

Temperature Dependence of Ester Hydrolysis in Water

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Aksnes, G. and Libnau, F. O., 1991. Temperature Dependence of Ester Hydrolysis in Water. – *Acta Chem. Scand.* 45: 463–468.

The rate of the hydroxyl-promoted hydrolysis of ethyl acetate has been determined at every second degree between 4 and 50°C in water and 50% (w/w) ethanol–water mixtures (10–40°C). Similarly, the rate of the proton-catalyzed hydrolysis of propyl formate has been determined in water at the same temperatures. It is found that the Arrhenius activation energy of the alkaline and acid hydrolysis shows an oscillatory dependence on temperature in water, but not in 50% (w/w) ethanol–water. The results are in accordance with previously reported findings of the acid hydrolysis of acetal in water and 55% (v/v) ethanol–water. The results are discussed in relation to proton-transfer reactions and recent relaxation data of water.

The outstanding role of water as solvent in inorganic and organic reactions has resulted in a tremendous number of investigations devoted to physical and chemical behaviour of water. However, many of the finer details of water as solvent still escape our understanding. The water structure specialist Dore¹ wrote “It sometimes seems that the more we learn from experimental studies, the less we understand about the microscopic properties of this important material”. When the physical properties of liquid water, composed of triatomic molecules, escape our understanding, we ought not be astonished that reactions in water, subjected to various temperature-dependent interactions with the water molecules, confront us with more complex problems.

We have for some time been interested in the temperature dependence of hydrolytic reactions in water. In a previous publication, Aksnes and Asaad² reported that the acid-catalyzed hydrolysis of an acetal in water, measured at one degree intervals between 8 and 50°C, resulted in an Arrhenius activation energy which appeared to vary in an oscillatory manner. Thermodynamic parameters of equilibrium reactions are known to vary with temperature. Usually, fittings of experimental data to the equilibrium equation ($\ln K = -\Delta G^\circ/RT$) are obtained by expansion of the standard Gibbs energy in power and/or exponential series of temperature.^{3,4} For non-equilibrium reactions the temperature dependence of the rate constants is usually expressed by the Arrhenius equation ($\ln k = \ln A - E_A/RT$). When the reaction rates are measured over a considerable temperature interval, the activation energies obtained from the Arrhenius equation are not constant. Various correction terms have been introduced to fit the equation to the experimental data.⁵⁻⁷

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It seems to us that complicated empirical equations used to describe the temperature dependence of reactions in water are of limited value, since they cannot shed light on the microscopic details of the processes taking place.⁷ If the solvent and the solvation processes undergo changes within short temperature intervals, empirical functions may miss the effect entirely. We felt that specific solvation changes with temperature could best be detected by measuring the reaction rates at narrow intervals (1–2°C) in the temperature region chosen for study (0–50°C). When reactions which can be measured with high accuracy in water are investigated and the Arrhenius equation is assumed to be valid within short intervals, a more veracious picture of the connection between rate and temperature of reactions in water and water–organic solvents ought to be obtained.

In the aforementioned study of acetal hydrolysis, the rate of acid hydrolysis of the diethyl acetal of 4-nitrobenzaldehyde in water and in 55% water–ethanol was reported. The activation energy was calculated in 25 short temperature intervals and was found to vary in an oscillatory manner in water, whereas in 55% water–ethanol the activation energy remained fairly constant within experimental error. The magnitude of the oscillation amplitude in water was in the region 5–10 kJ mol⁻¹, which was estimated to be 3–4 times the errors of the calculated activation energies.

Admittedly, it might be a hasty conclusion to claim that the acetal study reveals a general tendency regarding the influence of temperature-dependent water structure on reactions in water. Further accurate studies are required to reach a firmer conclusion, especially measurements where thorough error analyses of the rate data have been undertaken. In following up this intention, the present paper reports hydrolysis of acetate and formate esters in water and in water–ethanol mixtures.

Experimental

Materials. Ethyl acetate (p.a. grade), supplied by E. Merck, was carefully distilled in a fractionating column, b.p.₇₆₀ = 77 °C. The purity was tested by gas chromatography and found to be >99 %, and the refractive index, n_D^{23} , was 1.3707. (Literature: $n_D^{20} = 1.3723$, $n_D^{25} = 1.370$.)⁸

Propyl formate was prepared by customary methods from 1-propanol and formic acid⁹ and distilled twice in a fractionating column, b.p.₇₆₀ = 81 °C. The purity was tested by gas chromatography (>98 %), and the refractive index was $n_D^{23} = 1.3754$. (Literature: $n_D^{20} = 1.3779$ and $n_D^{25} = 1.375$.)¹⁰ The apparently lower gas-chromatographic purity of propyl formate relative to ethyl acetate may partly be caused by the fact that formic acid is a stronger organic acid and that the presence of exceedingly small amounts of formic acid and water in the ester may result in rapid hydrolysis at the high temperature (80–100 °C) inside the GC column. When the ester and its water solutions were stored at low temperature, hydrolysis was a minor problem within the time of the experiments and the small decrease in ester concentration was always corrected for in the start concentration during each run.

Concentrated hydrochloric acid (p.a. grade) was supplied by E. Merck and used without further purification.

NaOH (purum, >98 %) was supplied by Eka Nobel. The NaOH pellets were rinsed with distilled water prior to use to remove surface carbonate.

Stock solutions of HCl and NaOH of desired concentrations were prepared by customary methods.¹¹ The NaOH solution was standardized against potassium hydrogen phthalate (p.a. grade, >99.9 %, Baker Analyzed Reagent) and the HCl solution against the previously standardized NaOH solution.

Ethanol was rectified spirit used without further purification.

Water was distilled, de-ionized and boiled before placing under a CO₂-free atmosphere.

Apparatus. The analyses were performed by end-point titrations using an automatic titration assembly from Radiometer consisting of an ABU80 autoburette, a TTT80 titrator and a PHM82 standard pH-meter.

The temperature of the thermostatted water bath was held constant within 0.02 °C by a Heto 02PT623 thermostat. The temperature was measured with two YSI703 thermocouple probes connected to a Cole-Parker 8502-12 thermistor thermometer. The thermometer setup was calibrated against a Hewlett-Packard 2804A quartz thermometer.

NaOH solution of known concentration, kept free from CO₂, was pumped into a burette until the necessary volume was reached and then quickly transferred to a conical flask filled with nitrogen. The volume was determined by weighing. The catalyst solution and an accurate amount of ester solution, in a separate flask, were equilibrated in a thermostatted water bath until the reaction temperature was reac-

hed. The time for equilibration lasted 15–30 min, depending on the difference between the reaction temperature chosen and the room temperature. When the appropriate reaction temperature of the two separate solutions of ester and catalyst was reached, the reaction was started by rapidly mixing the two solutions. At fixed times samples were withdrawn with a syringe extending into the reaction solution through a rubber seal in the reaction flask. A second needle allowed for air inflow above the reaction medium during sample withdrawal.

Because of the low concentrations of substrate used, the densities of the water–substrate solutions were taken as identical to pure water, and the densities of 50 % (w/w) ethanol–water–substrate solutions as identical to 50 % (w/w) ethanol–water mixture. Density data are taken from the literature.^{12,13}

Kinetic measurements. The hydroxyl-promoted hydrolysis of ethyl acetate was run in water and in a 50 % (w/w) ethanol–water mixture. Immediately after the sample was withdrawn by a syringe from the reaction solution it was emptied into a solution of crushed ice containing a known amount of excess hydrochloric acid, which abruptly stopped the hydroxyl-promoted hydrolysis in the sample. The time was noted, the sample weighed on an automatic balance, and thereafter immediately back-titrated under nitrogen with NaOH. The end-point of titration was fixed at pH 8.00. Because of the volatility of ethyl acetate, the start

Table 1. Rate data for the alkaline hydrolysis of ethyl acetate in water.

$t/^\circ\text{C}$	$k_2/\text{M}^{-1} \text{s}^{-1}$	$e_k/\%$ ^a
4.05	0.029 7	0.5
6.05	0.036 7	0.7
8.04	0.041 5	0.6
9.96	0.044 6	0.9
12.05	0.053 4	0.5
14.02	0.071 3	1.0
15.97	0.077 3	1.0
18.07	0.080 0	0.4
20.03	0.085 2	0.5
22.09	0.099 6	0.6
24.01	0.104 1	0.3
26.13 ^b	0.128 9	0.2
28.15	0.131 6	0.3
29.94	0.174	1.4
31.95	0.182	0.6
34.06	0.227	0.5
36.15	0.249	0.4
38.16	0.271	0.3
39.91	0.280	0.5
41.99	0.322	0.4
44.05	0.389	0.5
46.07	0.448	0.7
47.96	0.444	0.4
49.85	0.483	0.6

^a e_k is the estimated standard deviation in k_2 . ^bTommila and Murto²⁵ have reported k_2 to be 0.111 M⁻¹ s⁻¹ at 25 °C.

concentration of ester in the reaction vessel was measured for each independent run. The hydrolysis was allowed to come to completeness (more than 10 half-lives of the reactants) and the concentration of acetate ion thus found was taken as the start concentration of ester. 14 samples, in addition to those taken to determine the final acetate concentration, were analyzed in each run to determine the reaction rate. The start concentrations of ester and NaOH in the aqueous reaction mixture were $(4-8) \times 10^{-3}$ and $(0.5-1) \times 10^{-2}$ M, respectively. In 50% (w/w) ethanol-water the start concentrations of ester and NaOH were $(0.9-1) \times 10^{-2}$ and 1×10^{-2} M, respectively.

The second-order rate constant, k_2 , is given by eqn. (1),

$$\frac{1}{(a-b)} \ln \left(\frac{b(a-x)}{a(b-x)} \right) = k_2 t \quad (1)$$

where a and b are the start concentrations of ethyl acetate and NaOH, respectively, and x is the amount (per unit volume) of the ester and base reacted after the time t . Any point of too great a residual was excluded from the computation of the rate constant. The magnitude of the residuals showed no appreciable systematic variation.

The rate constants for the ethyl acetate hydrolysis determined at 2°C intervals, in water from 4 to 50°C and in 50% (w/w) ethanol-water from 10 to 40°C, are listed in Tables 1 and 2, respectively.

The acid hydrolysis of propyl formate was run in water. Immediately after the sample had been withdrawn from the reaction solution the syringe was emptied into a solution of crushed ice to slow down the reaction in the sample. The time was noted, and after weighing, the sample was rapidly back-titrated under nitrogen with NaOH. The end-point of titration was fixed at pH 8.00. Because of the volatility of

propyl formate, the start concentration of ester in the reaction vessel was measured for each independent run. 14 samples, in addition to those taken to determine the final formate concentration, were analyzed in each run to determine the reaction rate. The start concentrations of ester and HCl in the reaction mixture were $(0.8-1.2) \times 10^{-2}$ and $(2.0-2.6) \times 10^{-2}$ M, respectively.

The pseudo first-order rate constant, k_1 , is given by eqn. (2), where a is the original start concentration of

$$\ln \left(\frac{a}{(a-x)} \right) = k_1 t \quad (2)$$

propyl formate and x is the amount (per unit volume) of the ester reacted after a time t .

By choosing the zero time as the time, t_n , when one of the samples, n , was taken, and substituting a by $(a-n)$, x by $(x-n)$, and t by $(t-t_n)$, eqn. (2) becomes eqn. (3),

$$\ln \left(\frac{a-n}{(a-x)} \right) = k_1 (t-t_n) \quad (3)$$

where a , x and n are given by eqns. (4)–(6), in which V_T is

$$a = \frac{V_{T_a} C_T - V_{S_a} C_{HS}}{V_{S_a}} \quad (4)$$

$$x = \frac{V_{T_x} C_T - V_{S_x} C_{HS}}{V_{S_x}} \quad (5)$$

$$n = \frac{V_{T_n} C_T - V_{S_n} C_{HS}}{V_{S_n}} \quad (6)$$

the volume of titre (NaOH) used, C_T the concentration of the titre, V_S is the sample volume and C_{HS} is the concentration of HCl in the sample. Substituting eqns. (4)–(6) into eqn. (3) leads to eqn. (7).

$$\ln \left(\frac{V_{T_a}/V_{S_a} - V_{T_n}/V_{S_n}}{V_{T_a}/V_{S_a} - V_{T_x}/V_{S_x}} \right) = k_1 (t-t_n) \quad (7)$$

Eqn. (7) shows that k_1 is determined independently of the concentrations of catalyst and titre as long as these are constant throughout the reaction. Assuming that the titre concentration is constant, one can test the constancy of the catalyst concentration by changing the number of samples, the time of which is taken as zero time, starting from the first to the second sample, and so on. If k_1 is constant throughout the set of values obtained, one may be confident that the constancy of the catalyst concentration holds. One can easily exclude samples out of range by comparing the residuals. The residuals showed no appreciable systematic variation. For each temperature, k_1 was computed using the times of the first 10 samples as zero times. k_1

Table 2. Rate data for the alkaline hydrolysis of ethyl acetate in 50% (w/w) ethanol-water.

$t/^\circ\text{C}$	$k_2/\text{M}^{-1} \text{s}^{-1}$	$e_k/\%^a$
10.05	0.009 66	0.8
12.14	0.011 2	1.0
14.20	0.013 48	0.3
15.99	0.014 8	1.0
18.14	0.018 23	0.3
20.13	0.020 54	0.2
22.02	0.023 6	0.7
24.08	0.026 8	0.5
26.03	0.029 9	0.7
28.05	0.035 6	0.3
30.08	0.040 7	0.4
32.12	0.046 6	0.3
33.96	0.051 6	0.3
36.15	0.058 7	0.4
38.16	0.067 1	0.4
40.02	0.074 8	0.4

^a e_k is the estimated standard deviation in k_2 .

Table 3. Rate data for the acid hydrolysis of propyl formate in water.

$t/^\circ\text{C}$	$k_2/\text{M}^{-1}\text{s}^{-1}$	$e_k/\%^a$
4.06	0.000 415	2.3
6.03	0.000 555	1.5
8.01	0.000 81	2.8
10.03	0.000 95	1.7
12.10	0.001 03	1.3
14.05	0.001 25	1.6
16.05	0.001 36	1.8
18.00	0.001 69	0.9
20.11	0.002 05	2.8
22.07	0.002 82	1.1
24.00	0.003 39	1.2
26.03	0.003 48	1.5
28.02	0.004 18	0.8
30.08	0.005 01	1.8
32.01	0.006 04	1.3
34.00	0.007 08	1.1
35.99	0.008 10	0.6
38.09	0.009 97	0.8
39.95	0.011 6	1.2
42.00	0.013 1	1.5
43.97	0.015 3	1.0
45.99	0.017 7	1.2
47.97	0.020 2	1.3
49.98	0.022 9	1.8

^a e_k is the estimated standard deviation in k_2 .

showed no appreciable deviation from constancy. The average of a set of values of k_1 was obtained by using the times for the first 6–9 samples taken as zero times. Beyond this the standard deviation in k_1 was too large for these k_1 values to be considered meaningful in the calculation of the average k_1 value.

Values for the second-order rate constant, k_2 , obtained after dividing the average values of k_1 by the respective hydrogen ion concentration, determined at 2°C intervals from 4 to 50°C , are listed in Table 3.

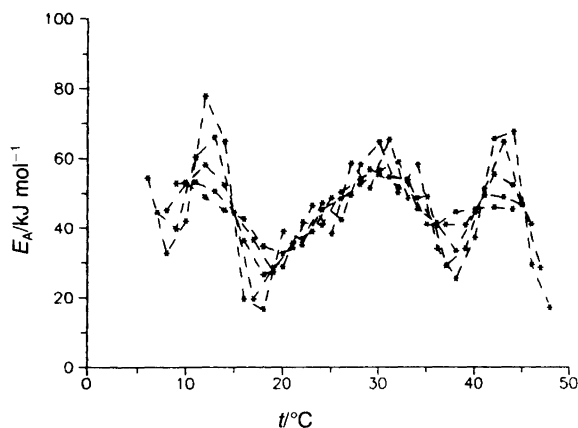


Fig. 1. The activation energy, E_A , of hydroxyl-promoted hydrolysis of ethyl acetate in water plotted versus temperature.

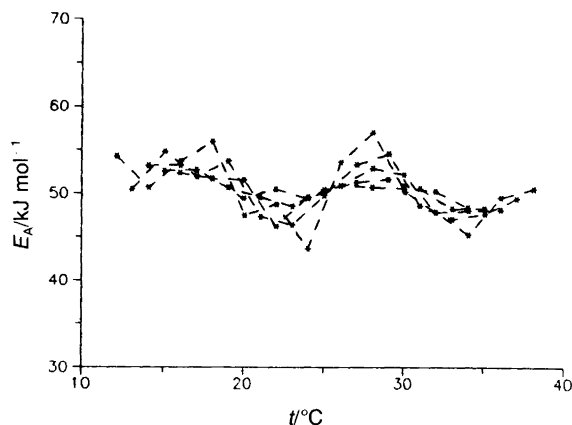


Fig. 2. The activation energy, E_A , of hydroxyl-promoted hydrolysis of ethyl acetate in 50% (w/w) ethanol-water plotted versus temperature.

Activation energy. To estimate the temperature dependence of the activation energies, the activation energies were estimated in successive, short temperature intervals. The sub-intervals contained from 3 to 7 data points, and the calculations covered the entire temperature interval investigated. The activation energies thus obtained are plotted against the middle temperature of the respective intervals in Figs. 1–3. The average activation energies, \bar{E}_A , are shown in Fig. 4. When two or three of the activation energies based on the sub-intervals were located at the same temperature (difference $<0.1^\circ\text{C}$), the average was used and others were excluded.

Gibbs energy of activation. According to Eyring,¹⁴ the Gibbs energy of activation, ΔG^\ddagger , may be written as eqn. (8),

$$\Delta G^\ddagger = -RT \ln k + RT \ln \left(\frac{k_B T}{h} \right) \quad (8)$$

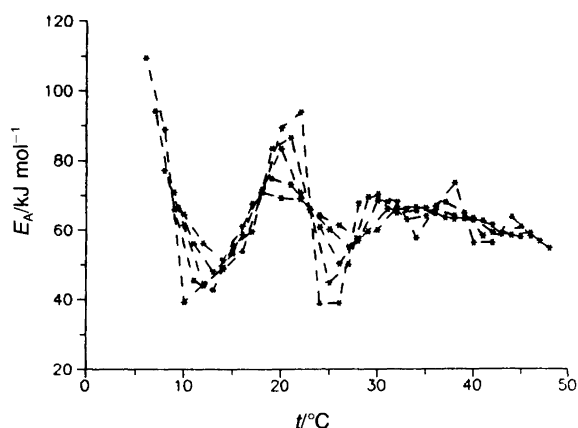


Fig. 3. The activation energy, E_A , of acid-catalyzed hydrolysis of propyl formate in water plotted versus temperature.

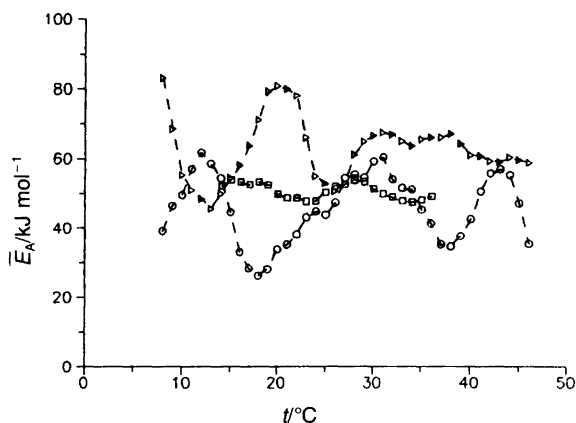


Fig. 4. The average activation energy, \bar{E}_A , obtained from Figs. 1–3, plotted versus temperature of (a) base hydrolysis of ethyl acetate in water (○), (b) base hydrolysis of ethyl acetate in 50% (w/w) ethanol-water (□) and (c) acid hydrolysis of propyl formate in water (△).

where k is the rate constant, R the gas constant, T the absolute temperature, h Planck's constant, and k_B Boltzmann's constant.

Discussion

When the Arrhenius activation energy, E_A , is determined as the average value over the entire temperature interval studied, the HO^- -promoted hydrolysis of ethyl acetate in water and in 50% (w/w) ethanol-water resulted in E_A values of 45.2 ± 0.7 and $50.4 \pm 0.3 \text{ kJ mol}^{-1}$, respectively. The acid-catalyzed hydrolysis of propyl formate in water gave an E_A value of $63.5 \pm 0.7 \text{ kJ mol}^{-1}$. With such small standard deviations it may seem obvious that the average E_A values should be taken as the best E_A values in each temperature interval over the region between 0 and 50°C,

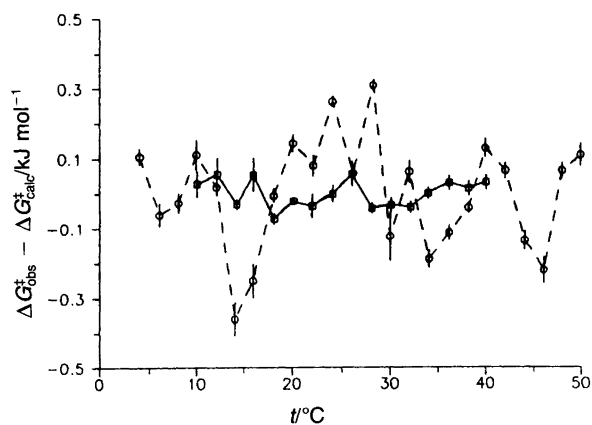


Fig. 5. The deviation $\Delta G_{\text{obs}}^{\ddagger} - \Delta G_{\text{calc}}^{\ddagger}$ plotted versus temperature, of the base hydrolysis of ethyl acetate in (a) water (○) and (b) 50% (w/w) ethanol-water (□). Vertical lines are the estimated standard deviation (95% conf. int.) in $\Delta G_{\text{obs}}^{\ddagger}$.

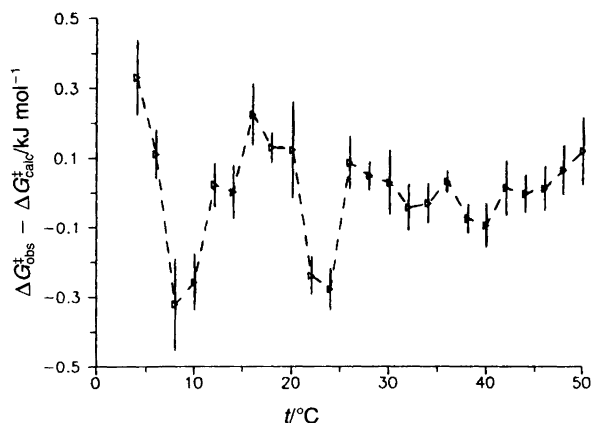


Fig. 6. The deviation $\Delta G_{\text{obs}}^{\ddagger} - \Delta G_{\text{calc}}^{\ddagger}$ plotted versus temperature, of the acid hydrolysis of propyl formate in water. Vertical lines are the estimated standard deviation (95% conf. int.) in $\Delta G_{\text{obs}}^{\ddagger}$.

because the calculation of E_A values over the shorter temperature intervals with fewer rate constants results in greater standard deviations in E_A . If random errors in the rate values have been the cause of the errors in E_A , the latter values should be scattered randomly around the average E_A value calculated from the entire interval. However, the E_A values for the hydrolyses in water are seen to be systematically distributed in a wave-like manner with temperature in Figs. 1–3. The activation energy is a derived function of temperature, proportional to $d(\ln k)/d(1/T)$, and accordingly critically dependent on the accuracy of the rate data, as well as on the length of the temperature intervals chosen in the calculations. On the other hand, the Gibbs energy of activation, $\Delta G_{\text{obs}}^{\ddagger}$, obtained by inserting the k values in the equation of Eyring [eqn. (8)], also gives rise to an irregular temperature function. This behaviour is well illustrated in Figs. 5 and 6, where the difference,

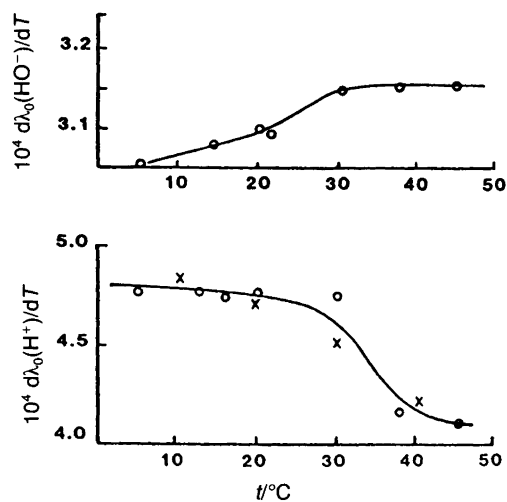


Fig. 7. The temperature gradients of the molar conductivities (in $\Omega^{-1} \text{ m}^2 \text{ mol}^{-1} \text{ K}^{-1}$) plotted versus temperature, of HO^- (upper curve) and H^+ (lower curve).^{15,16}

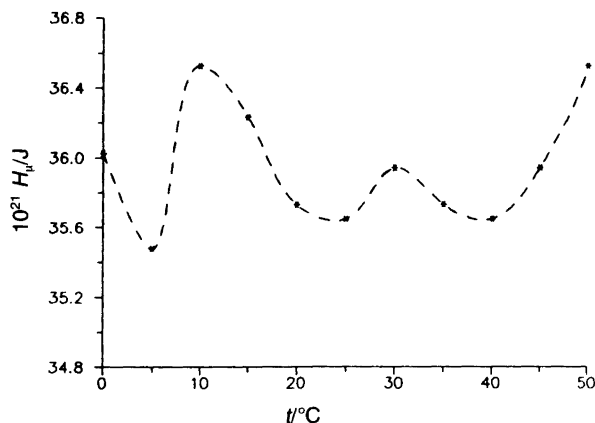


Fig. 8. The rotational barrier, H_{\ddagger} , of water plotted versus temperature, as calculated by Johri and Roberts.²³

$\Delta G_{\text{obs}}^{\ddagger} - \Delta G_{\text{calc}}^{\ddagger}$, is plotted as a function of T . $\Delta G_{\text{calc}}^{\ddagger}$ is obtained assuming the free energy to be a linear function of T ($\Delta G_{\text{calc}}^{\ddagger} = a_0 + a_1T$). Introducing a quadratic term into T ($\Delta G_{\text{calc}}^{\ddagger} = a_0 + a_1T + a_2T^2$) does not alter the picture shown in Figs. 5 and 6. The present activation parameters of the hydrolysis of esters in water accord with the previously reported data for the hydrolysis of the diethyl acetal of 4-nitrobenzaldehyde, where E_A for hydrolysis was found to vary in an oscillatory manner with temperature in water, but not in 55% (v/v) water-ethanol.²

The \bar{E}_A values obtained from Figs. 1–3 are plotted vs. temperature in Fig. 4. The almost opposite oscillatory course, with maxima and minima in reversed order, is striking, and cannot be regarded as wholly accidental. From existing literature data,^{15,16} the temperature gradients of the molar conductivities of H^+ and HO^- are calculated and recorded in Fig. 7. The opposite temperature dependence of $d\lambda_{\text{H}^+}/dT$ and $d\lambda_{\text{HO}^-}/dT$ is unquestionable, although the accuracy of the derived values is insufficient to determine the true temperature course. It may be that the wave-shaped variation of E_A in the ester hydrolysis is connected with the temperature dependence of the proton-transfer reactions in water.

Theoretical calculations¹⁷ of the barrier of proton transfer in $[\text{HOHOH}]^-$ and $[\text{H}_2\text{OH}_2]^+$ complexes reveal that they are oppositely dependent on the angle of the H-bond connecting the oxygen atoms. Increased bending of H-bonds in water with rising temperature is a vital part of modern theories of water.^{18–20} Studies of ultrafast protolytic reactions in water have also shown that the rate of proton transfer is proportional to the rotational barrier of water.^{21,22} In a recent paper, Johri and Roberts²³ have studied the dielectric response of water at 1–2°C intervals between 0 and 50°C and calculated the temperature dependence of the rotation barrier (Fig. 8). They stress that: "Discontinuities in the observed parameters and in the correlation factor, under the significant liquid structure model, indicate higher order transitions in the examined

temperature range". This observation supports the working hypothesis put forward in previous publications^{2,24} that the oscillatory behaviour of E_A versus temperature in water is caused by higher-order transitions, possibly between four-, three- and two-coordinated, cooperatively H-bonded structures. Further studies are in progress at our institute on spontaneous and general acid/base-catalyzed reactions in water.

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Received November 8, 1990.