

Kinetics of Solvolysis of Acetic Anhydride in Methanol-Water Mixtures

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The rates of simultaneous hydrolysis and methanolysis of acetic anhydride in various methanol-water mixtures were measured at three different temperatures. The great variation in the second-order rate constants of the solvolysis reactions when the composition of the solvent mixture is altered is discussed and it is concluded that both methanolysis and hydrolysis are catalysed by the weak base water. The changes observed in the ratio methanolysis/hydrolysis are discussed in terms of hydrogen bonding in the methanol-water mixtures.

In addition to the spontaneous hydrolysis and alcoholysis of acetic anhydride, these reactions are catalysed by acids and bases¹⁻². The spontaneous solvolyses of acetic anhydride in alcohol-water mixtures could be described as reactions catalysed by the weak base water. In order to study this problem the rates of hydrolysis and methanolysis of acetic anhydride were measured in different methanol-water mixtures.

EXPERIMENTAL

The water used was freshly distilled. The methanol (Merck, analytical grade) was dried with aluminium methylate³ and distilled. Finally it was distilled over anhydrous copper sulphate. The amount of water remaining after this treatment, usually about 0.005 mole/litre, was determined by the Karl Fischer method. The aniline was freshly distilled. The acetic anhydride used was a product of Merck, analytical grade.

The solvent mixtures were made up by volume in a 100 ml volumetric flask and the components were also weighed. The solvent mixture and anhydride were separately allowed to obtain the temperature of the thermostat during about one hour. At 0°C a stirred 10 l Dewar flask thermostat, half filled with ice, was used and for other temperatures the thermostats were electrically controlled to within $\pm 0.01^\circ$. The reaction was started by adding about one milliliter of acetic anhydride to 100 ml of the solvent which yielded an approximately 0.1 M anhydride solution. The reaction was followed by taking 5 ml samples at suitable time intervals in order to cover the range from about 10 % to 90 % change. One sample was mixed with 15 ml of saturated aniline water (about 0.3 M aniline) and titrated with 0.02 M baryta. Another sample was taken immediately after the first (about 1 min) and mixed with 20 ml of 0.6 M ammonia. The mixture

was made slightly acid by adding 1–3 ml of 0.1 M hydrochloric acid and then titrated with 0.6 M ammonia potentiometrically (Radiometer PHM 22h). These results were interpolated to correspond to the same reaction time. The difference between these two titrations gives the amount of anhydride present in the sample.

During the reaction of acetic anhydride with methanol in dry methanol the acetic acid produced in the reaction was esterified to some extent (2–3 %). This did not interfere with the calculation of the rate of methanolysis of acetic anhydride when the method of two different titrations was used. In methanol-water mixtures the consecutive reactions of esterification of acetic acid or hydrolysis of methyl acetate would have complicated the calculations of the ratio of the rates of simultaneous hydrolysis and methanolysis of acetic anhydride. Fortunately these consecutive reactions were so slow, when compared with the solvolysis of acetic anhydride, that they could be neglected. This was verified by taking samples from mixtures in which all the anhydride had reacted.

The rate constants were calculated from the usual first-order equation, which in the case of two simultaneous first-order reactions gives the sum of the two rate constants $k_1^h + k_1^m$. The ratio of these rate constants was obtained from the mean of the ratios of the changes in the values of the aniline and ammonia titration. Thus the first-order rate constants of hydrolysis k_1^h and methanolysis k_1^m could be calculated in each solvent mixture from a single run. The experimental error of the rate constants is of the order of magnitude of about 1–2 % in cases where the rates of hydrolysis and methanolysis do not much differ from each other and increases as the proportion of the rate of reaction decreases. The results are given in Table 1.]

RESULTS AND DISCUSSION

From Table 1 it is seen that the first-order rate constant of hydrolysis of acetic anhydride k_1^h decreases continuously when methanol is added to water, but the first-order rate constant of methanolysis k_1^m shows a maximum. This contrast in the behaviour of hydrolysis and methanolysis disappears in the second-order rate constants k_2^h and k_2^m . Over the whole range of solvent mixtures there is nevertheless a considerable change of the second-order rate constant, of about 80-fold in the case of hydrolysis and 320-fold in methanolysis. There are different ways of explaining these great changes in rates. If the transition state in the hydrolysis and methanolysis of acetic anhydride is much more polar than the reactants, a solvent of lower solvating power such as methanol would retard the rate. Still, methanol is a solvent of fairly high dielectric constant ($D = 35.0$ at 0°) and good solvating power. Therefore it would be necessary to postulate an highly polar transition state. But it would then be difficult to account for the increase in the second-order rate constant of methanolysis of acetic anhydride when a solvent of low dielectric constant and poor solvating power such as benzene ($D = 2.29$ at 18°) is added to methanol ⁴.

An other possible explanation is based on changes in the acid-base properties in the methanol-water mixtures. Water is 137 times as strong a proton acceptor as methanol ⁵ at 25° and about one-eighth as strong a proton donor as methanol ⁶ at 25° . When water is replaced by methanol there is a considerable decrease in the basicity of the solvent. The solvolyses of acetic anhydride are known to be accelerated by various bases such as hydroxyl ion ⁴, acetate ion ², pyridine ^{1,2} and various tertiary amines ¹. The great sensitivity of acetic anhydride towards bases makes it possible to assume that the spontaneous

Table 1. The first-order k_1 , second-order k_2 and catalytic k_k rate constants of hydrolysis and methanolysis of acetic anhydride in methanol-water mixtures.

t°	wt. % MeOH	mole · l ⁻¹		sec ⁻¹		l · mole ⁻¹ · sec ⁻¹		l ² · mole ⁻¹ · sec ⁻¹		k_2^m / k_2^h
		[H ₂ O]	[MeOH]	10 ⁵ · k_1^h	10 ⁵ · k_1^m	10 ⁷ · k_2^h	10 ⁷ · k_2^m	10 ⁷ · k_k^h	10 ⁷ · k_k^m	
0	100	0.007	25.2		0.258	1.0 *	1.02			
	98.9	0.507	25.0	0.009	0.483	1.8	1.93	1.6	1.8	1
	97.8	1.01	24.8	0.019	0.728	1.9	2.94	0.9	1.9	1.5
	95.0	2.28	24.5	0.060	1.41	2.6	5.75	0.7	2.08	2.2
	93.4	3.03	24.1	0.11	1.88	3.6	7.80	0.85	2.24	2.2
	89.0	5.06	23.3	0.25	2.96	5.0	12.7	0.8	2.12	2.5
	83.6	7.57	22.3	0.56	5.07	7.4	22.8	0.85	2.88	3.1
	73.2	12.9	20.1	1.63	9.44	12.7	47	0.90	3.57	3.7
	42.5	29.6	12.5	8.21	17.4	27.8	139	0.90	4.67	5.0
	16.2	45.5	4.96	24.1	13.1	52.4	246	1.13	5.78	4.7
	8.03	50.4	2.48	31.9	7.14	63.4	290	1.23	5.7	4.6
	5.00	52.5	1.49	36.8	4.80	70.0	320	1.31	6.1	4.6
	2.50	54.0	0.743	40.3	2.85	74.7	320	1.36	5.9	4.3
	0	55.5	0	46.5		83.8		1.46		
	25	100	0.001	24.6		2.15	10 *	8.75		
99.87		0.057	24.6		2.26		9.20			
99.74		0.113	24.6		2.36		9.60			
99.46		0.224	24.5		2.63		10.7			
97.5		1.10	24.2	0.16	4.04	15	16.7	4.5	7.2	1.1
95.1		2.20	23.8	0.41	6.52	19	27.4	4.1	8.5	1.4
87.8		5.50	22.4	1.86	16.2	34	72.3	4.3	11.6	2.1
76.6		11.0	20.3	6.41	32.7	58	161	4.4	13.8	2.8
0		55.5	0	255		460		8.1		
50		100	0	23.9		20.9	60 *	87.5		
	95.1	2.14	23.1	2.0	32.7	95	141	16	25	1.5
	87.8	5.36	21.8	8.3	57.6	155	264	18	33	1.7
	76.6	10.7	19.8	24	96.7	230	489	16	37.6	2.1
	0	54.9	0	972		1 770		31		

* extrapolated values.

solvolysis of acetic anhydride in methanol-water mixtures is catalysed by the weak base water. The catalytic rate constant of methanolysis k_k^m is obtained when the second-order rate constant of methanolysis in pure methanol k_2^m is subtracted from the rate constants in methanol-water mixtures and divided by the concentration of water. The catalytic rate constant k_k^m decreases much less than k_2^m when methanol is added to water (Table 1 and Fig. 1). The catalytic rate constant of hydrolysis k_k^h is obtained in the same way when an extrapolated value of k_2^h in absolute methanol is used. Such an extrapolation may not be quite justified, but the choice of the extrapolated value only affects the value of k_k^h at low water concentrations and has a negligible effect upon their

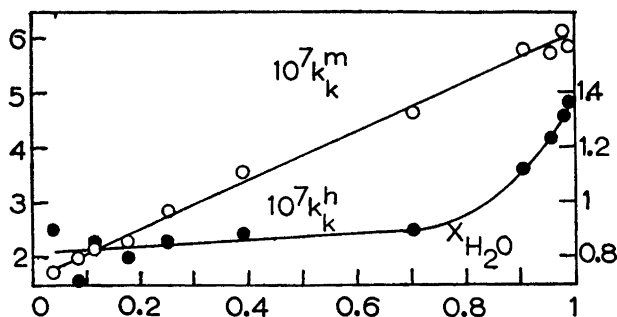


Fig. 1. The variation of the water-catalysed rates of hydrolysis and methanolysis of acetic anhydride in methanol-water mixtures.

values at water concentrations higher than 50 %. Furthermore, these rate constants change much less than the corresponding second-order rate constants k_2^h . The variation of the catalytic rate constants when the composition of the solvent is altered at the temperatures 0°, 25° and 50° is essentially the same. The remaining small changes in k_k -values with changing composition of the solvent mixture may be ascribed to solvent effects, for example hydrogen bonding.

Further insight into these "second-order" effects can be obtained from a comparison of the ratios of the rates of hydrolysis and methanolysis, because this treatment excludes the effect of water as a catalyst. From Table 1 and Fig. 2 it is seen that considerable changes in these ratios occur when temperature or solvent composition is altered. For comparison the writer's ⁴ previous values in ethanol-water mixtures are included, and likewise the values of Caundri ⁷. In both cases the ratio of the rate constants changes in the same way when the composition of alcohol-water mixtures are altered, but the reactivities of the alcohols and water are in an unexpected order of magnitude. The rates of hydrolysis and ethanolysis are not very different from each other but the rate of methanolysis is considerably greater than that of hydrolysis, especially in mixtures with a high water concentration. This high reactivity of methanol in methanol-water mixtures may be attributed to hydrogen bonding in solvent mixtures. When methanol and water are mixed, considerable amounts of heat are evolved ⁸. The strong interaction between methanol and water molecules probably occurs *via* hydrogen bonding. This can take place in two different ways, but because of the dominating acidic properties of methanol and the basic properties of water, it is likely to occur in the way: $MeOH \cdots OH_2$. Higher hydrogen-bonded associations also occur, but their occurrence does not invalidate the following argument. The hydrogen bonding between methanol and water molecules would then make the oxygen of methanol more and the oxygen of water less nucleophilic or reactive to the anhydride molecule. The same argument also applies to ethanol-water mixtures. When the temperature is increased, the hydrogen bonds are partially broken and the ratios of the rates of alcoholysis and hydrolysis decrease. At

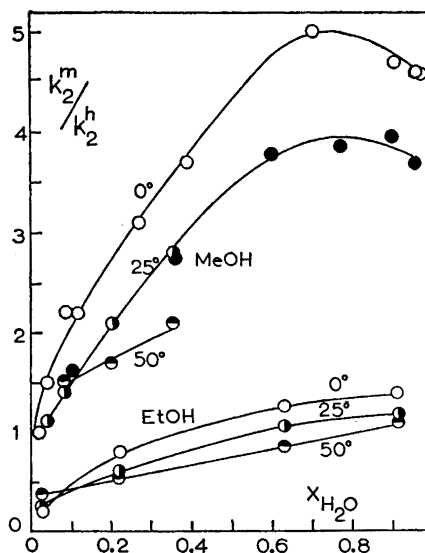


Fig. 2. The variation in the ratio of the second-order rate constants of hydrolysis and alcoholysis of acetic anhydride in methanol-water mixtures. In addition to the present values the writers previous⁴ data and those of Caundri⁷ (black points) are also included.

high enough temperatures the ratios could well be less than one in all mixtures of water and alcohol.

In mixtures containing less water than alcohol the ratio is decreased as the amount of water is decreased. In mixtures containing little water, all the water is hydrogen-bonded, mainly in the form $\text{MeOH}\cdots\text{OH}_2$, and in addition the excess of methanol molecules are associated between themselves $\text{MeOH}\cdots\text{OHMe}$. Therefore there is no change in the species reacting in the hydrolysis but an increasingly greater proportion of methanolysis occurs between the anhydride and various polymers of methanol as the amount of water in the solvent mixture decreases. On steric grounds the rate of methanolysis will decrease as compared with that of hydrolysis and the ratio of the rates will decrease as the proportion of water decreases. The reverse effect of temperature at very low water concentrations may likewise be explained on the same lines (Fig. 2).

In mixtures containing small amounts of methanol the ratio also decreases as the amount of methanol decreases. In these mixtures the methanol is mainly bonded as $\text{MeOH}\cdots\text{OH}_2$ but the excess of water forms associations with itself $\text{HOH}\cdots\text{OH}_2$ and these may be slightly more reactive in the hydrolysis than the associations with methanol.

The low reactivity of acetic anhydride with associations of alcohol is clearly seen from the increase in the rate when the associations are depolymerised by addition of an inert solvent such as benzene⁴ and change of temperature which yields high apparent activation energies⁴ in alcohols (about 18 kcal) compared with those in benzene (14 kcal) or water (10 kcal).

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