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The Kinetics of the Base-Catalysed Hydrolysis of Acetic Anhydride in Dioxan-Water Mixtures

JOUKO KOSKIKALLIO

Department of Chemistry, University of Oulu, Oulu, Finland

The kinetics of the hydrolysis of acetic anhydride catalysed by sodium acetate, pyridine and triethylamine in dioxan-water mixtures has been studied. The reaction mechanisms proposed by Butler and Gold [1-3] and by Koskikallio [4] are not in agreement with the weak solvent effect of the acetate-catalysed hydrolysis in dioxan-mixtures, whereas the mechanism proposed by Johnson [5] is in agreement with the kinetic data for the hydrolysis in these mixtures as well as in methanol-water mixtures [4].

The rate of the acetate-catalysed hydrolysis greatly increases when the concentration of water in dioxan-water mixtures of low water content is decreased and decreases when the acetic acid content is increased. These effects are in accord with the mechanism of Johnson.

The effect of solvent composition on the hydrolysis catalysed by pyridine in dioxan-water mixtures was large, in agreement with the mechanism proposed by Butler and Gold [6-7]. Sodium acetate does not retard the pyridine-catalysed hydrolysis, whereas perchloric acid greatly accelerates this reaction in dioxan-water mixtures of low water content. Mechanisms differing from the mechanism proposed by Butler and Gold for the hydrolysis in dioxan-water mixtures of low water content are discussed.

A number of mechanisms have recently been proposed for the hydrolysis of acid anhydrides catalysed by carboxylate ions [1-5,8] and pyridine [6-8] and for the hydrolysis of esters catalysed by bases other than the hydroxide ion [8-12]. As a continuation of kinetic investigations of solvolytic reactions, the catalysis by sodium acetate, pyridine and triethylamine of the hydrolysis of acetic anhydride in dioxan-water mixtures has been examined in the hope that information would be obtained which would permit a decision between the proposed mechanisms.

EXPERIMENTAL

Materials. All the chemicals except dioxan were guaranteed reagents from E. Merck AG, and were used as such. The dioxan (Fluka AG, purified by the method of Hess and Frahm) was retreated according to the method of Hess and Frahm [13] to remove all traces of hydroxylic compounds.

Kinetic experiments. Samples taken from the reaction mixture were analysed by the aniline method [14]. The rate constants were calculated from the first-order rate equation. The initial concentration of acetic anhydride was usually about 0.05 mole/l. The calculated rate constants for each run were constant within the experimental error over the whole range used in the experiments, *i.e.* from about 10 to 80 % change except for the acetate-catalysed reaction in the dioxan-water mixture containing 0.22 mole of water per litre, which was retarded by the acetic acid produced. The mean values of the rate constants are given in Tables 1 and 2.

DISCUSSION

Hydrolysis of acetic anhydride catalysed by sodium acetate

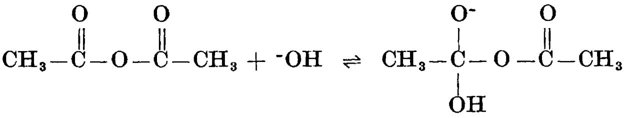
Acetate ion catalyses the solvolysis of several compounds containing the acetate group, for example, the hydrolysis [1-3] and methanolysis [4] of acetic anhydride and the hydrolysis of phenyl acetate [8-12]. The hydrolysis of acetic anhydride is catalysed also by formate ions [1,2,8] and that of benzoic anhydride by acetate ions [5]. In these last two cases a more readily hydrolysed interme-

Table 1. Hydrolysis of acetic anhydride in the presence of different catalysts in dioxan-water mixtures containing 4.44 moles of water per litre 40°C.

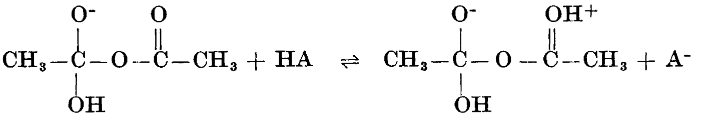
No.	Catalyst	[Catalyst]	Catalyst	[Catalyst]	10^5k s^{-1}	10^4k l $mole^{-1}s^{-1}$
1	—		—		0.485	
2	pyridine	0.124			2.03	1.24
3	”	0.248			3.59	1.24
4	”	0.496			6.35	1.20
5	”	0.800			12.1	1.45
6	CH_3COONa	0.001			1.80	131
7	”	0.002			3.01	126
8	”	0.004			4.99	113
9	”	0.008			9.02	107
10	CH_3COOH	0.080			0.56	0.20
11	”	0.160			0.61	0.15
12	CH_3COOH	0.080	CH_3COONa	0.008	7.25	
13	$HClO_4$	0.0019	”	”	1.80	69
14		0.0102	”	”	8.25	75
15	$N(C_2H_5)_3$	0.020	”	”	2.09	8.0
16	”	0.040	”	”	4.22	9.3
17	”	0.080	”	”	7.52	8.8
18	pyridine	0.250	$HClO_4$	0.000103	9.60	5850
19	”	0.250	”	0.000412	20.2	4030
20	”	0.250	”	0.00206	73.7	3400
21	”	0.250	”	0.00824	247	2950
22	”	0.250	”	0.0424	615	1450
23	”	0.020	”	0.0424	18.2	8.26
24	”	0.125	”	0.00206	60.21	
25	”	0.500	”	0.00206	109	
26	”	0.250	CH_3COOH	0.104	4.05	
27	”	0.125	CH_3COONa	0.001	2.96	
28	”	0.125	”	0.004	6.41	
29	”	0.125	”	0.008	10.45	
30	”	0.250	”	0.004	7.91	
31	”	0.500	”	0.004	11.1	
32	$N(C_2H_5)_3$	0.040	$HClO_4$	0.0212	2.28	9.5

diate, a mixed anhydride, is formed and the mechanism of the catalysis is obvious. The catalysis of the hydrolysis of acetic anhydride by acetate ion is more difficult to explain, and three different mechanisms have been proposed for this reaction.

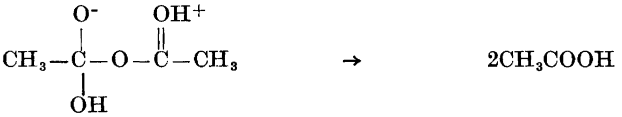
Mechanism I. Butler and Gold[1–3] suggested the following mechanism for the acetate-catalysed hydrolysis of acetic anhydride:



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + {}^{-}OH \rightleftharpoons CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 \qquad \text{fast} \quad (1)$$



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + HA \rightleftharpoons CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-O-\overset{\overset{\displaystyle OH^+}{\|}}{C}-CH_3 + A^- \qquad \text{slow} \quad (2)$$



$$CH_3-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle O^-}{|}}{C}}-O-\overset{\overset{\displaystyle OH^+}{\|}}{C}-CH_3 \rightarrow 2CH_3COOH \qquad \text{fast} \quad (3)$$

This mechanism was recently criticized by Johnson[4] because according to it the carbon-oxygen bond should be broken faster in reaction (3) than the proton is transferred between two oxygen atoms in reaction (2). According to this mechanism the rate should be proportional to the product of the concentrations of acetic anhydride and acetate ion. The mechanism[1,4] implies that the experimental second-order rate constant of the acetate-catalysed hydrolysis reaction can be expressed as

$$k_{\mathrm{AcO^-}} = K_1 \times k_2 \times K_w/K_a \tag{4}$$

where K_1 is the equilibrium constant of reaction (1), k_2 the rate constant of reaction (2), K_w the ionic product of water, and K_a the acid constant of acetic acid.

The weak solvent effect observed in the acetate-catalysed hydrolysis of acetic anhydride in dioxan-water mixtures in the present study (Table 2) is not in accord with this mechanism. According to eqn. (4), a strong decrease in the rate would be expected when dioxan is added to water. The ratio K_w/K_a decreases[15,16] from the value 5.73×10^{-8} in water to the value 2.41×10^{-8} in 70 % dioxan-water at 25°. The variation of K_1 is not known, but because reaction (1) is symmetrical with respect to the charged species, K_1 can be expected to remain almost unaltered in dioxan-water mixtures. Hence K_1K_w/K_a should remain approximately constant in these solvent mixtures. The reaction (2) involves an increase in the number of charges and the transition state should therefore be much more polar than the reactants. The addition of the non-polar solvent dioxan to polar water should therefore lead to a strong lowering of the rate constant k_2, and hence of the experimental rate constant $k_{\mathrm{AcO^-}}$ if the reaction occurs by mechanism I. The observed solvent effects shown in Table 2 are small and of the order of magnitude found for many reactions between an ion and an uncharged molecule[17–19] in which the

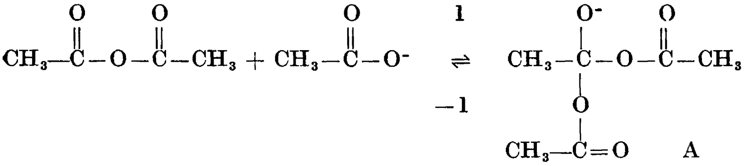
Table 2. Hydrolysis of acetic anhydride catalysed by sodium acetate or pyridine in dioxan-water mixtures at 40°C. Initial acetic anhydride concentration about 0.05 mole/l.

$[H_2O]$ mole/l	$[CH_3COONa]$ mole/l	$10^4 k_{CH_3COONa}$ l mole^{-1}s^{-1}	[Pyridine] mole/l	$10/k_{py}$ l mole^{-1}s^{-1}
55.5	0.5	95		
22.2	0.08	51	0.0992	715 *
11.1	”	”	0.496	17.6
4.44	0.002	126	0.496	1.20
1.11	0.001	355	0.496	0.085
0.22	0.0002	> 2000	0.496	0.0059

* Initial anhydride concentration 0.01 mole/l

number of charges does not change. On these grounds, this mechanism cannot be accepted.

Mechanism II. Mechanism I does not take into account the rapid exchange of acetate groups that occurs between acetic anhydride and the acetate ion [7] in water. This latter reaction and the acetate-catalysed hydrolysis may occur by a similar mechanism. The exchange reaction of the acetate group involves the formation of a symmetrical intermediate which may decompose in the reverse reaction into the reactants in two ways:



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + CH_3-\overset{O}{\overset{\|}{C}}-O^- \underset{-1}{\overset{1}{\rightleftharpoons}} CH_3-\overset{O^-}{\overset{|}{C}}(-O-COCH_3)-O-\overset{O}{\overset{\|}{C}}-CH_3 \quad \text{A} \tag{5}$$

$$A + H^+ \rightleftharpoons AH \tag{6}$$

$$A + H_2O \xrightarrow{2} 2CH_3COOH + CH_3COO^- \tag{7}$$

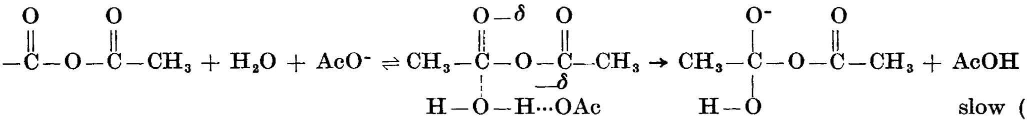
If the intermediate A reacts faster with water than acetic anhydride does, this stage could be the first stage in the acetate-catalysed hydrolysis. This mechanism has been discussed previously by this author [4] in a study of the solvolysis of acetic anhydride in methanol-water mixtures. The intermediate A is in equilibrium with its protonated form AH, but the latter cannot be the intermediate in the hydrolysis reaction because the acetate-catalysed hydrolysis of acetic anhydride [4] in water is insensitive to changes in pH.

The exchange [7] of acetate group is about four times faster than the hydrolysis of acetic anhydride in water at 0°. Hence $k_{-1} \approx 4\ k_2$. As the rate is proportional to the concentration of acetate ion, only a small fraction of the anhydride can be present in the form of the intermediates A and AH in the reaction mixture. Reaction (5) is therefore the slow process in this mechanism, but the rate constant k_1 does not alone determine the rate of the hydrolysis reaction because the reverse reaction is also taking place. The experimental rate constant of the acetate-catalysed hydrolysis of acetic anhydride in water should then be about 0.2 k_1 at 0° if the mechanism II is correct.

The mechanism II is also in accord with the observed[1] solvent isotope effect, $k_{H_2O}/k_{D_2O} = 1.69$, in the acetate-catalysed hydrolysis of acetic anhydride. Reaction (5) would be expected to be insensitive, but reaction (7) sensitive to the change in solvent from water to deuterium oxide.

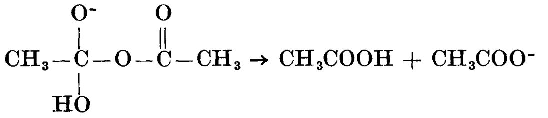
The mechanism is not, however, in agreement with the weak solvent effect observed in the hydrolysis in dioxan-water mixtures (Table 2). The equilibrium is not expected to be greatly affected by the change in the solvent composition, but the reaction (7) can be expected to be strongly retarded when dioxan is added to water as solvent because additional charges should arise when the transition state is formed from water and the intermediate A. Mechanism II does not therefore contribute to the acetate-catalysed hydrolysis of acetic anhydride to any greater extent.

Mechanism III. Johnson[5] has suggested the following mechanism for the acetate-catalysed hydrolysis of acetic anhydride:



$$CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + H_2O + AcO^- \rightleftharpoons CH_3-\underset{\underset{H-O-H\cdots OAc}{\vdots}}{\overset{O-\delta}{\overset{\|}{C}}}-O-\underset{-\delta}{\overset{O}{\overset{\|}{C}}}-CH_3 \rightarrow CH_3-\underset{\underset{H-O}{|}}{\overset{O^-}{\overset{|}{C}}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + AcOH$$

slow (8)



$$CH_3-\underset{\underset{HO}{|}}{\overset{O^-}{\overset{|}{C}}}-O-\overset{O}{\overset{\|}{C}}-CH_3 \rightarrow CH_3COOH + CH_3COO^-$$

fast (9)

The rate-determining step is then either a thermolecular reaction between anhydride, water and acetate ion, or a bimolecular reaction between the anhydride and a solvated water molecule in the solvation shell of the acetate ion. In this mechanism the acetate ion acts as a base and not as a nucleophilic catalyst. Acetate ions are solvated by water molecules in solution and these water molecules are more nucleophilic than water molecules not involved in solvation. On the other hand, water is a weaker nucleophilic reagent than the hydroxide ion, which reacts very rapidly with acetic anhydride[4]. The inreased nucleophilicity of water greatly accelerates the hydrolysis of acetic anhydride. A mechanism of the hydrolysis reaction involving a bimolecular reaction between anhydride and a water molecule associated with the acetate ion seems therefore probable.

The solvent isotope effect, k_{H_2O}/k_{D_2O}, is 2.9 for the spontaneous hydrolysis of acetic anhydride[1] and 1.67 for the acetate-catalysed hydrolysis of acetic anhydride.[1] The solvent isotope effect in the alkaline hydrolysis of acetic anhydride is not known but a value of 1.33 has been obtained for the alkaline hydrolysis of ethyl acetate[20]. The value 1.67 for the acetate-catalysed hydrolysis agrees well with the weaker nucleophilic properties of water as compared with the hydroxide ion.

Additional evidence in favour of mechanism III is provided by data for the solvolysis of acetic anhydride in methanol-water mixtures[4,21]. The ratio of the second-order rate constants of the spontaneous methanolysis and hydrolysis reactions of acetic anhydride in methanol-water mixtures, $k_m/k_h = 4.7$, at 0° remains almost constant in solvent mixtures of higher water content, but decreases to about unity when the concentration of water is decreased until it is much lower than that of methanol [21].

The ratio, k_m/k_h, of the corresponding rate constants for the alkaline solvolysis is about 13 at 25° in water-rich methanol-water mixtures as calculated from the value $K = 4.5$ of the methoxide-hydroxide equilibrium [22] and the reaction product ratios in the alkaline solvolysis of acetic anhydride in methanol-water mixtures [23].

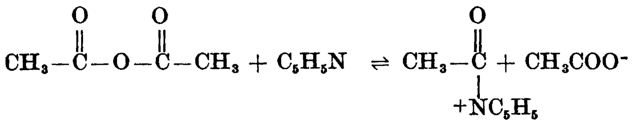
The ratio [4] of the rate constants of the methanolysis and hydrolysis reactions of acetic anhydride catalysed by acetate ion in water-rich methanol-water mixtures is about 19 at 0°. This value is larger than the respective values for the spontaneous and alkaline hydrolysis reactions. One reasonable explanation for this large value can be given if the mechanism III of Johnson is accepted. Methanol is known to be a stronger acid than water and the methoxide-hydroxide equilibrium constant has a value [22] of about 7.7 in methanol-water mixtures containing small amounts of methanol at 0°. The mole ratio of methanol to water is thus higher in the solvation shell of the acetate ion than in the bulk of the solution. The methanolysis is therefore favoured more than hydrolysis in acetate-catalysed solvolysis reactions. The experimental ratio of the rate constants, about 19, is therefore too high. If it is divided by the methoxide-hydroxide equilibrium constant, about 7.7, a value of about 2.5 is obtained which can be taken as minimum value. The true ratio of the rate constants of the acetate-catalysed solvolysis reaction has a value between 2.5 and 19 and is then most probably between the values 4.7 and 13 obtained for the spontaneous and alkaline solvolysis of acetic anhydride in methanol-water mixtures. Neither mechanism I nor II can explain this large value [19] of the rate constant ratio in the acetate-catalysed solvolysis reaction.

The rate constant of the acetate-catalysed hydrolysis of acetic anhydride decreases at first slightly and then increases when dioxan is added to water (Table 2). With the exception of dioxan-water mixtures containing only low concentrations of water, the observed solvent effects are comparatively small and in good accordance with mechanism III where the number of charges do not change when the transition state is formed (reaction [8]). The rapid increase in the value of the rate constant when the concentration of water decreases to low values is probably due to a decrease in the number of water molecules in the solvation shell of the acetate ion and an increase in the nucleophilic properties of the water molecules remaining in the shell.

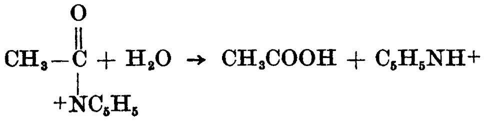
From experiments 9 and 12 in Table 1 it can be seen that acetic acid retards the acetate-catalysed hydrolysis of acetic anhydride slightly. With decreasing water content, acetic acid becomes even more effective in retarding the hydrolysis and the experimental first-order rate constant becomes proportional to the inverse of the acetic acid concentration in the reaction mixture. Only a lower limit can be estimated from the experimental values for the rate of the acetate-catalysed hydrolysis not affected by acetic acid. The retarding effect of acetic acid is also in accord with mechanism III. Acetic acid is bound to the acetate ion (or ion pair) more strongly than water because it is a stronger acid and decreases the number of water molecules in the solvation shell of the acetate ions, and thereby retards the acetate-catalysed hydrolysis.

Hydrolysis of acetic anhydride catalysed by pyridine

The pyridine-catalysed hydrolysis of acetic anhydride has been studied recently by several authors [4-7]. The mechanism [5-6] involves two consecutive reactions:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + C_5H_5N \rightleftharpoons CH_3-\underset{\underset{+NC_5H_5}{|}}{\overset{\overset{O}{\|}}{C}} + CH_3COO^- \qquad \text{fast} \quad (10)$$



$$CH_3-\underset{\underset{+NC_5H_5}{|}}{\overset{\overset{O}{\|}}{C}} + H_2O \rightarrow CH_3COOH + C_5H_5NH^+ \qquad \text{slow} \quad (11)$$

The existence of an intermediate addition product like that formed in reaction (10) has been verified spectrophotometrically in the case of a similar reaction [10-11], the imidazole-catalysed hydrolysis of phenyl acetate. In the present case the formation of an addition product by pyridine and acetic anhydride is confirmed [6] by data which show that acetate ion retards the hydrolysis catalysed by pyridine. In another recent work [7] it was shown with the aid of isotope indicators that the reverse of reaction (10) is about 25 times faster than reaction (11) in water at 0°. The concentration of the intermediate formed in reaction (10) is too small for it to be detected spectrophotometrically. Reaction (10) is then a fast pre-equilibrium followed by a slow reaction of the intermediate to the products (eqn. [1]).

The large solvent isotope effect observed,[2] $k_{H_2O}/k_{D_2O} = 5.9$, is due to reaction (11) as the equilibrium (10) is not expected to be much different in deuterium oxide than in water.

When dioxan is added to water, the pyridine-catalysed hydrolysis of acetic anhydride is strongly retarded (Table 2), approximately to the same extent as other ionization reactions in the same solvent mixtures [24,25]. The rate of the pyridine-catalysed hydrolysis reaction decreases because the equilibrium constant of reaction (10), in which two ions are formed from neutral molecules, decreases when the polarity of the solvent mixture is decreased.

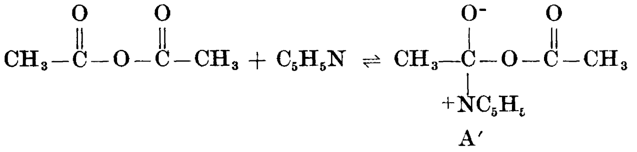
In dioxan-water mixtures of low water content (< 4 M), pyridine is no longer an highly effective catalyst, whereas sodium acetate and perchloric acid are more powerful catalysts (Table 3). In these dioxan-water mixtures the pyridine-catalysed hydrolysis of acetic anhydride is not retarded by sodium acetate (Table 1, Expts. 2—9 and 27—31). With both sodium acetate and pyridine present the first-order experimental rate constant can be expressed as

Table 3. Second-order catalytic rate constants of the hydrolysis of acetic anhydride in dioxan containing 4.4 moles of water per litre at 40°.

Catalyst	Pyridine	CH_3COONa	CH_3COOH	$HClO_4$	$N(C_2H_5)_3$
k_1[l.mole^{-1}·s^{-1}]	1.25×10^{-4}	1.20×10^{-2}	1.7×10^{-5}	7.2×10^{-3}	8.7×10^{-4}

$$k_{exp} = k_0 + k_{AcONa}\,[CH_3COONa] + k_{py}\,[Pyridine] \qquad (12)$$

where k_0, k_{AcONa} and k_{py} are the rate constants for the spontaneous, acetate-catalysed and pyridine-catalysed hydrolysis reactions of acetic anhydride. There is then no evidence that sodium acetate retards the pyridine-catalysed hydrolysis as in the 50 % acetone-water mixture [6]. This means that in solvent mixtures of low polarity such as dioxan containing 4.4 moles of water per litre, either reaction (10) is slow compared with reaction (11) and rate determining, or reactions (10) and (11) have to be replaced by the following reactions:



$$CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3 + C_5H_5N \rightleftharpoons \underset{A'}{CH_3-\overset{\overset{O^-}{|}}{\underset{\underset{+NC_5H_5}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-CH_3} \qquad (12)$$

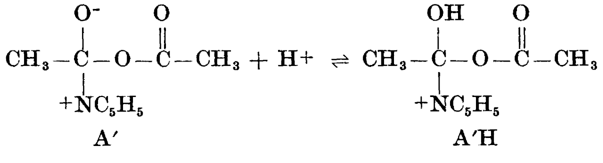
$$A' + H_2O \rightarrow 2\ CH_3COOH + C_5H_5N \qquad (13)$$

The present results do not permit one to distinquish between these two possibilities.

When perchloric acid is added simultaneously with pyridine to the reaction mixture, the rate of the hydrolysis is greatly increased (Table 1, Expts. 18—25). The pyridinium ion PyH^+ formed in these mixtures is not catalytically active. This is seen from the experiment in which perchloric acid was used in an excess over pyridine (Table 1, Expt. 23).

When pyridine is present in large excess over perchloric acid and the concentration of perchloric acid is increased, the first-order rate constant is only approximately proportional to the concentration of perchloric acid. When the concentration of pyridine is increased at constant perchloric acid concentration, the first-order rate constant increases but slightly. The second-order rate constant obtained by dividing the first-order rate constant with the concentration of pyridine then increases with increasing acidity. The acid catalysis observed in the pyridine-catalysed hydrolysis reaction may be due to the protonation of acetic anhydride prior to the reaction between anhydride and pyridine (12). A similar pre-equilibrium exists in the acid-catalysed hydrolysis of acetic anhydride in dioxan-water mixtures [26]. In this case the rate of hydrolysis is closely proportional to the acid concentration. Therefore the same mechanism is probably not applicable in the acid-catalysed reaction of acetic anhydride with pyridine present.

Another possible explanation for the acid catalysis of the pyridine-catalysed hydrolysis is that the intermediate formed in reaction (12) is in equilibrium with its protonated form



$$\underset{A'}{CH_3-\overset{\overset{O^-}{|}}{\underset{\underset{+NC_5H_5}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-CH_3} + H^+ \rightleftharpoons \underset{A'H}{CH_3-\overset{\overset{OH}{|}}{\underset{\underset{+NC_5H_5}{|}}{C}}-O-\overset{\overset{O}{\|}}{C}-CH_3} \qquad (14)$$

If A'H reacts faster to products and decomposes less rapidly into the starting materials than A', an increase in acidity would increase the rate of the hydrolysis reaction.

The acid catalysis is not observed in the hydrolysis of acetic anhydride catalysed by triethylamine, probably because the p*K* values of the intermediate similar to A'H and triethylamine do not have suitable values in this solvent mixture. (Table 1, Expt. 32).

The addition of acetic acid increases the rate of the pyridine-catalysed hydrolysis only slightly (Table 1, Expts. 25 and 3), in accordance with the fact that acetic acid is a very weak acid in dioxan containing only small amounts of water. Addition of acetate does not either have any additional catalytic effect upon the rate of the pyridine-catalysed reaction. The catalytic effect is then observed only in the presence of a strong acid such as perchloric acid.

Triethylamine is only about seven times more effective a catalyst (Table 3) in the dioxan-water mixture although it is more than 10^5 times as strong a base as pyridine in water. It is the nucleophilic properties and not the basicity of the amine that is important in the catalysis of the hydrolysis of acetic anhydride.

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