Influence of the Water Structure on Chemical Reactions in Water. A Study of Proton-Catalysed Acetal Hydrolysis

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The rate of the specific proton-catalysed hydrolysis of the diethylacetal of 4-nitro-benzaldehyde has been determined at temperature intervals of 1 °C between 8 and 50 °C, in water, and in 55 % (v/v) water/ethanol. The activation energy of the hydrolysis in water, calculated for 25 short intervals, is found to vary with temperature in an oscillatory manner, with amplitudes of 5–10 kJ mol⁻¹ above and below the average Arrhenius value of 86.4 kJ mol⁻¹. In 55 % water/ethanol the rate data lie, within experimental error, on the straight line of the function log k versus $1/T$, giving an activation energy of 90.7±2 kJ mol⁻¹. The reaction anomaly in water is assumed to arise from minor phase transitions between different temperature-dependent, cooperatively hydrogen-bonded dynamic structure entities in the water bulk, and in the solvation shell (clathrate) of the reactants.

Water, and mixtures of water with organic solvents, are commonly used as reaction media for a large variety of chemical reactions. Water itself is of course unique, since all life processes have evolved, and still proceed, in intimate contact with this solvent. From a great number of studies it is known that addition of organic solvents has profound effects on thermodynamic, as well as activation, parameters of reactions in water/organic-solvent mixtures.[1-11] The effect on the Gibbs free energy, ΔG, or on the activation free energy, ΔG^*, is usually less conspicious than the effect on the corresponding enthalpy and entropy parameters, owing to compensating effects that arise between the latter parameters.

When the activation energy of organic reactions in water/organic-solvent mixtures is plotted as a function of mol % organic solvent, the first few per cent normally have the strongest effect on the thermodynamic or activation parameters. This observation suggests that modest amounts of foreign molecules disturb or disrupt the original network structure of water, giving rise to profound effects on reactants, activation complexes and/or products.

Accurate data on the temperature dependence of thermodynamic and/or activation parameters of reactions in water, and in water/organic solvents, are scarce. This is easy to understand, since evaluation of temperature derivatives requires high accuracy and a great number of individually measured data in the temperature range studied. Most studies seldom operate with measurements at closer than 5 °C intervals. A search of the literature shows, however, that measurements of the equilibrium constants of
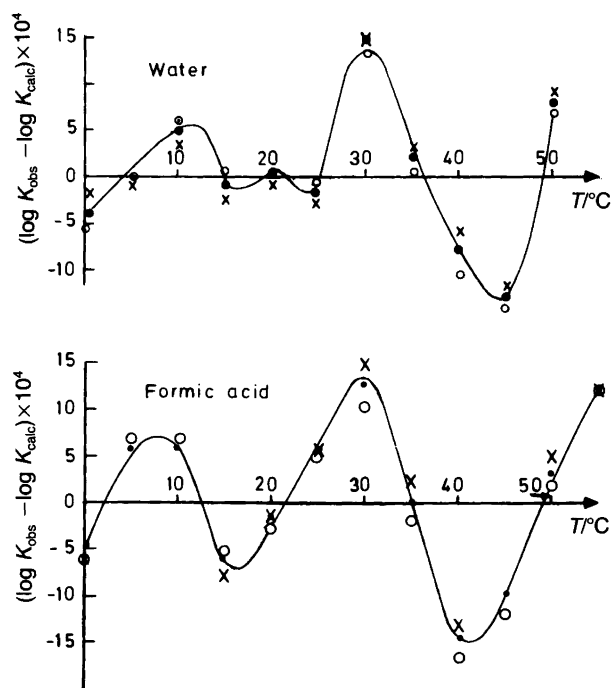

Fig. 1. Plot of log K_{obs} − log K_{calc} vs.:

(a) Ionization of formic acid.[2,3]
log K_{calc} = 30.9965 − 2013.5/T − 0.075841 T − 10.4000 log T
log K_{calc} = 56.7186 − 2684.1/T − 20.8000 log T
log K_{calc} = 1342.85/T + 5.2744 − 0.0151682 T

(b) Ionization of water.[2,3]
log K_{calc} = −5242.39/T + 35.39944 − 0.008530 T − 11.8261 log T
log K_{calc} = − 6013.79/T − 23.6521 log T + 64.7013
log K_{calc} = − 4470.99/T + 6.0875 − 0.017060 T.

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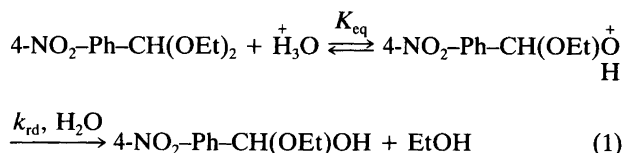
weak acids and the solubilities of sparsely soluble gases often fulfil the above requirements.

The measured ionization constants of weak acids in water (extrapolated to zero concentration) reveal interesting temperature-dependent deviations from the most accurate empirical functions of their temperature dependence.[2,3] This is illustrated for the ionization of formic acid, and the self-ionization of water, where the deviation between the observed and calculated values of log K is plotted against temperature, using three different empirical functions of comparable accuracy for the calculation of log K (Fig. 1). The wave-like form of the deviation vs. temperature curve is difficult to characterize as arising from random error, especially since the greatest deviations are 3–4 times the estimated errors in the measurements. Similar anomalies can be found in other ionization data.[3]

La Mer and Miller[4] showed that the activation energy of the hydroxide-catalysed decomposition of diacetone alcohol in water passed through a profound maximum around 34 °C. The maximum disappeared entirely in water containing 18.5 % methanol. The many individually measured rate constants, and the high accuracy of the dilatometric technique used, left little doubt about the reliability of the data [Figs. 2(a) and (b)].

Since the decomposition of diacetone alcohol is a true specific base-catalysed reaction, the rate of transfer of the hydroxide ion to the substrate is intimately dependent on the rate of the Grotthus movement of hydroxide ions in the hydrogen-bonded network of water. Current theories stress the importance of cooperative forces in the H-bonded network of water.[5,6] This means that clusters of H-bonded molecules might break down rather abruptly within narrow temperature intervals, with possible observable effects on the rate of hydroxide movement in the water network. In order to test the latter idea, we decided to study the proton-catalysed hydrolysis of the diethylacetal of 4-nitrobenzaldehyde (hereafter abbreviated acetal). The hydrolysis of acetals is well known to show specific proton catalysis, and the reaction rate is accordingly intimately connected with the ease of proton transfer in the water bulk, and in the solvation shell of the substrate. The reaction mechanism is well understood, consisting of protonation of one of the acetal oxygens, followed by the rate-determining splitting of the C–O bond. The further hydrolysis of the semiacetal is much more rapid, and does not influence the overall rate [eqn. (1)].

$$4\text{-}NO_2\text{-}Ph\text{-}CH(OEt)_2 + \overset{+}{H_3O} \overset{K_{eq}}{\rightleftharpoons} 4\text{-}NO_2\text{-}Ph\text{-}CH(OEt)\overset{+}{\underset{H}{O}}$$

$$\xrightarrow{k_{rd},\ H_2O} 4\text{-}NO_2\text{-}Ph\text{-}CH(OEt)OH + EtOH \qquad (1)$$

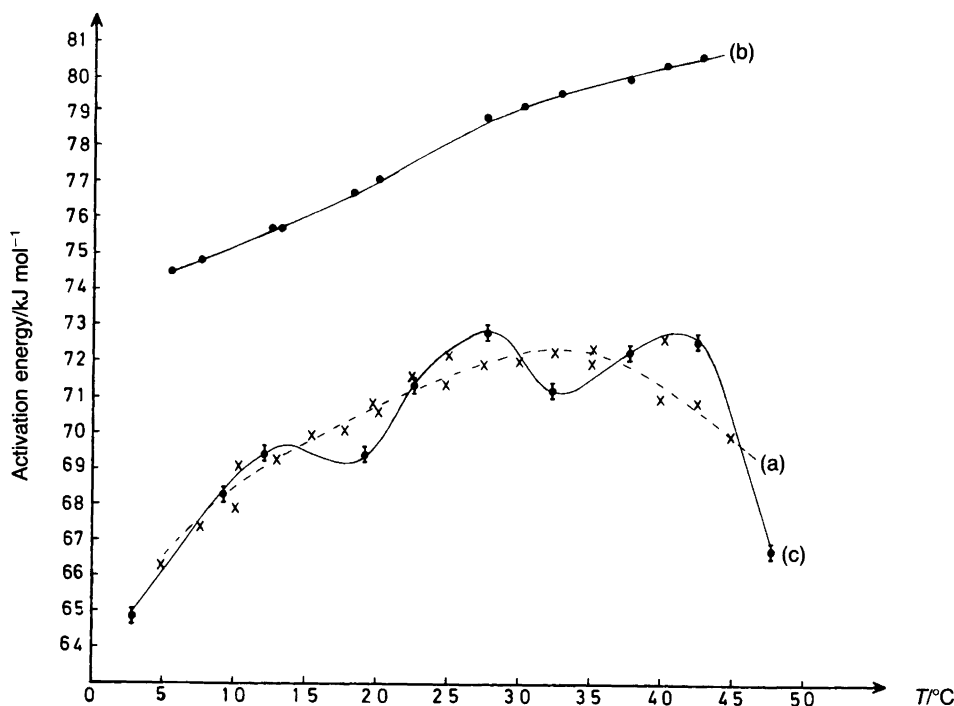A summary of the present work has been presented.[7]

Fig. 2. Plot of the activation energy for the hydroxide-catalysed decomposition of diacetone alcohol vs. temperature: (a) in water, calculated at intervals of 10, 15 and 20 °C;[4] (b) in 18.5 % methanol/water at intervals of 10, 15 and 20 °C;[4] (c) the data from (a) calculated at 5 °C intervals.

Experimental

Materials. The diethylacetal of 4-nitrobenzaldehyde was prepared according to the method of Fife and Jao.[8] Ethanol was purified using magnesium filings. Water was freshly distilled from potassium permanganate.

Kinetic measurements. The rate of hydrolysis of the acetal was measured with a Hewlett Packard Fourier-transform spectrophotometer (HP8450A UV/VIS) by following the increase in absorbance of 4-nitrobenzaldehyde at 267 nm. The reaction temperature, measured directly in a quartz cuvette (Helma 160 QS), was kept constant to within ±0.01 °C. The concentrations of acetal and HCl in the reaction solution were 5×10^{-5} M and $(1-5) \times 10^{-2}$ M, respectively. Approximately 100 separate readings, at each temperature of absorbance, with time were treated by a least-squares method in obtaining the pseudo-first-order rate constant. The second-order rate constant, k_2, obtained after dividing the former by the hydrogen ion concentration, was determined to better than ±2 %. The experimental rate constants, determined at 46 temperatures between 8 and 50 °C in water and in 55 % water/ethanol, are listed in Table 1.

Activation energy. The average values of the activation energy in water and in 55 % water/ethanol, between 8 and 50 °C, were calculated from the slope of the Arrhenius plot in Fig. 3. The temperature dependence of the activation energy in water was estimated by calculating individual values of the activation energy in 25 short intervals between 8 and 50 °C. Each interval varied from 3 to 10 °C, and the number of individual measured rate constants in each interval between 8 and 18. The data are recorded in Table 2.

Error calculations. The Arrhenius activation energy calculated in short intervals between temperatures T_j and T_i, with rate constants k_j and k_i, respectively, is expressed by eqn. (2).

$$ E = \frac{RT_jT_i}{T_j - T_i} \ln \frac{k_j}{k_i} \tag{2} $$

Since the maximum error in all the measured rate constants was less than ±2, one obtains eqn. (3) for the error in E when the error in temperature is ignored.

$$ E = \frac{RT_jT_i}{T_j - T_i} \ln \frac{k_j}{k_i} \pm \frac{RT_jT_i}{T_j - T_i} (0.02^2 + 0.02^2)^{\frac{1}{2}} \tag{3} $$

With n individually measured rate constants in each interval, the standard error in E is given by eqn. (4).

$$ \sigma_s = \pm 0.02 \times \frac{2}{n} \frac{RT_jT_i}{T_j - T_i} \tag{4} $$

Table 1. Rate data for the specific acid-catalysed hydrolysis of the diacetal of 4-nitrobenzaldehyde in water, and in a 55 % water/ethanol mixture.

| $T/°C$ (± 0.01)	$10^2 \, k_2/M^{-1} \, s^{-1}$		$T/°C$ (± 0.01)	$10^2 \, k_2/M^{-1} \, s^{-1}$	
	H_2O	55 % H_2O–EtOH		H_2O	55 % H_2O–EtOH
8.56	4.117	0.107	28.05	41.90	1.291
9.34	4.460	0.118	28.96	47.24	1.441
10.14	4.783	0.132	29.88	53.26	1.592
10.94	5.286	0.147	30.80	60.06	1.777
11.75	5.784	0.164	31.73	67.03	1.984
12.56	6.204	0.184	32.66	73.35	2.215
13.38	6.788	0.203	33.60	78.66	2.472
14.21	7.427	0.224	34.54	84.37	2.760
15.03	8.208	0.248	35.49	93.24	3.112
15.87	9.442	0.279	36.45	102.0	3.473
16.70	10.75	0.312	37.41	110.5	3.939
17.56	12.00	0.348	38.38	121.0	4.243
18.39	13.53	0.389	39.25	135.0	4.783
19.25	15.26	0.429	40.33	150.6	5.340
20.10	17.00	0.479	41.31	169.9	5.960
20.97	18.64	0.535	42.32	189.6	6.654
21.83	19.99	0.598	43.31	216.0	7.427
22.71	21.65	0.667	44.32	243.5	8.291
23.59	22.99	0.745	45.32	277.3	9.163
24.47	25.41	0.823	46.34	309.6	10.33
25.36	28.08	0.928	47.36	349.0	11.53
26.25	31.66	1.036	48.39	389.6	12.87
27.15	36.06	1.156	49.43	426.3	14.58
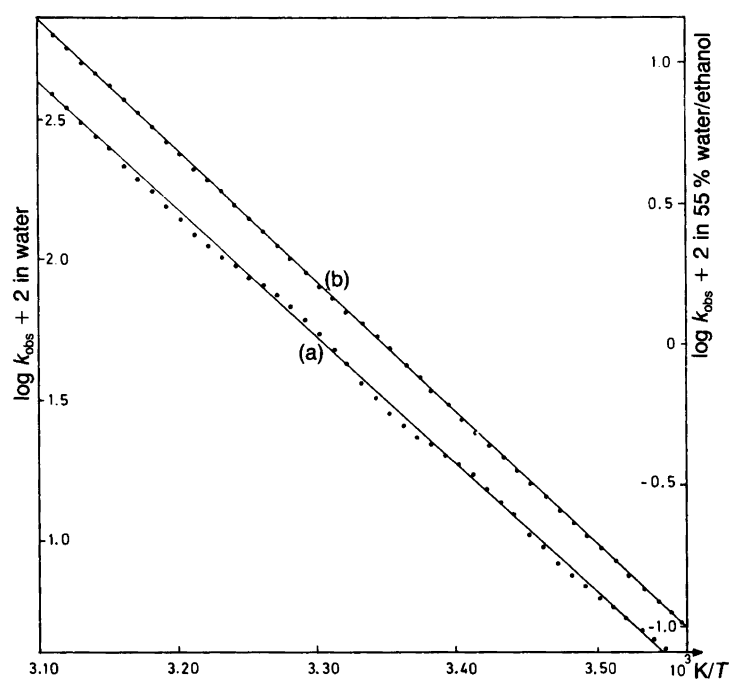
Fig. 3. The Arrhenius plot (log k_{obs} vs. $1/T$) for the proton-catalysed hydrolysis of the diethylacetal of 4-nitrobenzaldehyde: (a) in water; (b) in 55 % water/ethanol (by volume).

Table 2. Energy of activation at different temperature intervals of the specific acid-catalysed hydrolysis of 4-nitrobenzaldehyde diethylacetal in water.

| Interval/°C	Mid-point of temp. interval	E/kJ mol^{-1}	No. of points, n	Correlation factor, r	Standard error/ kJ mol^{-1}
8.54–14.21	11.37	70.97	8	0.999	±1.3
9.34–15.87	12.60	75.66	9	0.997	±1.0
10.14–16.70	13.42	82.65	9	0.994	±1.0
12.56–17.56	15.06	93.24	7	0.997	±1.6
10.14–20.10	15.12	90.59	13	0.997	±0.6
12.56–21.83	17.19	93.20	12	0.998	±0.6
13.38–24.47	18.92	86.78	14	0.995	±0.5
15.03–26.25	20.62	82.38	14	0.995	±0.5
16.70–28.05	22.37	81.15	17	0.996	±0.5
18.39–30.80	24.59	86.11	15	0.995	±0.5
20.10–34.54	27.32	89.07	17	0.996	±0.4
22.71–36.45	29.58	89.88	16	0.996	±0.4
24.47–38.38	31.42	86.99	16	0.995	±0.4
25.36–40.33	32.84	84.16	17	0.996	±0.4
26.25–42.31	34.28	82.72	18	0.997	±0.4
28.05–44.31	36.18	81.75	18	0.998	±0.4
29.88–46.34	38.11	83.80	18	0.997	±0.4
31.73–47.36	39.74	86.49	17	0.996	±0.4
32.66–48.39	40.52	88.57	17	0.997	±0.4
33.60–49.43	41.51	90.99	17	0.998	±0.5
35.49–49.43	42.66	92.68	15	0.999	±0.5
37.41–49.43	43.42	96.57	13	0.999	±0.6
39.35–49.43	44.39	97.81	11	0.999	±0.8
41.31–49.43	45.37	97.55	9	0.999	±1.0
43.31–49.43	46.37	95.32	7	0.999	±1.4
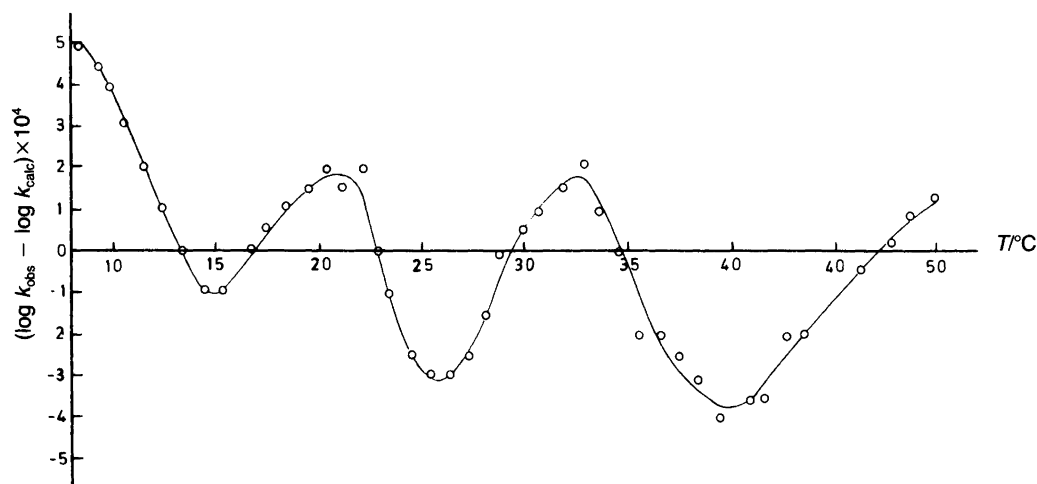
Fig. 4. The deviation of (log k_{obs} − log k_{calc}) vs. temperature for the hydrolysis of the diethylacetal of 4-nitrobenzaldehyde in water.

The activation energy values, together with error-estimation data, are recorded in Table 2. In Fig. 8 (see later) the values of the activation energy in water and in 55 % water/ethanol are plotted as a function of temperature.

Discussion

A first glance at the Arrhenius plot for the acetal hydrolysis in water [Fig. 3(a)] may give the impression that the rate data in Table 1 give a fairly good linear dependence between log k and the inverse of the absolute temperature. Closer inspection of the curve reveals, however, that the rate data are distributed in an oscillatory manner along the straight line. Irrespective of how the Arrhenius line is drawn, the experimental log k values will in certain temperature regions fall above or below the line. The greatest differences between experimental and calculated values are

of the order of 3–4 times the estimated errors in the rate constants. In the short temperature interval of the present study (42 °C) the magnitude of the deviations was quite unexpected, especially since the rate data for the same reaction in 55 % water/ethanol, with an identical experimental set-up and similar accuracy, are in excellent accordance with the linear Arrhenius plot [Fig. 3(b)].

From the slope of the line in Fig. 3(a) an average activation energy of 86.4 kJ mol^{-1} is calculated. When the difference (log k_{obs} −log k_{calc}), where log k_{calc} is the calculated value derived from the straight line and log k_{obs} is the experimental value, is plotted as a function of temperature, the oscillatory curve in Fig. 4 is obtained. In the following discussion, evidence will be brought forward which supports the view that the anomalies are due to inherent properties of water.
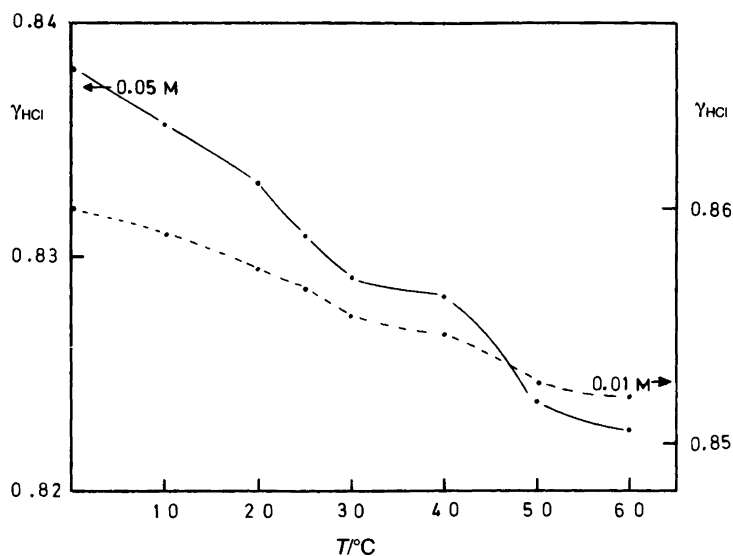

Fig. 5. Plot of the activity coefficient for HCl in water vs. temperature at concentrations of 0.01 and 0.05 M.[9]

The hydrolysis of acetals is specifically proton-catalysed. In the present study HCl was used as the catalyst, and it was therefore of interest to check the temperature dependence of the activity coefficient of HCl in water in the concentration range used in the hydrolysis. Accurate measurements are reported by Bates and Bower,[9] and their data have recently been confirmed by Dickson[10] (Fig. 5). Admittedly, the data are few and the effects are small. However, an oscillatory appearance of the activity coefficients with temperature is clearly recognized.

Returning to the hydrolysis of acetal, the rate constants determined at 1 °C intervals between 8 and 50 °C (Table 1) enabled us to calculate the temperature gradients of the rate constants with reasonable accuracy. The data are plotted as a function of temperature in Fig. 6. In spite of considerable errors in the gradient values, the maxima and minima in the curve must be considered to be real.

With regard to the proton-catalysed acetal hydrolysis, it was mentioned in the introductory section that the acetal hydrolysis has a protonation step before the rate-determining step where the semiacetal is formed. The hydrolysis of the latter is much faster, and does not influence the overall rate [eqn. (1)]. The observed rate constant is accordingly a product of an equilibrium constant, K_{eq}, and a rate-determining constant, k_{rd}. This means that the influence of the pre-equilibrium step might show up in the temperature dependence of the observed rate of acetal hydrolysis. In

fact, the deviation plot, (log k_{obs} − log k_{calc}) vs. T, in Fig. 4 is remarkably similar in form to the plot of (log K_{obs} − log K_{calc}) vs. T for formic acid and water in Fig. 1.

A common feature characterizes proton-transfer reactions in water: the proton movements to and from the substrate ought to be quite sensitive to minor changes in the H-bonded water network in the bulk, and in the solvation shell around the substrate (clathrate water). It is known that the formation and/or breaking of H-bonds in water is a cooperative phenomenon, i.e. the formation or breaking of a H-bond influences the strength as well as the structure of nearby H-bonded water molecules in the network. However, the thermal stability of the water network in the bulk need not be the same as the stability of the clathrates. When H-bonded entities in the bulk change from a 4-, via a 3-, to a 2-coordinate type of network with increasing temperature, resulting in energetic and conformational changes, phase transitions between bulk entities and the clathrate water might take place which will influence the proton movement.

The encounter between the proton and the substrate can also be considered from a macroscopic point of view in which the approaching proton is separated from the substrate by water of dielectric constant ε. Following the suggestion of Moelwyn-Hughes,[11] the activation energy of the reaction can be divided into an electrostatic, E_e, and a non-electrostatic, E_n, term [eqn. (5)].
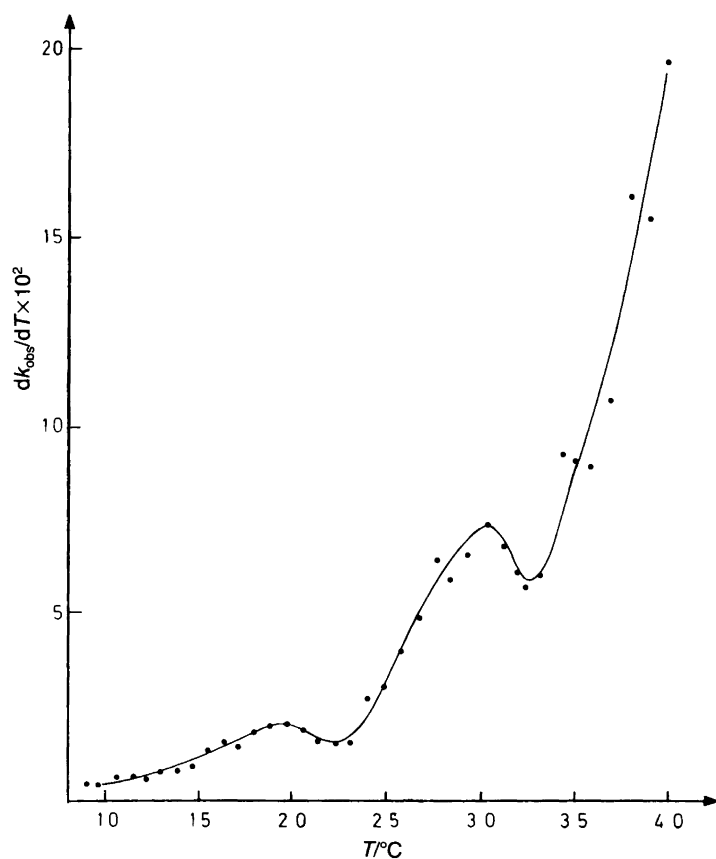

Fig. 6. Plot of the temperature gradient, dk_{obs}/dT, vs. temperature for the proton-catalysed hydrolysis of acetal in water.
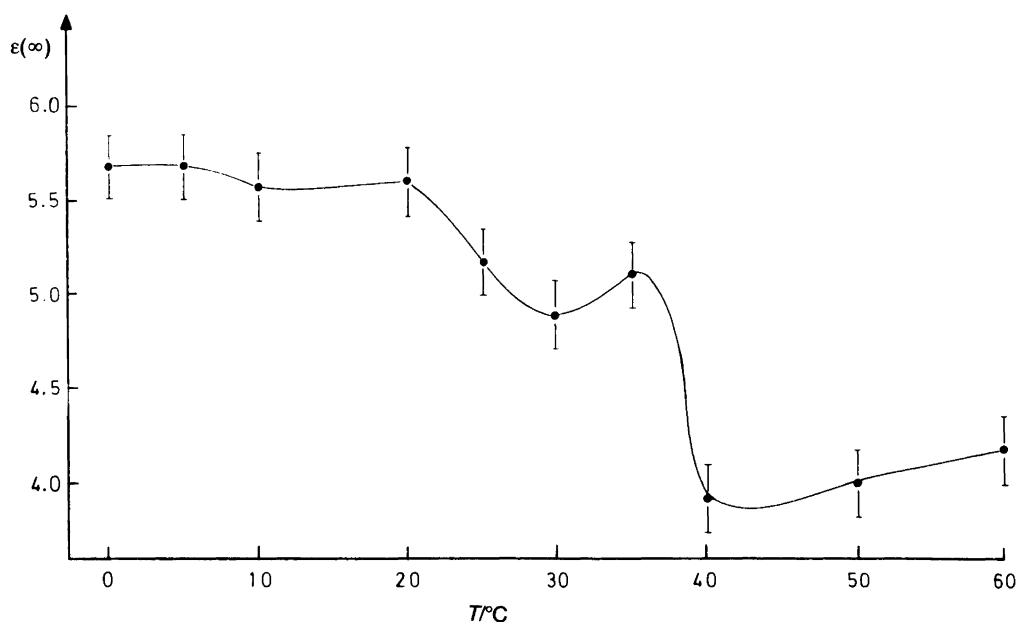
Fig. 7. Plot of the high-frequency permittivity of H_2O, $\varepsilon(\infty)$, vs. temperature. Data from Kaatze and Uhlendorf.[12]

$$E = E_n + E_e = E_n + e\mu\cos \Theta/\varepsilon r^2 \qquad (5)$$

Here, r is the distance between the centre of the proton and that of the dipole of the substrate, Θ is the angle subtended between the directions of the polar axis and the line of centres, ε is the macroscopic static dielectric constant, and e is the charge of the proton. However, the static dielectric constant is an inadequate measure, since no reorientation of water molecules can take place within the time-scale of the proton transfer. More realistic ε values are presumedly the $\varepsilon(\infty)$ values calculated from microwave measurements up to 100 GHz, which are of the same order of magnitude as the proton jump. The most recent data of Kaatze and Uhlendorf[12] are reproduced in Fig. 7. The curve has been drawn by the present authors. It is intriguing that the $\varepsilon(\infty)$ values seem to reveal three temperature regions in which rapid changes in water take place. They correspond to the regions where anomalies in the parameters of reactions in water are observed. If the $\varepsilon(\infty)$ values of Katze and Uhlendorf are used in the equation above, choosing parameter values of $r = 4$ Å, $\Theta = 50°$ and $\mu = 1.5$ D, the electrostatic term E_e varies from 4 to 6 kJ mol^{-1} between 20 and 50 °C, which is of the same order of magnitude as the deviations from the activation energy calculated from the Arrhenius equation. However, the uncertainty in the choice of the parameters makes more detailed quantitative calculations of little interest, especially since the activation energy for the rate-determining step might also be somewhat dependent on the structure changes in water.

How can the constancy of the activation energy of the acetal hydrolysis in 55 % water/ethanol be explained? According to the previous line of reasoning it is natural to assume that 45 % ethanol, approximately 20 mol %, breaks down the original structure of water to such an extent that

structure transitions from 4-, via 3-, to 2-coordinated water have already taken place. It can be understood if the linearly 2-coordinated ethanol enforces a similar structure on water. This means that an increase in temperature will only influence the length of the H-bonded chains, and thus have a minor effect on its solvent properties. A recent mass-spectrometric analysis of association in water/ethanol mixtures, using an adiabatic liquid jet expansion technique,[13] has shown that both the types and the sizes of the H-bonded polymers have very little temperature dependence in the region 40–70 % (17–42 mol %) ethanol. This result corresponds well with the temperature-independent activation energy of the acetal hydrolysis in 55 % water/ethanol (Fig. 8).

The hydrolysis in water/ethanol might also shed light on the hydroxide-catalysed decomposition of diacetone alcohol mentioned in the introductory section (Fig. 2). We have recalculated the activation-energy data of La Mer and Miller[4] from their experimental values reported in steps of 5 °C, instead of intervals of 10, 15 and 20 °C used in their calculation [Figs. 2(a) and (c)]. This gives rise to an activation-energy curve with three maxima instead of one, a result which is very similar to our findings in the acetal hydrolysis. Since the diacetone alcohol of La Mer and Miller was studied at concentrations of 2 % in water, the alcoholic substrate will influence the original water structure to a considerable extent, wiping out details of the original water structure. This view is strengthened by the fact that the same reaction performed in 18.5 % methanol/water results in a monotonic rise in the activation energy with no maxima [Fig. 2(b)].

Inspection of the temperature gradient curve for the rate constant for acetal hydrolysis in water (Fig. 6) reveals that a calculation of the Arrhenius activation energy in short tem-
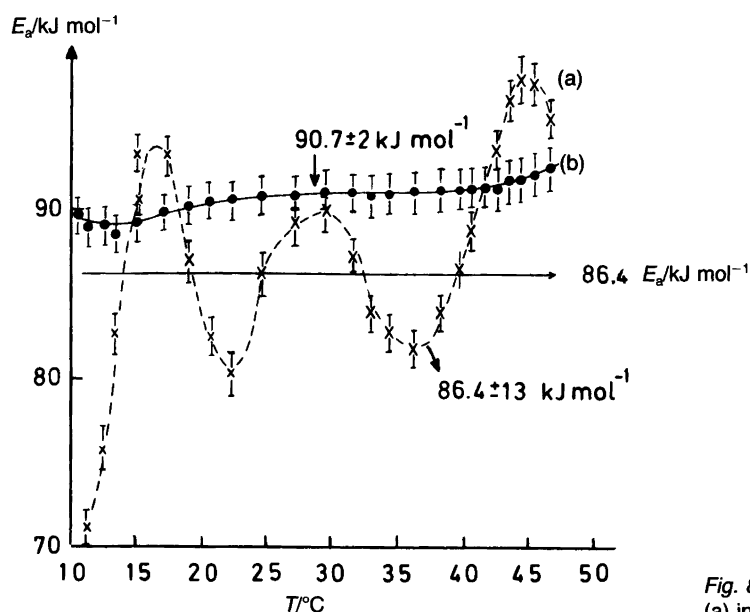
$E_a/\text{kJ mol}^{-1}$

90.7 ± 2 kJ mol^{-1}

(a)

(b)

90

86.4 $E_a/\text{kJ mol}^{-1}$

80

86.4 ± 13 kJ mol^{-1}

70

10 15 20 25 30 35 40 45 50

$T/^{\circ}C$

Fig. 8. The temperature dependence of the acetal hydrolysis; (a) in water; (b) in 55 % (v/v) water/ethanol.

perature intervals, as performed by La Mer and Miller, will be critically dependent upon where the intervals are chosen. One is faced with the problem that very short intervals give a higher error in the calculation, whereas longer intervals will average out any structural water effect. In spite of these complications we have attempted a stepwise calculation of the activation energy from the data in Table 1. The data are collected in Table 2, and the variation of the activation energy with temperature is illustrated in Fig. 8, where the activation energy of the same reaction in 55 % water/ethanol (almost independent of temperature) is plotted for comparison [Fig. 8(b)]. The maxima and minima of the activation energy in water [Fig. 8(a)] are approximately 5 kJ mol^{-1} above and below the average value of 86.4 kJ mol^{-1}, which is of the magnitude estimated for the electrostatic term in the activation-energy equation previously discused.

So far the discussion of reactions in water has been limited to small molecules. With regard to biomolecules, enzymes constitute a material for which usually quite abrupt changes in rate and activation parameters take place with increase in temperature, these most certainly being caused by conformational changes of the active enzyme centre.[14,15] However, since enzymes are encaged by huge solvation shells of many more water molecules than the clathrates of small solutes, much stronger effects are also to be expected upon sudden changes or collapse of the solvation shell (Fig. 9).

Drost-Hansen[16-18] has for three decades been an active proponent of the view that interfacial water plays a critical role in abrupt changes in reaction parameters at around 15, 30, 45 and 60°C. He is of the opinion, however, that the effect is limited to water at interfaces with solids or macromolecules of molecular weight not less than 1000–5000 Da. The present work supports the idea of phase-transition-like changes of reaction in water. However, the phenomena

appear to be of a more general character than suggested by Drost-Hansen and coworkers.[17] As a working hypothesis we suggest that the effect is an inherent property of water, and originates from short-lived water assemblies whose dynamic structures owe their transient stability to cooperatively H-bonded entities which, with rising temperature, shift more or less gradually from 4-coordinative entities, to 3- and 2-coordinative ones, of condensed rings and open chains. Various H-bonded entities of water with different structures and stabilities might arise from proton resonance stabilization.[5] A comparison with the electronic resonance concept, which shows that maximum stabilization is obtained with identical hybrid forms, suggests that proton resonance stabilization might promote different "pure" structural entities as 4-coordinative ("iceberg"), 3-coordi-
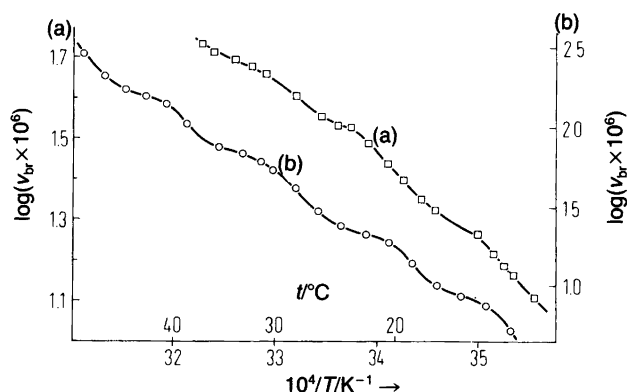

Fig. 9. Temperature dependence of the overall reaction rate (log v_{br}) of: (a) hydrolysis of N^{α}-benzoylargenine ethylester (3.8×10^{-3} mol dm^{-3}) by trypsine (1 mg dm^{-3}) at pH 9.4; (b) oxidation of salicylaldehyde (1.5×10^{-2} mol dm^{-3}) by xanthine oxidase (10 µg dm^{-3}) in the presence of methylene blue (6.25×10^{-5} mol dm^{-3}) and phosphate buffer (5×10^{-2} mol dm^{-3}, pH 7.4) (reproduced from Talsky[14]).

native ("iceflake") and 2-coordinative ("ring-and-chain") forms.

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