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Kinetics of hydrolysis of 1-benzoyl-1,2,4-triazole in aqueous solution as a function of temperature near the temperature of maximum density, and the isochoric controversy

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At temperatures above and below the temperature of maximum density, TMD, for water at ambient pressure, pairs of temperatures exist at which the molar volumes of water are equal. First-order rate constants for the pH-independent hydrolysis of 1-benzoyl-1,2,4-triazole in aqueous solution at pairs of such isochoric temperatures show no unique features. Taken together with previously published kinetic data for the hydrolysis of a range of simple organic solutes in both water and D_2O near their respective TMDs, we conclude that special significance in the context of rates of chemical reactions in aqueous solutions should not be attached to the isochoric condition.

Introduction

In 1935 Evans and Polanyi[1] suggested that isochoric activation parameters for chemical reactions in aqueous solution might be more mechanistically informative than conventional isobaric activation parameters; *i.e.* $[\partial\ln(k)/\partial T]_v$ rather than $[\partial\ln(k)/\partial T]_p$ where k is the rate constant for spontaneous chemical reaction.[2,3] This proposal sparked enormous interest in several subject areas including ionic transport[4] and chemical equilibria[5] in solution.

With reference to chemical reactions in dilute aqueous solution the isochoric standard internal energy of activation $\Delta^{\neq}U^{\circ}_{v}$ is related to the isobaric standard enthalpy of activation $\Delta^{\neq}H^{\circ}_{p}$ at temperature T and the standard volume of activation $\Delta^{\neq}V^{\circ}$ using equation (1) where α^{*}_{p1} and κ^{*}_{T1} are, respectively, the isobaric expansibilities and isothermal compressibilities of water (l).

$$\Delta^{\neq}U^{\circ}_{v} = \Delta^{\neq}H^{\circ}_{p} - T\ [\alpha^{*}_{p1}/\kappa^{*}_{T1}]\Delta^{\neq}V^{\circ} \qquad (1)$$

Baliga and Whalley[6] noted that the dependence on solvent mixture composition of $\Delta^{\neq}U^{\circ}_{v}$ is less complicated than that for $\Delta^{\neq}H^{\circ}_{p}$ for solvolysis of benzyl chloride in ethanol–water mixtures at 298.15 K. A similar pattern was reported by Baliga and Whalley[7] for the hydrolysis of 2-chloro-2-methylpropane in the same mixture at 273.15 K. Nevertheless the significance of isochoric parameters in the context of both kinetic[8] and equilibrium parameters[9] has been extensively debated.[10–15]

Much of the debate centred on the isochoric condition and the answer to the question "which volume is held constant?".[9] With reference to equation (1) α^{*}_{p1} and κ^{*}_{T1} depend on temperature. Then the volume identified by subscript V on $\Delta^{\neq}U^{\circ}_{v}$ is dependent on temperature. Further, the molar volumes of binary liquid mixtures at fixed T and p (*cf.* kinetic data in reference 7) depend on composition so that in the context of $\Delta^{\neq}U^{\circ}_{v}$, the volume identified by subscript V is not constant across a range of solvent mixtures. In 1985, Haak *et al.*[8] noted that above and below the temperature of maximum density (TMD) of water there are pairs of temperatures where the molar volumes of water at ambient pressure are equal. Hence rates of reaction for chemical reactions in dilute aqueous solution at such temperatures would yield pairs of isochoric rate constants. The suggestion was not taken up. However, another controversy had arisen concerning chemical reactions in aqueous solutions at low temperatures. Hills and Viana[16] reported that rate constants for hydrolysis of benzyl chloride (see above) in very dilute aqueous solutions increased with increase in temperature above the TMD of water and, significantly, increased with decrease in temperature below the TMD. Albery and Curran[17] were unable to confirm the pattern in rate constants reported by Hills and Viana.[16]

Therefore we turned our attention to the suggestion made by Haak *et al.*[8] concerning rates of reaction at isochoric pairs of temperatures. For this study to be meaningful, the studied reaction had to satisfy at least three criteria:

(i) the rate of chemical reaction can be precisely measured;
(ii) the mechanism of reaction is well understood, and
(iii) the rate of reaction is sensitive to temperature.

These three criteria are satisfied by the spontaneous first-order hydrolysis of 1-benzoyl-1,2,4-triazole in aqueous solution. The mechanism of hydrolysis involves water-catalysed nucleophilic attack at the carbonyl group.[8]

The dependence of rate constants on temperature near the TMD of water is examined in terms of the dependence of the molar volume of water on temperature reported by Kell and Whalley[18] and summarised by Kell.[19] We show that the 'isochoric condition' does not reveal novel features concerning the hydrolysis reaction in aqueous solution. We draw attention to published kinetic data which support our conclusion but which, in the debate over isochoric kinetics, were overlooked.

Results

First-order rate constants for the hydrolysis of 1-benzoyl-1,2,4-triazole in aqueous solution (Scheme 1) are reported at 12 different temperatures between 276.15 and 278.15 K; Table 1. The difference between the temperatures in the series is generally between 0.1 and 0.3 K. At three temperatures, 276.25, 276.45 and 277.25 K, repeat experiments yielded rate constants which agree to better than ±0.42%. The resulting plot (Fig. 1) of (k/s^{-1}) against $(T/\mathrm{K})^{-1}$ is linear. The dependences of (k/s^{-1})

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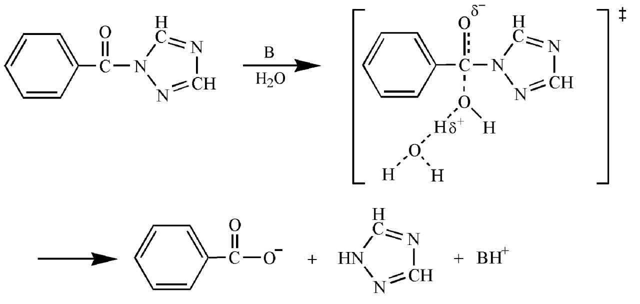
Table 1 First-order rate constants for the spontaneous hydrolysis of 1-benzoyl-1,2,4-triazole as a function of temperature in aqueous solution at temperatures close to the TMD[a]

T/K	k/10^{-4} s^{-1}
276.15	3.91
276.25	3.92; 3.93; 3.95
276.45	3.93; 3.96; 3.97
276.65	4.04
276.95	4.11
277.05	4.16; 4.26
277.25	4.20; 4.22; 4.25
277.35	4.29
277.45	4.29; 4.32
277.65	4.37
277.85	4.51
278.15	4.59

[a] At 298.15 K, $k = 21.2 \times 10^{-4}$ s^{-1}.



Scheme 1

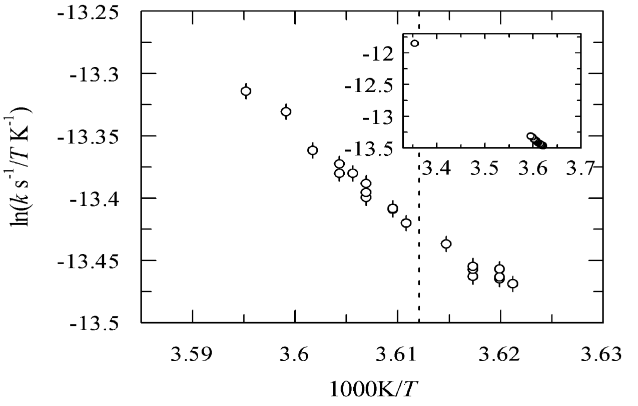


Fig. 1 Dependence of ln(k/T) on reciprocal temperature for the hydrolysis of 1-benzoyl-1,2,4-triazole in aqueous solution. The dotted line marks the TMD. The inset plot shows the dependence in relation to the previously reported[21] rate constant at 298.2 K.

and molar volume V_1^* (l) on temperature are compared in Fig. 2. These plots show no novel features as the temperature increases from below to above the TMD which is estimated to be 276.85 K; see Experimental section. The dependence of rate constants on temperature[20] was analysed using equation (2) where θ is a reference temperature.

$$\ln\left(\frac{k}{T}\right)=\ln\left(\frac{k(\theta)}{\theta}\right)+\left(\frac{\Delta^{\ddagger}H^{0}(\theta)}{R}\right)\times\left[\frac{1}{\theta}-\frac{1}{T}\right]+\left(\frac{\Delta^{\ddagger}C_{p}^{0}(\theta)}{R}\right)\times\left[\frac{\theta}{T}-1+\ln\left(\frac{T}{\theta}\right)\right] \quad (2)$$

The analysis yields estimates of rate constant at $k(\theta)$, the standard enthalpy of activation $\Delta^{\neq}H^{o}$ (θ) and the standard isobaric heat capacity of activation $\Delta^{\neq}C_p^{o}$ (θ) at reference temperature θ. A statistically significant estimate of $\Delta^{\neq}C_p^{o}$ (θ) requires kinetic data over an extended temperature range. The temperature range covered by the results in Table 1 are too small and so the experimental data were analysed using two parameters $k(\theta)$ and $\Delta^{\neq}H^{o}$ (θ). Hence (Fig. 3) with θ = 276.85 K, $k(\theta)/10^{-4}$ s^{-1} equals 4.106 ± 0.006 and $\Delta^{\neq}H^{o}$ (θ) equals 49.8 ± 1.6 kJ mol^{-1}, in agreement with previous results.[21]

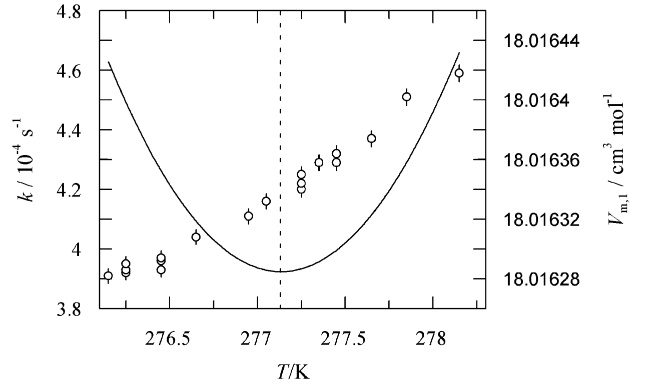


Fig. 2 Dependence of rate constant for the hydrolysis of 1-benzoyl-1,2,4-triazole and molar volume of the aqueous solution on temperature. The dotted line marks the TMD.

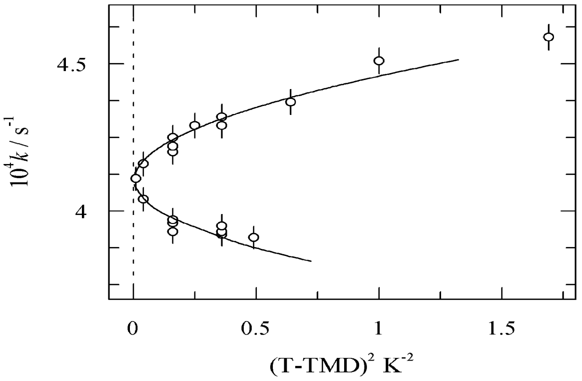


Fig. 3 Dependence of rate constant for the hydrolysis of 1-benzoyl-1,2,4-triazole on $(T\text{-TMD})^2$ over the temperature range 276.15 ≤ T/K ≤ 278.15. The solid line shows the calculated rate constant using equation (1) with θ = 276.85 K, $k(\theta)$ = 4.106 × 10^{-4} s^{-1} and $\Delta^{\neq}H^{o}$ (θ) = 49.8 kJ mol^{-1}.

Discussion

The careful and detailed investigation reported here was prompted by the idea that isochoric rate constants for reactions in solution might contribute to the problem of understanding the role of solvents in controlling activation parameters for reactions in solution. In general terms, activation parameters for a given reaction in aqueous solution are determined in part by solute–solvent interactions between both initial and transition states and neighbouring solvent molecules. Solvent–solute intermolecular distances and solvent organisation around solutes are functions of temperature. Therefore the case was made[1] that by keeping the volume constant these distances remain constant when the temperature is changed. The expectation was therefore that as one increases the temperature the influence of changes in solute–solvent distances are minimal under isochoric conditions. Hence by 'removing' this influence one can direct attention to the changes taking place in the reactants on going from initial to the transitions states. The question[9] which 'volume is constant?' was raised.

The importance of the experimental results presented here is that they illustrate how

$$\left(\frac{\partial \ln(k)}{\partial T}\right)_{V_1^*(\ell)}$$

can be calculated with respect to isochoric conditions. Interestingly there are pairs of isochoric data points on the plot shown in Fig. 1. All the data points, both above and below the TMD, show that the rate of reaction is insensitive to the presence of the TMD. In fact, this pattern is shown by published kinetic data for hydrolysis reactions in aqueous solutions as reported by Robertson and co-workers. These data sets also include kinetic data for solvolysis of a range of compounds in water[22–30] and in D_2O,[22,23,25,31] the TMD of the latter being 284.35 K. The compounds included methyl trifluoroethanoate, succinic and phthalic anhydride,[22] dimethylsulfamoyl chloride,[23] diethyl and methyl(ethyl)sulfamoyl chloride,[24] methanesulfonyl and benzenesulfonyl chloride,[25] methyl chlorosulfate and ethyl chlorosulfate,[27] 2-chloroethyl(methyl) sulfide,[28] methyl methanesulfonate[29] and 4-substituted benzenesulfonyl chlorides.[30] Moelwyn-Hughes *et al.*[26] reported rate constants for the solvolysis of 2-chloro-2 methylpropane in aqueous solution at intervals of 1 K from 273.15 to 298.15 K. Novel features in the kinetic data can neither be discerned from isobaric pairs of temperatures nor from around the TMD.

We note that most of these data were published before the claim by Hills and Viana[16] was published concerning 'negative activation energies'. In other words published data was available to show that the TMD of water plays no real part in determining rate constants for solvolytic reactions. In fact, the interest of the senior author Robertson on many of these publications[22–31] was directed towards determining the isobaric heat capacity of activation for solvolytic reactions in water and D_2O; *e.g.* 2-chloro-2-methylpropane (aq).[26]

These comments do not, of course, detract from the importance of the original proposal by Evans and Polanyi.[1] We simply suggest that in many cases where isochoric activation parameters have been reported the proper meaning of the term 'isochoric' has not been recognised. However, we have shown that in the important case of aqueous solutions no unique feature emerges in the kinetic data for hydrolysis reactions in the region of the TMD.

Experimental

Materials

1-Benzoyl-1,2,4-triazole was synthesised according to published procedures.[21,32,33] Water was distilled twice from an all-quartz distillation unit.

Kinetics

The spontaneous hydrolysis of 1-benzoyl-1,2,4-triazole was followed using a Shimadzu Diode-array spectrophotometer, absorbances being recorded between 200 and 400 nm. The cell compartment of the spectrophotometer was thermostatted to a preset temperature using a Haake thermostatting unit equipped with a Pt100 electrode for direct temperature control of the cell block in the spectrophotometer. The temperature was checked using a copper/constantin thermocouple and found to deviate by no more than 0.05 K from the preset temperature during the kinetic experiments. Experience showed that control of temperature was improved by using ethanol rather than water as a bath liquid. We attribute the problems with using water to the formation of ice in the refrigeration unit.

A quartz cuvette, path length 1cm, contained approx. 2.75 cm^3 of water for which the pH had been adjusted to 3.8 ± 0.3 using HCl (aq). The cuvette had a stopper fitted with two small holes. The cuvette was thermostatted overnight. The cell compartment was sealed with cling film so that the air-flow in the spectrophotometer did not affect the temperature of the cell compartment. The cell compartment was continually flushed with dry pre-cooled air. The latter was important in order to avoid condensation of water vapour on the cell walls.

The cell compartment was fitted with a hole in the cover through which wires and tubing could be led into the sealed cell compartment. Through this hole 1.5 cm^3 of solution in the sample cell was withdrawn. Between 4 and 8 μL of a stock solution containing 5 mg of 1-benzoyl-1,2,4-triazole in 1 cm^3 cyanomethane was injected into the cuvette. The solution in the cuvette was withdrawn and re-injected several times. Finally the solution was injected into the cuvette very slowly in order to prevent the formation of air bubbles. After the reaction had been initiated the temperature of the cell was monitored. Only after the temperature had returned to the required temperature were data points recorded of absorbance and time. During a given kinetic run the absorbances were measured during a brief exposure (1 second in each minute) of the cell to the incident UV–visible beam of light. Poor kinetic data resulted if the solution was subjected to continuous radiation.

The TMD of the solutions used in the experiments was slightly lower than the TMD of water at ambient pressure. The lowering of the TMD was caused by the use of cyanomethane in the reaction medium injected as stock solution of the substrate. In a typical experiment 6 ± 2 μl of a stock solution in cyanomethane was injected together with 2.75 cm^3 of water (l) resulting in a 0.126 ± 0.040 mol% aqueous solution of cyanomethane. The TMD of water (l) is lowered[34] by 0.28 ± 0.09 K to 276.85 ± 0.09 K. In the following we assume that the molar volume of water + cyanomethane binary liquid mixture at ambient pressure is a quadratic function of the temperature around the TMD. Nevertheless the conclusions presented here are not affected by setting the TMD to either 276.85 or 277.13 K.

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References

1 M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1935, **31**, 875.
2 M. G. Evans and M. Polyani, *Trans Faraday Soc.*, 1937, **33**, 448.
3 D. M. Newitt and A. Wassermann, *J. Chem. Soc.*, 1940, 735.
4 See, for example, G. J. Hills, P. J. Ovenden and D. R. Whitehouse, *Discuss. Faraday Soc.*, 1965, **39**, 207 and references therein.
5 D. A. Lown, H. R. Thirsk and Lord Wynne-Jones, *Trans. Faraday Soc.*, 1970, **66**, 51.
6 B. T. Baliga and E. Whalley, *J. Phys. Chem.*, 1967, **71**, 1166.
7 B. T. Baliga and E. Whalley, *Can. J. Chem.*, 1970, **48**, 528.
8 J. R. Haak, J. B. F. N. Engberts and M. J. Blandamer, *J. Am. Chem. Soc.*, 1985, **107**, 6031.
9 M. J. Blandamer, J. Burgess, B. Clark and J. M. W. Scott, *J. Chem. Soc., Faraday Trans. 1*, 1984, **80**, 3359.
10 P. G. Wright, *J. Chem. Soc., Faraday Trans. 1*, 1986, **82**, 2557.
11 L. M. P. C. Albuquerque and J. C. R. Reis, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 207.
12 E. Whalley, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 2901.
13 M. J. Blandamer, J. Burgess, H. J. Cowles, I. M. Horn, J. B. F. N. Engberts, S. A. Galema and C. D. Hubbard, *J. Chem. Soc., Faraday Trans. 1*, 1989, **85**, 3733.
14 J. B. F. N. Engberts, J. R. Haak, M. J. Blandamer, J. Burgess and H. J. Cowles, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1059.
15 L. M. P. C. Albuquerque and J. C. R. Reis, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 1553.
16 G. Hills and C. A. N. Viana, *Nature*, 1971, **229**, 194.
17 W. J. Albery and J. S. Curran, *J. Chem. Soc., Chem. Commun.*, 1972, 425.
18 G. S. Kell and E. Whalley, *Philos. Trans. R. Soc. London, A*, 1965, **258**, 565.
19 G. S. Kell, *J. Chem. Eng. Data*, 1967, **12**, 66.
20 E. C. W. Clarke and D. N. Glew, *Trans. Faraday Soc.*, 1966, **62**, 539.
21 W. Karzijn and J. B. F. N. Engberts, *Tetrahedron Lett.*, 1978, **19**, 1787.

22 B. Rossall and R. E. Robertson, *Can. J. Chem.*, 1975, **53**, 869.
23 E. C. F. Ko and R. E. Robertson, *J. Am. Chem. Soc.*, 1972, **94**, 573.
24 E. C. F. Ko and R. E. Robertson, *Can. J. Chem.*, 1972, **50**, 946.
25 R. E. Robertson, B. Rossall, S. E. Sugamori and L. Treindl, *Can. J. Chem.*, 1969, **47**, 4199.
26 E. A. Moelwyn-Hughes, R. E. Robertson and S. Sugamori, *J. Chem. Soc.*, 1965, 1965.
27 E. C. F. Ko and R. E. Robertson, *Can. J. Chem.*, 1972, **50**, 434.
28 M. J. Blandamer, H. S. Golinkin and R. E. Robertson, *J. Am. Chem. Soc.*, 1969, **91**, 2678.
29 P. W. C. Barnard and R. E. Robertson, *Can. J. Chem.*, 1961, **39**, 881.
30 R. E. Robertson and B. Rossall, *Can. J. Chem.*, 1971, **49**, 1441.
31 B. Rossall and R. E. Robertson, *Can. J. Chem.*, 1971, **49**, 1451.
32 H. A. Staab, M. Luking and F. H. Durr, *Chem. Ber.*, 1962, **95**, 1275.
33 H. J. Mooij, J. B. F. F. N. Engberts and M. Charton, *Recl. Trav. Chim. Pays-Bas*, 1988, **107**, 185.
34 G. Wada and S. Umeda, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 1797.