

## Kinetics of the Acid-Catalysed Solvolysis of Acetic Anhydride in Methanol-Water Mixtures

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The rate constants of the acid-catalysed hydrolysis and methanolysis of acetic anhydride were measured in various methanol-water mixtures. In solvent mixtures containing more than 27 % of water, the third-order rate constants are almost unaffected by the change of solvent composition. In solvent mixtures containing less than about 27 % of water, the increase of the rate constant is due to a shift in the proton transfer equilibria between the methoxonium ion, water and anhydride. From these values of the rate constants the equilibrium constant of the proton transfer reaction between methoxonium ion and water was calculated. The values obtained are  $K = 209$  at 0° and 118 at 25° and they agree well with the previous investigations. With the aid of these values it was concluded that the acid-catalysed solvolysis of acetic anhydride involves a proton transfer pre-equilibrium instead of a bimolecular reaction between hydroxonium or methoxonium ions and acetic anhydride.

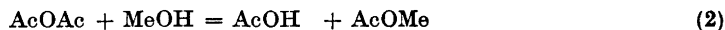
The hydrolysis of acetic anhydride in water and the alcoholysis in alcohols are catalysed by strong acids<sup>1,2</sup>. In organic solvents or in solvent mixtures with water, the rate of spontaneous hydrolysis is much less than in water, and acetic anhydride becomes more sensitive towards acids. In the present study the rates of the acid-catalysed methanolysis and hydrolysis of acetic anhydride in methanol-water mixtures were measured. From these measurements it is possible to calculate the equilibrium constant for the proton transfer reaction (1) between methoxonium ion and water and compare these values with those previously obtained by the author<sup>3</sup> from e.m.f. measurements.



### EXPERIMENTAL

The materials used in the experiments were the same as in the previous work<sup>4</sup>. Gaseous hydrogen chloride obtained from sodium chloride and concentrated sulphuric acid was absorbed in methanol and a sample of the solution obtained was titrated with baryta before use. The amounts of water remaining in the dried methanol were titrated by the

Karl Fischer method. The rate measurements and the calculations of the rate constants were made as before<sup>2</sup>. In dry methanol and also in mixtures containing less than 6 % of water the acetic acid formed in the reaction between anhydride and methanol (2)



was slowly esterified with methanol (3) during the experiments. Because the method of taking two samples simultaneously<sup>2</sup>, mixing with aniline and ammonia, and titrating, allows the calculation of the amount of anhydride in the mixture, the sum of the first-order rate constants of hydrolysis and methanolysis in methanol-water mixtures could be exactly calculated. The consecutive reaction (3) interfered only with the calculations of the ratio of the rate constants of hydrolysis and methanolysis. Fortunately, the rate of hydrolysis of acetic anhydride was small compared with that of methanolysis in the mixtures containing 6 % or less of water and hence it could be neglected. In the 5.4 % water mixture the hydrolysis was estimated at about 5 % of the methanolysis and in mixtures containing less water it was a proportionally smaller fraction of the total rate. The esterification of acetic acid (3) also produced water and since the rate of methanolysis in absolute methanol was especially sensitive to small amounts of water, the rate constants in each run decreased as the reaction proceeded. Between 0 and 50 % change the decrease was about 10 %. These rate constants were extrapolated to zero reaction time. In methanol-water mixtures the change of rate constants was much less, and the mean of the rate constants and the mean of the water concentrations were used. In mixtures containing 27 % or more water, the esterification of acetic acid or the hydrolysis of methyl acetate were negligible. Thus it was possible to calculate separately the rates of simultaneous hydrolysis and methanolysis of acetic anhydride catalysed by hydrochloric acid.

The estimated error in the rate constants of methanolysis is about  $\pm 2$  % except in the two mixtures containing more water, in which the error is about  $\pm 5$  %. In view of the unfavourable conditions for measuring the acid-catalysed hydrolysis of acetic anhydride owing to the comparatively high proportion of the spontaneous reaction and the simultaneous, faster methanolysis, these rate constants are subject to an error of about  $\pm 20$  % and are included only for a rough comparison. The results are given in Table 1, which contains the first-order rate constants of methanolysis  $k_1^m$  and hydrolysis  $k_1^h$ , from which the rate constants of the respective spontaneous solvolyses<sup>4</sup> have been subtracted, the catalytic rate constants  $k_k^m$  and  $k_k^h$  obtained from the first-order rate constants by dividing by the concentration of hydrochloric acid, the third-order rate constants  $k_3^m$  and  $k_3^h$  obtained by dividing the catalytic constants by the concentrations of water and methanol, respectively, and in the last columns the equilibrium constants calculated for the proton transfer equilibria 1.

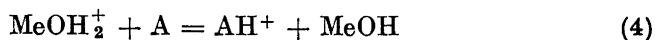
## RESULTS AND DISCUSSION

The equilibrium constant of the proton transfer reaction 1 is known from previous measurements (see Table 2). This equilibrium constant can also be calculated from the present kinetic measurements. The methanolysis of acetic anhydride catalysed by hydrogen chloride is especially suitable for this purposes, because the rate of the reaction is very little affected by the change in the composition of the methanol-water mixtures used as solvents. From Table 1 it is seen that between 27 % and pure water the rates of acid-catalysed methanolysis and hydrolysis change very little; the small changes observed are probably due to experimental error. At low water concentrations the rate increases as the proportion of water decreases and the change is about 30-fold between 27 and 0 % water. This change can be ascribed to changes in the distribution of protons between methanol, water and anhydride.

Table 1 shows the difference between the first-order experimental rate constants of methanolysis  $k_1^m$  and hydrolysis  $k_1^h$  in a solvent mixture containing hydrochloric acid and the rate constant of the spontaneous reaction  $k_0$ , the respective catalytic rate constants  $k_k = (k_1 - k_0)/c_{\text{HCl}}$ , the third-order rate constants  $k_3^m = k_k^m / c_{\text{MeOH}}$  and  $k_3^h = k_k^h / c_{\text{H}_2\text{O}}$  and the equilibrium constant of the proton transfer reaction 1.

$t^\circ$	wt. % H <sub>2</sub> O	mole · l <sup>-1</sup>		CHCl	sec <sup>-1</sup>		l · mole <sup>-1</sup> · sec <sup>-1</sup>		l <sup>2</sup> · mole <sup>-2</sup> · sec <sup>-1</sup>		l · mole <sup>-1</sup> $K = \frac{[\text{H}_3\text{O}^+]}{[\text{MeOH}_2^+] \cdot [\text{H}_2\text{O}]}$
		CH <sub>2</sub> O	CMeOH		10 <sup>5</sup>	10 <sup>6</sup>	10 <sup>4</sup>	10 <sup>4</sup>	10 <sup>6</sup>	10 <sup>5</sup>	
					$k_1^m - k_0$	$k_1^h - k_0$	$k_k^m$	$k_k^h$	$k_3^m$	$k_3^h$	
0	0	0	25.2	0.00250	10.05			422		168	
	0	0.001	25.2	0.00250	10.00			400		159	
	0.55	0.250	25.2	0.00245	3.28			138		54.8	7.6
	1.09	0.495	25.1	0.00243	1.96			81		32.2	7.9
	0	0	25.2	0.00525	21.1			402		160	
	0	0.007	25.2	0.00525	20.4			388		81	
	0	0	25.2	0.0130	55.0			424		168	
	0	0.007	25.2	0.0130	52.3			402		160	
	0.20	0.103	25.2	0.0129	29.1			226		90	8.8
	0.40	0.204	25.2	0.0128	20.8			163		64.7	8.1
	1.11	0.504	25.1	0.0127	10.6			83		33.1	8.2
	2.17	0.983	25.0	0.0126	6.54			52		20.8	7.2
	5.40	2.47	24.4	0.0121	3.16			26.1		10.7	6.0
	27.0	13.0	19.8	0.099	9.9	0.9	10.0	0.9	5.2	0.8	
	27.0	13.0	19.8	0.198	21.0	2.5	10.6	1.2			
	57.5	29.6	12.3	0.099	7.6	4.0	7.6	4.0	5.6	1.3	
	57.5	29.6	12.3	0.198	12.3	7.4	6.2	3.7			
	100	55.5	0	0.099			5.3	5.3		0.89	
100	55.5	0	0.198			9.1	4.6				
10	100	55.5	0	0.198		31.7	16.0		2.88		
20	100	55.5	0	0.099		41	41.4		7.45		
20	100	55.5	0	0.198		86	43.4		7.80		
25	0	0	24.6	0.00237	54.5			2 300		935	
	0	0.003	24.6	0.00237	54.0			2 280		925	
	0.23	0.103	24.6	0.00236	37.4			1 585		644	4.7
	0.45	0.201	24.5	0.00235	28.4			1 210		494	4.7
	0.91	0.398	24.4	0.00235	18.4			783		321	5.0
2.31	1.01	24.3	0.00234	9.5			416		171	4.7	
30	100	55.5	0	0.198		225	113		20.4		

This problem was first discussed by Goldschmidt<sup>5</sup>, but he did not take into account the decrease in the concentrations of water when hydroxonium ions are formed in reaction 1. In absolute methanol there is a proton transfer equilibrium between methoxonium ions and anhydride



The rate of the acid-catalysed methanolysis of acetic anhydride is proportional to the concentration, or rather to the activity of the protonated anhydride. In the following calculations concentrations are used instead of activities because both the rate constants and the equilibrium constants involve only

ratios of similarly charged species and at the low electrolyte concentrations used in the experiments the changes of the ratios of the activity coefficients were small compared with the experimental error involved in determining the rate constants. The equilibrium constants obtained from rate measurements at two different acid concentrations do not differ more from each other than the experimental error (Table 1, last column).

When a base such as water is added to methanol, the concentration of methoxyl ions decreases according to reaction 1. Since only a small fraction of the protons were combined with anhydride, the concentration of the protonated anhydride is decreased in proportion to the concentration of methoxonium ions. Therefore the ratio of the rate constants of the acid-catalysed methanolysis of acetic anhydride in absolute methanol and in a methanol-water mixture is equal to the ratio of the concentrations of protonated anhydride and also the methoxonium ions in the two solvents. The difference between the total acid concentration and the methoxonium ion concentration is equal to the concentration of hydroxonium ions. Finally the concentration of water is obtained by subtracting the concentration of hydroxonium ions. All the necessary equilibrium concentrations for calculation of the equilibrium constant of reaction 1 are now known. As a first approximation, a  $K$ -value was obtained which was used to calculate the rate constant in absolute methanol from the rate constants at the lowest water concentrations. The correction was only about 1–2 %, as is seen from Table 1. The mean of these rate constants was then used to calculate the  $K$ -values shown in Table 1 in the last column. The error in  $K$  is estimated as about  $\pm 3$  %. The  $K$ -values decrease as the concentration of water increases and are probably slightly affected by the change in the concentration of hydrochloric acid, too. An extrapolation to zero water concentration yields  $K = 8.3$  at  $0^\circ$  and  $K = 4.8$  at  $25^\circ$ . When these values are multiplied by the concentration of methanol, values of 209 and 118 are obtained. These values may be compared with the previous values obtained by various methods.

Table 2. Values of the equilibrium constant  $K = [\text{ROH}] \cdot [\text{H}_3\text{O}^+] / [\text{H}_2\text{O}] \cdot [\text{MeOH}_2^+]$ .

$t^\circ$	kinetically *	Method			kinetically <sup>b</sup>
		e.m.v. <sup>a</sup>	indicator <sup>c</sup>	conductivity <sup>d</sup>	
$0^\circ$	209				
$25^\circ$	118	137	111	107	109

\* present work

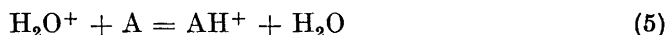
The heat of the proton transfer reaction 1 is  $\Delta H = -3.7$  kcal mole<sup>-1</sup> and the entropy  $\Delta S = -2.7$  cal degree<sup>-1</sup> mole<sup>-1</sup> as calculated from the values of  $K$  of the present work. The great difference in the basicity between methanol and water is probably due to the strong hydrogen bonding occurring in methanol. In acetic acid <sup>9</sup> water is only about eight times as strong a base as methanol at  $25^\circ$ . The heat of depolymerisation of hydrogen-bonded polymers of alcohols is of the same order of magnitude as the heat of the proton transfer reaction 1.

The activation energies and entropies calculated from the rate constants of hydrolysis in water and methanolysis in methanol given in Table 1 are

	$E$ kcal · mole <sup>-1</sup>	$A$ l · mole <sup>-2</sup> · sec <sup>-1</sup>	$\Delta S^*$ at 25° cal · degree <sup>-1</sup> · mole <sup>-1</sup>
Hydrolysis	17.13	$3.95 \cdot 10^9$	-17.06
Methanolysis	10.97	$1.4 \cdot 10^6$	-33.2

The values of the activation energy is not far from the respective value obtained for the acid-catalysed hydrolysis of simple esters, *e. g.* ethyl acetate<sup>10</sup>  $E = 16.76$  kcal mole<sup>-1</sup>,  $A = 3.75 \times 10^6$  l · mole<sup>-2</sup> · sec<sup>-1</sup> and  $\Delta S^* = -30.5$  cal · degree<sup>-1</sup> · mole<sup>-1</sup>. Although the entropies of activation differ considerably the mechanism of the two reactions is probably the same, involving a fast proton transfer equilibrium 4 and a subsequent bimolecular reaction between the protonated anhydride and a water molecule to form either an intermediate addition product or a transition state. A unimolecular mechanism was proposed by Gold<sup>1</sup> for the acid-catalysed hydrolysis of acetic anhydride in water at 0° on the grounds that the rate was proportional to the Hammett acidity function  $h_0$  and not to the concentration of the catalyst at high acid concentrations. The validity of this method has recently been criticized in a work of Koskikallio and Whalley<sup>11</sup> concerning the volume of activations of acid-catalysed hydrolyses.

The experimental activation energies given above are actually the sums of the activation energies of the slow step of the reaction and the proton transfer equilibria 4 and 5 in methanol and water, respectively.



The ratio of the equilibrium constants of the two proton transfer reactions 4 and 5 in the same solvent, *e. g.* a methanol-water mixture, is equal to the equilibrium constant of the proton transfer reaction 1 in the same solvent. Because the solvent effects are small for these reactions the above statement is approximately valid for values obtained in different solvents, *e. g.* pure methanol and water. Thus the greatest part of the difference between activation energies in water and in methanol,  $\Delta E = -7.2$  kcal · mole<sup>-1</sup>, is due to the heat of the proton transfer reaction 1,  $\Delta H = -3.7$  kcal · mole<sup>-1</sup>, and the rest of the difference is due the difference between the activation energies of the two reactions, hydrolysis and methanolysis, and their solvent effects.

Similarly, differences in the entropies of activation can be corrected for the changes in the proton transfer equilibria 4 and 5. If the concentrations of the protonated anhydride in water and in methanol containing hydrochloric acid were known, the entropies of activation of the slow step of the solvolysis of acetic anhydride could be calculated. Assuming the value of the equilibrium constant of the reaction 1 to be unaffected by the change in the composition of the solvent mixture,  $K = 209$  at 0°, the ratio of the concentrations of the protonated anhydride in methanol and in water can be calculated to be  $25.2 \cdot 209/55.5 = 94.2$ . Because the rate is proportional to the concentrations of the protonated anhydride, this would also be the ratio of the rate constants.

It would cause a difference of about 9.0 units in the experimental activation entropies. The observed difference in the entropies is 16.1 units. Thus the differences in the rates, activation energies and entropies of the acid-catalysed solvolysis of acetic anhydride in methanol-water mixtures are partly explained by the changes in the proton transfer equilibria when the composition of the solvent mixture is altered and the remaining small differences indicate that other solvent effects are only of minor importance.

That there are fast proton transfer pre-equilibria (4 and 5) in the acid-catalysed solvolyses of acetic anhydride is obvious from the observation of Gold<sup>1</sup> that the rate of the hydrolysis is much more closely proportional to the Hammett acidity function  $h_0$  than to the concentration of the catalyst at high acid concentrations. The same result is obtained from the present experiments. One of the possible mechanisms of the acid-catalysed solvolysis of acetic anhydride in addition to that involving a fast proton transfer pre-equilibria is a bimolecular reaction between methoxonium or hydroxonium ions and the uncharged anhydride. Because all the species are thermodynamically in equilibrium, a choice between these two mechanisms is impossible. For the following reasons the mechanism which includes the proton transfer equilibrium is more probable. If the value of  $K = 209$  is used to calculate the ratio of hydroxonium and methoxonium ions in the mixture containing 27 % water, a value of  $[\text{H}_3\text{O}^+]/[\text{ROH}_2^+] = 137$  is obtained. The ratio of the first-order rate constants of the acid-catalysed hydrolysis and methanolysis of acetic anhydride is  $k_1^{\text{H}}/k_1^{\text{M}} = 0.132$  in the same solvent mixture. Thus the bimolecular reaction between anhydride and hydroxonium ion would be about  $10^3$  times slower than the corresponding reaction between anhydride and methoxonium ion. Such a large difference between these two similar reactions is unexpected. Thus the mechanism is that involving a proton transfer pre-equilibrium. According to this mechanism the ratio of the acid-catalysed methanolysis and hydrolysis (about 4 to 6) is almost identical with the value for the ratio of the spontaneous reactions in the same solvent mixtures<sup>4</sup>. Also this observation is in accordance with the mechanism involving the proton transfer pre-equilibrium.

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