Kinetics of the Hydrolysis of Acetic Anhydride in Acetone-Water and Dioxane-Water Mixtures

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From the values obtained for the rate constants and activation entropies and energies of the acid hydrolysis of acetic anhydride in acetone-water and dioxane-water mixtures, it is concluded that the hydrolysis occurs simultaneously by two mechanisms, A-1 and A-2. When the composition of the solvent mixture is altered, one mechanism is favoured over the other. A-2 dominates in mixtures containing approximately 50 % acetone while A-1 dominates in mixtures containing only small amounts of water. An other important factor affecting the rate in solvent mixtures is the variation of the proton availability with solvent composition.

The acid-catalysed solvolysis of acetic anhydride involves, as do many other acid solvolyses, a fast proton transfer pre-equilibrium

$$Ac_2O + SH^+ = Ac_2OH^+ + S \tag{1}$$

followed by a slow reaction which may be either bimolecular, A-2,

$$Ac_2OH^+ + H_2O \xrightarrow{\text{slow}} AcOH + AcOH_2^+ \tag{2}$$
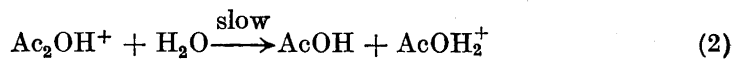
or unimolecular, A-1,

$$Ac_2OH^+ \xrightarrow{\text{slow}} AcO^+ + AcOH \tag{3}$$

The reactions following the step (2) or (3) that lead to the final products are all fast. The equilibrium of reaction (1) is far on the left and therefore the experimental rate constant

$$k_{exp.} = Kk \tag{4}$$

is equal to the product of the equilibrium constant K of the proton transfer reaction (1) and the rate constant k of the slow reaction, either (2) or (3).

Table 1. Rate constants of the acid-catalysed (k_a) and spontaneous (k_w) hydrolysis reactions of acetic anhydride in acetone-water mixtures.

$t°$	Water wt. %	H_2O mole/l	HCl mole/l	$10^5 k_a'$ l^2/mole^2 sec	$10^5 k_w$ l/sec
0°	3.03	1.34	0.0205	12.4	
	5.43	2.47	0.0404	6.85	
	12.8	5.85	0.101	4.85	0.017
	23.7	11.5	0.101	6.07	0.108
	44.6	22.5	0.101	14.6	0.95
	63.8	33.7	0.101	29.6	4.76
	82.1	44.5	0.100	47.2	17.9
	100	55.5	0.199	50.5	47.4
20°	1.14	0.49	0.079	150	
	1.77	0.76	0.0098	167	
	3.03	1.30	0.0198	179	
	5.43	2.40	0.039	81.5	
	12.8	5.70	0.098	43.5	0.083
	12.8	5.70	0.0099	41.1	0.083
	23.7	11.2	0.099	47.7	0.56
	44.6	22.1	0.099	92	4.26
	63.8	33.1	0.099	177	19.6
	82.1	44.0	0.099	333	70.5
	100	55.5	0.199	447	190
40°	3.03	1.26	0.0191	1610	
	5.43	2.34	0.0384	950	0.166
	12.8	5.56	0.096	373	0.34
	23.7	10.9	0.097	371	2.40
	44.6	21.7	0.097	620	15.9
	63.8	32.6	0.097	1155	61.9
	82.1	43.5	0.098	2280	210

Table 2. Second-order (k_a) and third-order ($k_a' = k_a/[H_2O]$) rate constants of acid-catalysed and spontaneous (k_w) hydrolysis reactions of acetic anhydride in dioxane-water mixtures at 20°C.

| Water wt. %	H_2O mole/l	HCl mole/l	$10^5 k_a$ l/mole sec	$10^5 k_a'$ l^2/mole^2 sec	$10^5 k_w$ l/sec
0.19	0.107	0.0144		149	
0.19	0.106	0.0456		142	
0.27	0.150	0.0504		261	
0.44	0.249	0.0260		298	
0.49	0.276	0.0400		262	
0.46	0.262	0.0670		272	
0.49	0.274	0.117		241	
0.76	0.431	0.0078		372	
1.10	0.620	0.0101	198	320	
0.98	0.551	0.0574	204	370	
0.99	0.560	0.171	182	325	
2.03	1.17	0.0196	284	243	
3.87	2.21	0.0396	142	64.5	
9.65	5.53	0.099	88	16.0	
19.3	11.0	0.099	80	7.3	0.80
38.5	22.1	0.099	126	5.75	5.57
58.3	33.1	0.099	239	7.22	24.6
78.7	44.0	0.099	369	8.38	79.5
100	55.5	0.199	447	8.05	190
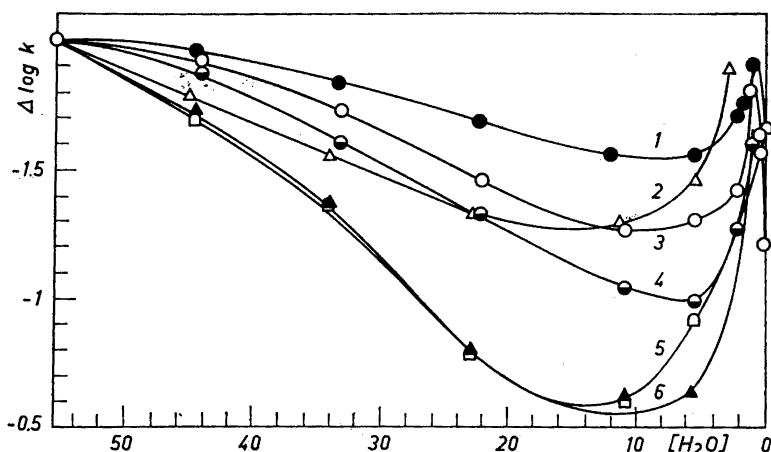
Fig. 1. Plot of log$k$ (solvent mixture) — log$k$ (water) and acidity function H_0 against [H_2O] for the hydrolysis of acetic anhydride in acetone-water and dioxane-water mixtures. 1. ethyl acetate, acetone-water. 2. diethoxymethane, dioxane-water. 3. acetic anhydride, dioxane-water. 4. acetic anhydride, acetone-water. 5. H_0, dioxane-water. 6. H_0, acetone-water.

It was found in a previous study [1] of the acid hydrolysis of acetic anhydride that the rate constant k varies only slightly over the whole range of methanol — water mixtures, whereas K, and therefore also $k_{exp.}$, changes considerably when the composition of the solvent mixture is altered. The change of K could be quantitatively explained by variations in the proton transfer equilibrium between water and methanol. The present investigation was undertaken in order to find out whether similar proton transfer equilibria are important in dioxane — water or acetone — water mixtures.

EXPERIMENTAL

Acetic anhydride (E. Merck AG, pro analysi), aniline (E. Merck AG, pro analysi) and acetone (E. Merck AG, pro analysi) were used as such. The water content of the acetone, 0.21 mole/litre, was determined by the Karl Fischer method. Dioxane (Fluka AG, purified by the method of Hess and Frahm) contained about 0.053 mole/litre of water. In order to remove any remaining hydroxylic compounds the dioxane was purified again by the method of Hess and Frahm [2]. After this treatment the dioxane contained less than 0.002 mole/litre of water. A stock solution of 1 N hydrochloric acid was prepared from a Titrisol ampoule (E. Merck AG). Solutions of hydrochloric acid in dioxane were prepared immediately before use by passing hydrogen chloride produced from sodium chloride and concentrated sulphuric acid into the dioxane. The acetone-water and dioxane-water mixtures were prepared by weighing in volumetric flasks.

Methods previously described [3] were used to determine the rate constants of the hydrolysis of acetic anhydride in the mixtures. The catalytic rate constant was obtained by subtracting the rate constant of the spontaneous reaction in the pure solvent mixture from the rate constant obtained in the same solvent mixture containing added hydrochloric acid. The second-order formula was used to calculate the rate constants when the concentration of water in the solvent mixture was less than 0.5 mole/litre, and the first-

order formula when the other solvent mixtures were employed. A good constancy of the rate constant was obtained in all cases except at the lowest water concentrations of 0.1 — 0.15 mole/litre. In these latter mixtures the second-order rate constant increases about 20 % when the reaction proceeds from 10 to 60 % change. The mean values of the rate constants are given in Tables 1 and 2.

DISCUSSION

In Fig. 1 are shown plots of $\log k$ (solvent mixture) — $\log k$ (water) against the water concentration of the solvent mixture for the acid hydrolysis of acetic anhydride, diethoxymethane [4], and ethyl acetate [5], and curves plotting values of the acidity function H_0 [6]. All these curves have a similar form and a minimum at a water concentration of about 10 moles/litre. The decrease in the rate at water concentrations below about 1 mole/litre is unexpected. Also the third-order rate constants obtained by dividing the second-order rate constant by the concentration of water vary similarly. The values of H_0 are too few in number to permit a decision as to whether they follow a similar course.

The acid hydrolysis of diethoxymethane is a typical example of the unimolecular reaction (3) with a positive entropy of activation [7] $\Delta S^* = +6.9$ e.u., a zero volume of activation [7] $\Delta V^* = 0$ cm^3 mole^{-1}, and a rate proportional to the acidity function H_0 in mixtures of a strong mineral acid and water [8]. The curve plotting the rate of acid hydrolysis of diethoxymethane is closest to the plot of the acidity function H_0 (Fig. 1). A complete agreement cannot be expected for mixtures of a organic solvent and water [8].

On the other hand, the acid hydrolysis of ethyl acetate is a typical example of a reaction occurring by the bimolecular mechanism (2). It has a negative entropy of activation in water [5]: $\Delta S^* = -22.5$ e.u. For methyl acetate which hydrolyses by the same mechanism as ethyl acetate a negative volume of activation [9] $\Delta V^* = -13.3$ cm^3 mole^{-1} was obtained in 44.1 % w/w acetone-water. The rate of acid hydrolysis of ethyl acetate is not proportional to H_0 in concentrated aqueous mineral acid solutions [10]. The curve for ethyl acetate in Fig. 1 deviates most from the H_0 curve.

The two reactions (2) and (3) probably occur concurrently in the acid hydrolysis of acetic anhydride. The activation entropy in water, $\Delta S^* = -12.3$ e.u. (Table 3), is higher than expected for a bimolecular reaction but

Table 3. Activation energies and entropies of the acid-catalysed hydrolysis of acetic anhydride calculated from the second-order rate constants and of the spontaneous hydrolysis calculated from the first-order rate constants in dioxane-water mixtures. Subscript *a* refers to acid-catalysed reaction and subscript *w* to the spontaneous reaction.

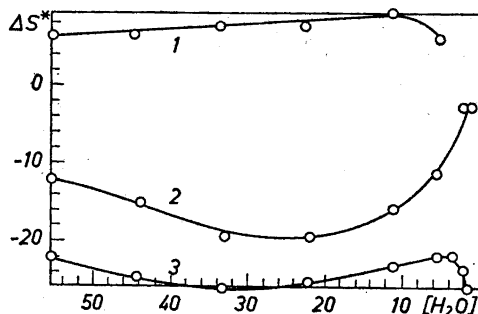| H$_2$O mole/l	E_a kcal/mole	ΔS_a^* e.u.	E_w kcal/mole	ΔS_w^* e.u.
1.30	20.65	− 2.6		
2.4	21.00	− 2.8		
5.7	18.97	−10.7		
11.2	17.44	−16.0	13.34	−39.0
22.1	16.01	−19.6	11.96	−39.7
33.1	15.64	−19.8	10.87	−40.5
44.0	16.52	−15.3	10.40	−39.5
55.5	17.25	−12.3	11.05	−35.1

Fig. 2. Plot of ΔS^* against $[H_2O]$. 1. diethoxymethane, dioxane-water. 2. acetic anhydride, acetone-water. 3. ethyl acetate, acetone-water.

lower than expected for a unimolecular reaction (Fig. 2). The rates of unimolecular hydrolyses increase faster than do the rates of bimolecular hydrolyses in aqueous solutions of strong mineral acids when the concentration of the acid is increased. The unimolecular reaction is thus favoured in concentrated mineral acid solutions and this may explain why the rate of acid hydrolysis of acetic anhydride has been found [12] to be proportional to the acidity function H_o.

In a mixture consisting of about half acetone and half water the activation entropy is small and reaches a minimum value $\Delta S^* = -20$ e.u. (Fig. 2). In this range the acid hydrolysis of acetic anhydride is thus mainly a bimolecular reaction. In agreement with this view a small negative volume of activation $\Delta V^* = -17.1$ cm³ mole⁻¹ was obtained [13] for the reaction in 44.1 % acetone-water. At high pressures the bimolecular reaction dominates even more than at low pressures because the rate of a bimolecular reaction is increased by pressure whereas an unimolecular reaction remains almost unaffected. The curve for acetic anhydride lies between those for the ester and the formal in water-rich mixtures (Fig. 1).
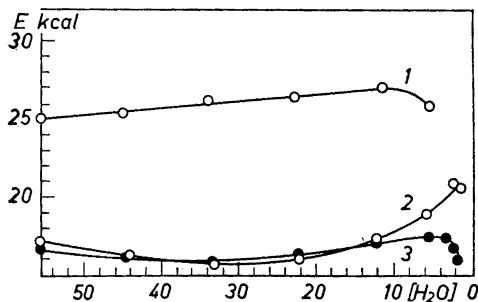

Fig. 3. Plot of E against $[H_2O]$. 1. diethoxymethane, dioxane-water. 2. acetic anhydride, acetone-water. 3. ethyl acetate, acetone-water.

The plots of the activation entropy against water concentration for ethyl acetate and diethoxymethane (Fig. 2) remain fairly horizontal over a wide range of solvent mixtures. The solvent effects in unimolecular and bimolecular reactions are hence small. On the other hand, the activation entropy of the acid hydrolysis of acetic anhydride varies much more when the composition of the solvent mixture is altered. In mixtures containing only small amounts of water the activation entropy ΔS^* reaches a high value of about —2.7 e.u. which is of the order of magnitude typical for unimolecular reactions. If all solvent effects remain insignificant when the concentration of water is decreased, the rate of the bimolecular reaction should be retarded and the unimolecular reaction should remain unaffected because the rate of the former reaction (2) is proportional to the water concentration, whereas the rate of the later (3) is of zero order with respect to water. The solvent effects of a unimolecular and a bimolecular reaction were found to be small. It is then not unexpected that a change occurs in the acid hydrolysis of acetic anhydride from two concurrent reactions in water to a typical unimolecular reaction in acetone containing only small amounts of water. Also the activation energies in Fig. 3 vary in a similar manner as the activation entropies and thus confirm the above conclusions.

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