The Influence of the Solvent on Reaction Velocity

III. The Hydrolysis of Valerolactone

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In the previous investigations [1,2] of this series the influence of the solvent on the alkaline hydrolysis of carboxylic esters was studied. It was found that a small addition of an alcohol, acetone, or dioxan into the water used as solvent often slightly enhances the velocity of the reaction, especially if the temperature is low, but that larger amounts of these organic substances always powerfully decrease the reaction rate. Much more interesting features revealed the determination of the parameters of the Arrhenius equation. In binary mixtures of water with aliphatic alcohols, acetone, or dioxan the activation energy and frequency factor have a minimum at the mole fraction x_{water} 0.94 —0.90, methanol-water and glycol-water being the only exceptions found to this rule. Besides, several other peculiarities appear, *e.g.* a steep fall of the frequency factor in aqueous alcohol at high alcohol percentages.

To see in what extent these observations have a wider bearing we have investigated the hydrolysis of valerolactone. The present communication contains the results of these experiments. The reaction has previously been studied by Hegan and Wolfenden [3] in ethanol-water, but their experiments did not cover the whole range of mixtures. However, on the ground of their results a minimum in E and A could be expected also in this case.

EXPERIMENTAL

Preparation of valerolactone. For the reduction of laevulinic acid to γ-hydroxyvaleric acid we used hydrogenation under pressure in presence of a catalyst, which is much more profitable than the older methods, *e.g.* that given by Taylor and Close [4]. 58 g (ca. 0.5 moles) of laevulinic acid was neutralized with 20 g of sodium hydroxide dissolved in 100 ml of water, this solution diluted up to 200 ml with water and introduced in a 500 ml hydrogenation bomb of stainless steel. Raney-nickel W6, prepared according to Adkins and Billica [5], was used as catalyst. The bomb was placed in an electric heater

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mounted on a shaking apparatus. Hydrogen of a pressure of 95 atmospheres was admitted to the bomb, while it was shaken, through a supply tube. The reaction set in at about 50° C, at which temperature the reduction was then performed. After two hours no more hydrogen was absorbed. The bomb was left to cool and opened; 65 ml of concentrated hydrochloric acid was added to the solution and the solution saturated with ammonium sulphate. The liberated γ-hydroxyvaleric acid was extracted with ether in an extraction apparatus. The extract was dried over anhydrous sodium sulphate, the ether distilled off, and the residue repeatedly distilled until a constant boiling point testified to the purity of the product. Usually two or three distillations are enough. The valerolactone obtained, a colourless liquid boiling at 207°, was practically pure. The yield depends greatly on the thoroughness of the extraction; a yield of 75 per cent is fairly easily reached.

The methanol, ethanol, acetone, and water used as solvent in the kinetic experiments were of the following qualities.

Methanol: A commercial synthetic product was distilled over anthranilic acid (10 g per 1 liter) and then treated by the method of Lund and Bjerrum [6], with the only exception that in the final distillation anthranilic acid was used instead of tribromo-benzoic acid. The purity of the product was checked by comparing its refractive index with that of methanol obtained from pure methyl oxalate.

Ethanol: Usual 95 per cent alcohol was dried by boiling with calcium oxide and finally purified by the method of Lund and Bjerrum.

Acetone: A commercial product of the quality "pure" was dried over ignited potassium carbonate and distilled.

Water: Only freshly distilled water was used.

Method. Wolfenden and Hegan used the conductivity method. Owing to the rapidity of the reaction in water, we, however, chose the titration method employed in this laboratory. The making use of the reaction vessels previously described [7] renders it possible to follow the course of fast reactions, too. The experiments were carried out by using both lactone and sodium hydroxide in equal concentrations. Except in experiments for the investigation of the dependence of the specific rate on the initial concentration of the reactants, 5 ml of a 0.05 M solution of the lactone was run into the one compartment of the reaction vessel, and 5 ml of a 0.05 M NaOH into the other, so that, after mixing, the initial concentration of each reactant was 0.025 moles/liter. The reaction vessel was kept in the thermostat until the reactants had acquired its temperature, and the reaction was then started by mixing of the two solutions. The reaction was stopped by adding a slight excess of 0.02 N hydrochloric acid and the acid titrated with 0.02 N baryta solution, cresol red being used as indicator.

The temperature of the thermostats could be held constant within ±0.02°. The thermometers used in the thermostats were checked against a thermometer calibrated by the National Bureau of Standards (U.S.A.).

The velocity constants were calculated by the ordinary bimolecular formula. To save space, merely the means of the runs (usually eight measurements) are given below. As an illustration the following two runs chosen at random may be sufficient.

1. Solvent water, $a = 0.025$ mol/l, temperature 40.00° C.

Time sec.	10	15	20	40	50	60	70	80
Percentage change	19.6	28.0	32.8	49.2	55.3	60.0	63.2	66.0
k l mol^{-1} sec.$^{-1}$	0.970	1.038	0.978	0.969	0.990	1.000	0.982	0.972

2. Solvent 60 per cent methanol, $a = 0.025$ mol/l, $0°$ C.

Time mins.	60	100	180	325	365	525	675	750
Percentage change	16.0	23.6	34.4	48.8	52.7	61.2	67.2	69.2
10^5 k 1 mol^{-1} sec.$^{-1}$	211	206	194	195	201	200	202	200

RESULTS AND DISCUSSION

The rate constants. The rate constant k is practically independent of the initial concentration a of the reactants and of an added salt, as is seen from the following results in water at $25°$ C:

a mol/l	0.05	0.025	0.01	0.025	0.025
KCl mol/l	—	—	—	0.1	0.2
k 1 mol^{-1} sec.$^{-1}$	0.411	0.400	0.412	0.411	0.409

This being stated, all the measurements were, as mentioned above, carried out using the initial concentrations 0.025 mol/l.

The experimental rate constants, corrected for change of concentration due to thermal expansion of the solvent, are given in Table 1. It is interesting to note that methanol always retards the reaction, whereas ethanol, when present in small amounts accelerates, but when present in large amounts retards it. The lower the temperature, the greater is the accelerating effect, and obviously it does not occur above a certain temperature. A corresponding acceleration is observed also in the alkaline hydrolysis of ethyl acetate [1,8]. A possible explanation is that in this composition range of the solvent the solvation of the transition state is strongly increased [1], which causes a great decrease in the energy of activation.

The retarding influence of methanol is much greater than that of ethanol, as is the case also in the alkaline hydrolysis of ethyl acetate [1]. Acetone has in greater concentrations a weaker effect than ethanol. No exact mathematical relationship between the rate constant and the composition of the solvent can be given, but it may be mentioned that in methanol-water in the range from pure water to the mole fraction $x_{MeOH} = 0.85$ (0—90 % by weight of methanol) log k is practically a linear function of the methanol content: at $25°$ log $k = -0.400 - 2.625$ x_{MeOH}. Log k then falls with rapidly increasing slope (Fig. 1). For the other mixtures only very rough relations can be given.

The Arrhenius equation. Table 1 also contains the values of the activation energy E and the frequency factor A, calculated by the Arrhenius equation $k = Ae^{-E/RT}$ from the experimental values of k at different temperatures using the method of least squares. In most cases the Arrhenius equation was
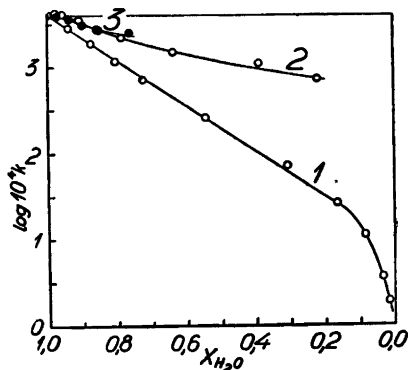
Fig. 1. Plot of log k vs. x_{water}, 25° c.

1. Methanol-water.
2. Ethanol-water.
3. Acetone-water.

obeyed within the limits of the experimental error, but in many methanol-water mixtures there appeared deviations from a linear relationship between log k and $1/T$. These will be treated later on separately. The data of Table 1 are mean values for the whole temperature range used, obtained by the method of least squares. They are fit enough for the examination of the general solvent effect.

It may be mentioned that our results are in good agreement with the data of Hegan and Wolfenden: | p % EtOH, E, log A | 0, 11 200, 7.89 | 21.5, 10 800, 7.46 | 40, 12 600, 8.57 | 60, 14 500, 9.78 |.

From the table or more cleary from Figs. 2 and 3 we see that E and A continuously rise with increasing methanol content of the solvent, the influence of methanol being very powerful. At the mole fraction $x_{\text{MeOH}} = 0.75$ A has its highest value, after which it rapidly falls. In ethanol-water and in acetone-
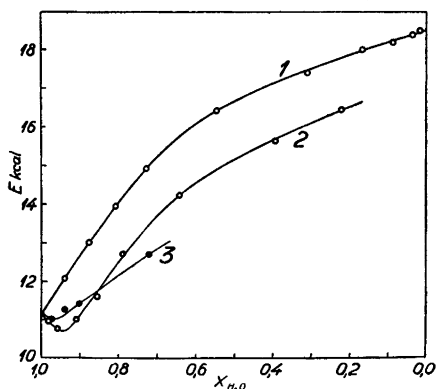

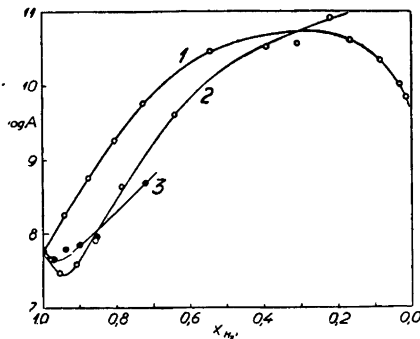Fig. 2. Graph to show the correlation between E and x_{water}.

Fig. 3. Graph to show the correlation between log A and x_{water}.

Table 1. The values of k, E, log A, and ΔS*.

Solvent	x_{H_2O}	k 1 mol^{-1} sec.$^{-1}$					E cal	log A	ΔS^* E.U.
		0.00°	15.00°	25.00°	40.00°	50.00°			
Water	1	0.0714	0.208	0.400	0.987		11 150	7.776	—25.0
10 wt. % Methanol	0.941	0.0434	0.137	0.283	0.732		12 050	8.286	—22.6
20 » »	0.877	0.0244	0.0873	0.187	0.516		13 000	8.772	—20.4
30 » »	0.806	0.0128	0.0510	0.115	0.341		13 950	9.282	—18.0
40 » »	0.727	0.00666	0.0291	0.0697	0.223		14 930	9.780	—15.8
60 » »	0.543	0.00198	0.00978	0.0255	0.0943		16 420	10.468	—12.6
80 » »	0.308	0.0_3454	0.00242	0.00663	0.0271		17 400	10.565	—12.2
90 » »	0.165	0.0_3160	0.0_3872	0.00260	0.0109		18 000	10.602	—12.0
95 » »	0.085		0.0_3380	0.00110	0.00465	0.0120	18 200	10.365	—13.1
98 » »	0.035			0.0_3359	0.00158		18 400	10.020	—14.7
99 » »	0.018			0.0_3190	0.0_3894	0.00519 (60°)	18 500	9.839	—15.5
5 wt. % Ethanol	0.980	0.0758	0.220	0.411	1.004		10 960	7.651	—25.5
10 » »	0.958	0.0775	0.217	0.405	0.969		10 730	7.471	—26.4
20 » »	0.910	0.0638	0.184	0.349	0.847		11 000	7.596	—25.7
30 » »	0.857	0.0432	0.136	0.269	0.656		11 600	7.912	—24.2
40 » »	0.788	0.0291	0.101	0.216	0.575		12 700	8.641	—21.0
60 » »	0.640	0.0158	0.0642	0.147	0.452		14 250	9.609	—16.6
80 » »	0.390	0.00878	0.0404	0.104	0.347		15 650	10.517	—12.4
90 » »	0.221	0.00526	0.0262	0.0708	0.251		16 450	10.906	—10.6
10 wt. % Acetone	0.972	0.0715	0.203	0.389	0.950		11 000	7.651	—25.5
20 » »	0.939	0.0636	0.183	0.355	0.898		11 250	7.800	—24.8
30 » »	0.900	0.0535	0.165	0.309	0.789		11 400	7.847	—24.6
40 » »	0.854	0.0461	0.141	0.274	0.712		11 600	7.956	—24.2
60 » »	0.721	0.0342	0.116	0.247	0.674		12 700	8.688	—20.7

water E and A have a minimum at $x_{water} = 0.95$. In these media E is always and A generally much lower than in methanol-water of the same molar composition. The curves in Figs. 2 and 3 have about the same form as those connected with the alkaline hydrolysis of carboxylic esters.

The correlation between E and log A is seen from Fig. 4. For ethanol-water and acetone-water the relationship is linear before and after the minimum. For methanol-water a slight deviation from linearity is observed, and besides, at high methanol contents the line is strongly curved. The linear relationship
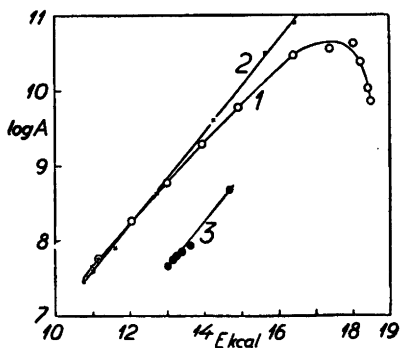
Fig. 4. Plot of log A against E.

1. Methanol-water.
2. Ethanol-water.
3. Acetone-water, E + 2 kcal.

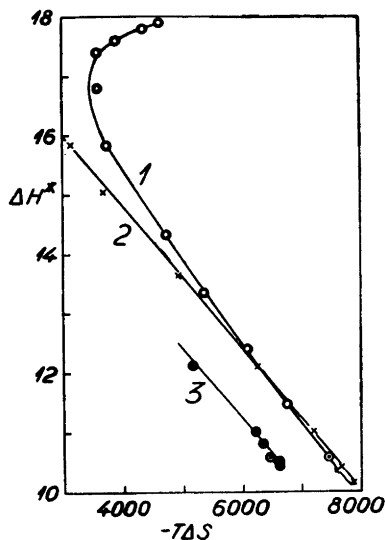Fig. 5. Plot of ΔH* vs. TΔS*.

1. Methanol-water.
2. Ethanol-water.
3. Acetone-water, −TΔS* + 1 000.

between E and log A is equivalent to a linear relationship between the heat of activation and the entropy of activation (Fig. 5), as expressed by the equation[1].

$$T\Delta S^* = a\Delta H^* + \beta$$

From Fig. 5 we obtain for ethanol-water and acetone-water mixtures in which the mole fraction of water is less than 0.9, $a = 0.84$, which corresponds to the ratio $\Delta \log A/\Delta E = 0.000616$ in Fig. 4. For the narrow region between pure water and the minimum $a \approx 1$. For methanol-water $a \approx 0.7$ or $\Delta \log A/\Delta E \approx 0.0005$. These values are thus of the same order of magnitude as for the alkaline hydrolysis of carboxylic esters.

The entropies of activation are calculated by the formula

$$\log A = e \frac{k\,T}{h} e^{\Delta S^*/R}$$

and the heats of activation from the equation $E = \Delta H^* + RT$.

The theory put forward in Part I of this series applies also to the case of the hydrolysis of valerolactone. According to this theory, if the transition state has a structure containing strongly hydrophilic and hydrophobic parts,

in some region of a continuous series of mixtures of water with an organic solvent a situation may arise, where the solvation of the transition state is greatly increased, which leads to a minimum in the curves representing E and A as functions of the composition of the solvent. Here the transition state may be written

$$CH_3 \cdot CH \cdot CH_2 \cdot CH_2$$
$$+O \text{-----------} C-O^-$$
$$\overset{-}{HO}\cdots H \qquad OH$$
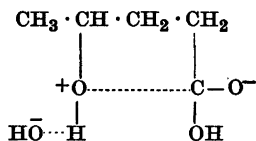
Thus it is of the type just mentioned. The reactants, *i.e.* the lactone and OH^-, are also strongly solvated by water, since valerolactone is in all proportions mixible with water. Probably owing to this the minima are not so pronounced as in the hydrolysis of carboxylic esters. The rise of E and A after the minimum indicates that here the total solvation of the transition state rapidly decreases or that of the lactone increases or, perhaps, that both of these processes occur. The increase of E in high alcohol percentages is probably due also to a shift of the alcoholate equilibrium [1].

An addition of an organic solvent which contains a very small hydrocarbon part, *e.g.* methanol, to the water, does not markedly increase the solvation of the transition state; on the contrary, since methanol molecules are only weakly attracted to the hydrocarbon part of the transition state, it is possible that with the decreasing concentration of the water molecules the total solvation of the activated complex continuously decreases and, accordingly, no minima appear in the curves of E and A.

The energy of activation and temperature. In aqueous methanol containing 20—60 per cent by weight of methanol the deviation of the ratio between $\log k$ and $1/T$ from linearity is very pronounced and far beyond the experimental errors connected with the reproducibility of the measurements. In these media the energy of activation is clearly the higher the lower the temperature. This seems to be the case also in aqueous ethanol between 30 and 60 per cent of ethanol (Table 2). In acetone-water no definite dependence of E on T could be ascertained.

A dependence of activation energy on temperature was found also in the alkaline hydrolysis of ethyl acetate in *tert.*-butanol-water mixtures *i.e.* in mixtures of water and an alcohol with a very great hydrophobic part [1]. Here, in the region of the minimum, E i n c r e a s e s with the temperature. The explanation given was that with the rise of the temperature the solvation of the activated complex decreases, which causes an increase in E. In the hydro-

Table 2. Values of the activation energies in various temperature ranges.

Solvent	E_{0-15}	E_{15-25}	E_{25-40}
Water	11 120	11 120	11 230
10 wt. % Methanol	12 000	12 380	11 860
20　　》　　　》	13 330	13 000	12 560
30　　》　　　》	14 410	13 880	13 450
40　　》　　　》	15 370	14 900	14 370
60　　》　　　》	16 650	16 360	16 180
80　　》　　　》	17 450	17 200	17 420
90　　》　　　》	17 680	18 650	17 730
10 wt. % Ethanol	10 740	10 650	10 790
20　　》　　　》	11 040	10 930	10 970
30　　》　　　》	11 960	11 650	11 200
40　　》　　　》	12 970	12 980	12 110
60　　》　　　》	14 620	14 140	13 900

lysis of valerolactone a shift of E is observed in aqueous ethanol and more powerfully in aqueous methanol, *i.e.* it is the more pronounced the more water-like the organic component of the solvent, and E d e c r e a s e s as the temperature rises. Besides, the phenomenon is here observed in the middle region of the mixtures, in aqueous ethanol after the minimum of E. Thus it is likely that here the situation is governed by a change in the solvation of the r e a c t a n t s with the temperature, for a decrease of the solvation of the reactants with rising temperature would tend to decrease the energy of activation. Such an assumption is well justified; the hydrocarbon heads of the alcohol molecules can attach to the hydrocarbon portion of the lactone, but the attraction is weak and easily disturbed by the thermal motion of the molecules. In the case of methanol this disturbance is greater than in the case of ethanol, where, owing to the greater hydrocarbon head, the attachement to the lactone must be firmer. If the alcohol concentration is high, this temperature-dependence is small. It is insignificant also in small alcohol concentrations in which the solvation by the alcohol molecules is very weak. Naturally also the transition state is less solvated at high than at low temperatures, which has a temperature effect opposite to the former, but this effect seems to be weaker than that caused by the change in the solvation of the reactants.

SUMMARY

The hydrolysis of valerolactone in methanol-water, ethanol-water, and acetone-water mixtures shows many common features with the alkaline hydrolysis of carboxylic esters. The details are discussed.

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