids as catalysts. In the solvent range from pure water to dioxane containing about 2 moles of water per litre the changes in the rate are small and similar for all the acids used as catalyst. When the concentration of water in dioxane is decreased below about 2 moles per litre, the rate constants decrease or increase depending on the acid catalyst. These results together with those⁶ obtained from spectrophotometric measurements show that the acid strength of perchloric acid increases, that of sulphuric acid remains almost unaltered, and that of hydrochloric acid decreases when the concentration of water in dioxane decreases.

The kinetics of the acid hydrolysis of acetic anhydride in acetone-water and dioxane-water mixtures¹ and also the kinetics of the acid hydrolysis of ethyl acetate in acetone-water mixtures have been studied² previously. Both reactions are of the bimolecular *A-2* type although the previous results for acetic anhydride indicate a possible change in mechanism from *A-2* to *A-1* as the amount of water in the solvent mixture is decreased. It was therefore of interest to investigate a unimolecular *A-1* type of hydrolysis reaction in the same solvent mixtures. The present investigation was undertaken in order to get values for comparison, the acid hydrolysis of diethoxymethane being chosen as a typical *A-1* reaction.

EXPERIMENTAL

Materials. All the chemicals (E. Merck AG, pro analysi) except dioxane were used as such. Traces of hydroxylic compounds were removed from the dioxane (Fluka AG, purified by the method of Hess and Frahm) by repeated treatment according to the method of Hess and Frahm³.

Anhydrous perchloric acid was prepared by the method of Smith⁴ from 70 % perchloric acid. The solutions of anhydrous perchloric acid and its monohydrate in dioxane were too unstable to be used in the kinetic experiments, but solutions of 70 % perchloric acid in dioxane remained uncolored for several days. Freshly prepared solutions were used in the kinetic experiments.

Table 1. Rate constants, activation energies and entropies of the acid hydrolysis of diethoxymethane in dioxane-water mixtures containing hydrochloric acid 0.100 mole per litre.

t°	$[\text{H}_2\text{O}]$ mole l ⁻¹	$[\text{HCl}]$ mole l ⁻¹	$10^4 \times k$ l mole ⁻¹ s ⁻¹	E kcal	ΔS^* e.u.	K mole ⁻¹ l
10	55.5	0.100	0.142			
25	55.5	0.100	1.39	25.12	6.03	
40	55.5	0.100	10.4			
50	55.5	0.100	38.2			
0	44.0	0.100	0.0188			
25	44.0	0.100	0.832			
40	44.0	0.100	6.67	25.44	6.26	
60	44.0	0.100	74.4			
25	33.9	0.100	0.482			
40	33.9	0.100	3.84	26.31	7.56	
60	33.9	0.100	51.9			
25	22.8	0.100	0.283			
40	22.8	0.100	2.33	26.54	7.52	
60	22.8	0.100	31.7			
25	11.4	0.100	0.267			
40	11.4	0.100	2.19	27.15	9.30	
60	11.4	0.0400	33.5			
40	11.0	0.0400	1.48			
40	5.5	0	1.35			
40	5.5	0.0496	2.96			70
40	5.5	0.0988	4.81			50
40	5.5	0.245	8.60			
40	2.22	0	5.3			
40	2.22	0.0197	8.3			50
40	2.22	0.0396	11.4			40
40	2.22	0.0968	19.4			
40	1.06	0.0194	8.40			60
40	0.52	0.0099	1.39			
40	0.52	0.0240	2.32			160
40	0.26	0.0121	0.88			240

Measurements. The kinetic experiments were performed in the same way as before ⁵. When the solvent mixtures contained 11 moles or more of water per litre ampoules were used as reaction vessels; in the case of the other solvent mixtures reaction vessels with no vapour space were used. These vessels were made from 50 ml all-glass syringes to which outlets of capillary tubes were fused. Samples of the reaction mixtures could be obtained within a few seconds by pressing the piston. The samples were weighed before analysis of the formaldehyde formed in the hydrolysis by the bisulphite method ⁵.

In each case the reaction was allowed to go to completion. Water and hydrochloric acid were added to a few samples which were then heated in ampoules at 60°C for a sufficient time for the reaction to proceed to completion. The equilibrium constant of the reaction was calculated from the analytical data obtained for these samples. The reverse reaction was taken into account when the rate constant of the hydrolysis reaction was calculated. In the rate equations

$$\frac{dx}{dt} = k(a-x) - k'x^3 = k(a-x) - k \frac{a-x_e}{x_e^3} x^3$$

$$\ln(a-x) = k \int \left(1 - \frac{a-x_e}{x_e^3} \frac{x^3}{a-x} \right) dt + \text{constant}$$

a is the initial concentration of diethoxymethane, x the concentration of formaldehyde produced in the reaction, x_e the concentration of formaldehyde at equilibrium, k the rate

Table 2. Rate constants, activation energies and entropies of the acid hydrolysis of diethoxymethane catalysed by perchloric acid in dioxane-water mixtures.

t°	$[\text{H}_2\text{O}]$ mole l ⁻¹	$[\text{HClO}_4]$ mole l ⁻¹	$10^4 \times k$ l mole ⁻¹ s ⁻¹	E kcal	ΔS^* e.u.	K mole ⁻¹ l
40	0.275	0	820			
	0.275	0.00051	900			200
	0.275	0.00099	980			260
20	0.55	0.00206	9.05			300
	0.55	0.0102	7.40			250
40	0.55	0	160	29.30	25.30	
	0.55	0.00100	180			180
	0.55	0.00200	210			170
	0.55	0.00490	238			140
60	0.55	0.00106	3290			150
	0.55	0.00199	3990			130
40	1.10	0	31			
	1.10	0.00407	37			80
	1.10	0.00992	45			110
20	2.10	0.0407	0.45			
	2.10	0.0783	0.74			64
40	2.10	0.0193	8.43	29.30	20.20	80
	2.10	0.0398	11.9			110
	2.10	0.0783	22.6			
60	2.10	0.0198	159			70
	2.10	0.075	283			89
40	5.50	0	1.53			
	5.50	0.0407	2.22			
	5.50	0.102	2.84			
	5.50	0.193	5.67			
40	11.0	0	0.81			
	11.0	0.102	1.49			
	11.0	0.203	2.00			
	11.0	0.385	3.84			

constant of the hydrolysis reaction and k' the rate constant of the reverse reaction. The integral on the right was evaluated graphically. The calculated values of k remained constant over the whole range of reaction studied, which was usually from about 10 % to 80 %. When water-rich solvent mixtures were used, the rate constants were calculated from the first-order rate equation. The results are given in Tables 1–4.

The second-order rate constants obtained by dividing the first-order rate constant by the concentration of the catalyst acid increased with the acid concentration; this salt effect was observed in the case of both water and dioxane-water mixtures. In some cases the rate constants were extrapolated to zero acid concentration; these values are also given in the tables.

DISCUSSION

The rate constant of the acid hydrolysis of diethoxymethane decreases when dioxane is added to water and has a minimum value when the solvent mixture contains water and dioxane in approximately equimolar ratio. When the proportion of water in the solvent mixture is decreased further, the rate increases rapidly when perchloric acid is used as catalyst. In the concentration range of water in dioxane from 2 to 0.3 mole per litre $\log k$ is a linear function of $\log [\text{H}_2\text{O}]$ with slope -2.5 , (Fig. 1).

The acidity function H_0 varies in a similar manner in dioxane-water mixtures when the solvent composition is altered^{1,6,7}. Measurements⁶ on perchloric acid and *o*-chloraniline in dioxane-water mixtures gave equilibrium constants

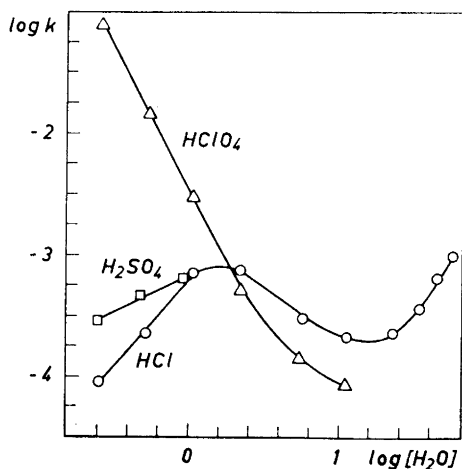
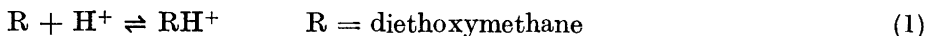


Fig. 1. Plot of $\log k$ versus $\log [H_2O]$.

for the acid-base reaction which varied linearly as $\log[H_2O]$ in the range of 0,5 to 11 moles of water per litre in dioxane. The slope of the plot was 1.9.

The similarity of the values of the slopes of the curves shows that the rapid increase of the rate of hydrolysis of diethoxymethane catalysed by perchloric acid is due to changes in the values of the equilibrium constant K of the proton transfer pre-equilibrium and that the rate constant k' of the hydrolysis of the protonated diethoxymethane is approximately independent of changes in the solvent composition as would be expected for a unimolecular reaction of this charge type. The experimental rate constant k of the acid hydrolysis of diethoxymethane is equal to the product of the equilibrium constant K of the proton transfer pre-equilibrium (1) and the rate constant k' of the subsequent slow reaction (2).



In dioxane-rich dioxane-water mixtures perchloric acid is present mainly as ion pairs. When water is added to dioxane the acid strength of perchloric acid decreases rapidly owing to the solvation of perchloric acid by water molecules. The value of the slope of about 2 indicates that in dioxane-rich solvent mixtures perchloric acid is solvated by two water molecules more than protonated diethoxymethane or *o*-chloraniline.

A different situation is found in the acid hydrolysis of diethoxymethane catalysed by hydrochloric acid in dioxane-water mixtures. In water-rich solvent mixtures the rate of hydrolysis changes similarly both when perchloric acid and when hydrochloric acid is the catalyst. The two curves in Fig. 1 differ because the rate constants in the case of perchloric acid were those obtained by extrapolation to zero acid concentration, whereas in the case of hydrochloric acid the rate constants were not extrapolated. In the solvent mixtures containing water less than about 2 moles per litre, the two curves

Table 3. Rate constants of the acid hydrolysis of diethoxymethane catalysed by sulphuric acid in dioxane-water mixtures at 40°C.

$[\text{H}_2\text{O}]$ mole l ⁻¹	$[\text{H}_2\text{SO}_4]$ mole l ⁻¹	$10^4 \times k$ l mole ⁻¹ s ⁻¹	K mole ⁻¹ l
0.250	0.0130	2.84	260
0.474	0.0255	4.43	120
0.93	0.0097	5.72	110
0.93	0.0488	6.85	91
2.14	0.0198	5.76	80
5.36	0.0399	1.43	
10.9	0.0403	0.95	

follow a different course. In the case of hydrochloric acid a maximum value of the rate is observed. When the amount of water is decreased below 1 mole per litre, the rate decreases and the plot of $\log k$ versus $\log[\text{H}_2\text{O}]$ is linear with slope 1.6.

Spectrophotometric studies⁶ reveal that when *o*-chloraniline is used as base the acid strength of hydrochloric acid decreases slightly in these solvent mixtures when the concentration of water decreases. Similarly as when perchloric acid is the catalyst, the changes in the rate of acid hydrolysis of diethoxymethane catalysed by hydrochloric acid are due to changes in the proton transfer pre-equilibrium (1). The rates of acid hydrolysis of acetic anhydride⁸ and ethyl acetate⁹ vary similarly in dioxane-water mixtures, respective slopes of the $\log k - \log[\text{H}_2\text{O}]$ plots being 1.5 and 1.9 for hydrochloric acid catalyst.

It is interesting to note that whereas the acid strength of hydrochloric acid in dioxane increases when water is added, the acid strength of perchloric acid decreases. The low acid strength of hydrochloric acid in dioxane may be due to a formation of covalent hydrochloric acid molecules which change to solvent separated ion pairs with an increase in acid strength when water is added to dioxane.

Similar curves are obtained with sulphuric acid as catalyst as with hydrochloric and perchloric acids in water-rich solvent mixtures containing two or more moles of water per litre but the curves for solvent mixtures containing only low concentrations of water are different. The rate in dioxane-rich solvent mixtures decreases slightly (Fig. 1) as the amount of water is decreased; the slope of the $\log k - \log[\text{H}_2\text{O}]$ plot is about 0.5. The spectrophotometric studies with *o*-chloraniline gave a similar result with a slope of 0.4.

The activation energies and entropies of the hydrolysis of diethoxymethane (Tables 1 and 2) increase slowly at first when dioxane is added to water and

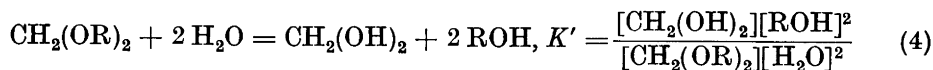
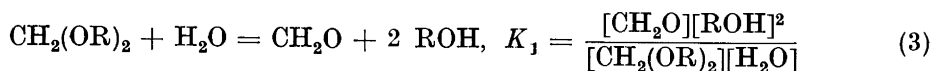
Table 4. Mean values of the equilibrium constants of the hydrolysis of diethoxymethane at 40°. $K = [\text{acetal}][\text{H}_2\text{O}]/[\text{CH}_2\text{O}][\text{ROH}]^2$ and $K' = [\text{acetal}][\text{H}_2\text{O}]^2/[\text{CH}_2(\text{OH})_2][\text{ROH}]^2$.

$[\text{H}_2\text{O}]$ mole l ⁻¹	K mole ⁻¹ l			mean	$K' = K[\text{H}_2\text{O}]$
	HClO ₄	HCl	H ₂ SO ₄		
0.25	230	240	260	240	60
0.50	160	160	120	150	75
1.0	95	60	100	85	85
2.1	95	45	80	75	160
5.4		60		60	320

more rapidly in the dioxane-rich solvent mixtures. Especially the activation entropy is unusually large in dioxane-water mixtures of low water content.

As shown by the mean values of the equilibrium constants collected in Table 4, the hydrolysis of diethoxymethane does not go to completion in dioxane-rich solvent mixtures. In spite of the fairly large experimental errors in these values, they exhibit no difference in the presence of different acid catalysts, hydrochloric, perchloric and sulphuric acids. This means that the rate of the reverse reaction, the formation of diethoxymethane from formaldehyde and ethanol, changes in a similar way as the rate of the hydrolysis reaction shown in Fig. 1. The variations of the rates of both forward and reverse reactions when the solvent composition is altered, are therefore due to changes in proton transfer pre-equilibria of the type 1.

The values of the equilibrium constants vary as the composition of the solvent mixture is altered. Formaldehyde is known¹⁰ to be present mainly as methylene glycol in water, but in dry dioxane the formaldehyde molecules are unaltered. It is likely that both forms of formaldehyde are present in concentrations of the same order of magnitude in dioxane-water mixtures containing small amounts of water. As the values of the equilibrium constant of the formaldehyde-methylene glycol reaction in dioxane-water mixtures were not known, the following two equilibria had to be considered:



Values of these two equilibrium constants were calculated and are given in Table 4. K decreases and K' increases as the amount of water in dioxane is increased. This suggests that both forms of formaldehyde are important in the solvent mixture range and therefore no constancy can be expected. In addition, formaldehyde is partly present as a monoacetal but the concentration of the latter is probably low because water is present in higher concentration than ethanol.

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