Thermodynamic functions of activation of the alkaline hydrolysis of ethyl benzoate and of ethyl *p*-nitrobenzoate in ethanol–water mixtures of various compositions at different temperatures

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This paper presents second-order rate constants for the alkaline hydrolysis of ethyl benzoate and of ethyl *p*-nitrobenzoate in ethanol–water mixtures in the ethanol mol fraction range 0.16–0.72 and at 278.15–318.15 K measured by a specially developed titrimetric technique. The results show interesting variations in the rate constants with ethanol content at the various temperatures, especially over the mol fraction ranges 0.16–0.25 and 0.4–0.5. The rate constant (k_2) data, the Arrhenius activation energy (E_A) and pre-exponential factor (A) for ethyl benzoate and the parameters of the fitted polynomials from which other derived thermodynamic functions may be calculated are provided as supplementary material.

Introduction

The main objectives of this study into solute–solvent interactions have been outlined elsewhere.[1,2] The interesting structural aspects and their correlation with thermodynamic functions have been amply reviewed by other workers.[3–5] Our titrimetric technique[6] has been used in preference to the conductimetric technique used by others[7] since our previous comparative studies had shown the latter to be inaccurate.[1]

We present in this paper second-order rate constants data (k_2) for the alkaline hydrolysis of ethyl benzoate and ethyl *p*-nitrobenzoate in ethanol–water mixtures over the ethanol mol fraction (X) range 0.16–0.72 (unfortunately restricted by solubility limitations) and the temperature (T) range 278.15–318.15 K. The k_2 data and the parameters of the fitted polynomials from which other functions of activation may be calculated are provided as supplementary material.‡

Results and discussion

The second-order rate constant k_2 was calculated according to eqn. (1), where:

$$k_2 = \frac{V(NV' - N'V_a + NV_t)}{NV't(N'V_a - NV_t)} \qquad (1)$$

V = volume of reaction mixture at the reaction temperature;
V' = volume of alkali solution added initially;
V_a = volume of acid used for quenching;
V_t = volume of alkali required for back-titrating excess acid;
M = molarity of alkali solution used in hydrolysis reaction and for back-titrating excess acid;
M' = molarity of acid used for quenching;
t = reaction period.

The maximum error in k_2 at the middle-of-range temperature and composition for both systems, evaluated from estimates of the errors of the above parameters according to the principle of superposition of errors, was ± 2.5%. As mentioned in a previous paper, our present technique has been proved to produce results in agreement with those by other workers using a titrimetric technique,[8] but not with those using a conductimetric technique.[7] In this work, results from duplicate runs consistent within this uncertainty limit were adopted. The k_2 data are given in Tables 1 and 2 in the supplementary material.

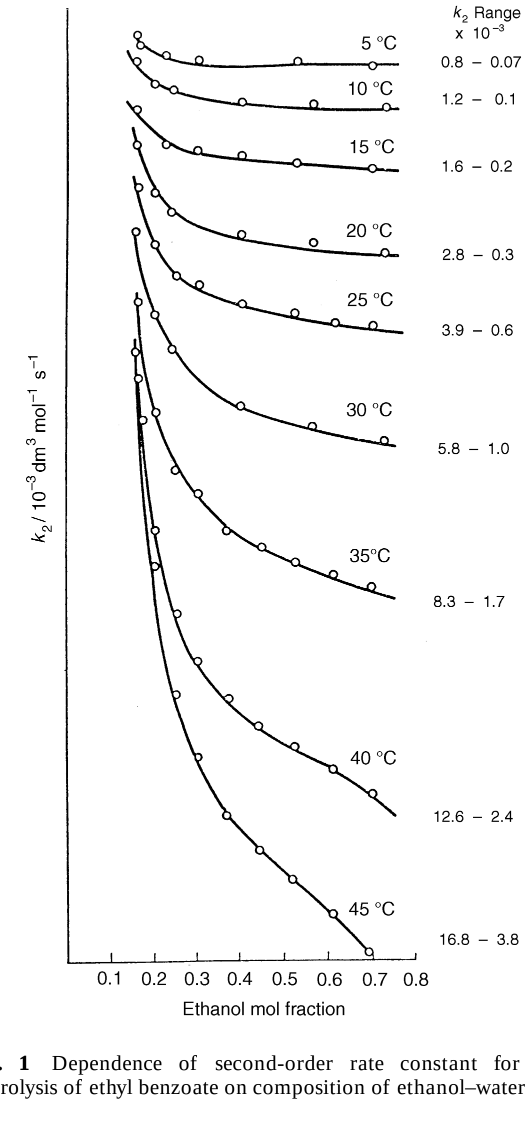

Fig. 1 Dependence of second-order rate constant for alkaline hydrolysis of ethyl benzoate on composition of ethanol–water solvent

The variation patterns of k_2 with ethanol mol fraction for the

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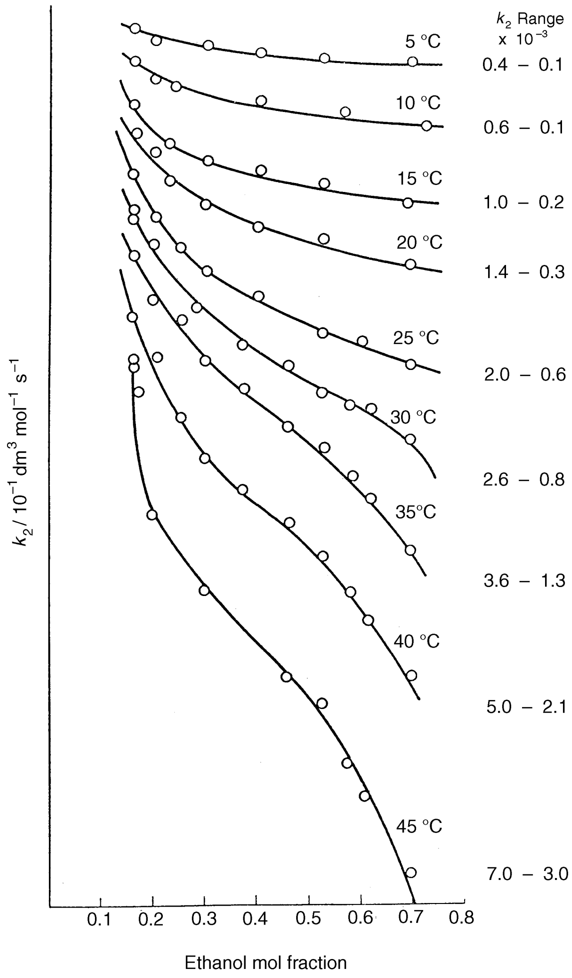

Fig. 2 Dependence of second-order rate constant for alkaline hydrolysis of ethyl *p*-nitrobenzoate on composition of ethanol–water solvent

two systems are shown in Figs. 1 and 2. The general features for both systems are a steep decrease of k_2 with increasing ethanol content over the mol fraction region from 0.16 to *ca.* 0.3. Thereafter the decrease becomes much smaller towards the end of the ethanol mol fraction scale. The initial sharp decrease becomes even steeper at higher temperatures, more so in the case of ethyl benzoate than that of ethyl *p*-nitrobenzoate. At higher temperatures, 40 °C for ethyl benzoate and 30 °C for ethyl *p*-nitrobenzoate, the curves appear to pass through an inflection towards higher ethanol content. The inflections appear to occur between 0.4 and 0.5 ethanol mol fractions. These variations should be reflected more profoundly in the derived functions of activation, *e.g.* $\Delta H^\ddagger$ if the ln k_2 data are of sufficient accuracy.

Initially, the simplistic linear correlation of ln k_2 with $1/T$ was tested. This was found to be fairly satisfactory for ethyl benzoate but not for ethyl *p*-nitrobenzoate. The Arrhenius activation energy E_A and the pre-exponential factor A were thus evaluated by linear least-square fitting of the data of the former system for the various ethanol mol fractions according to eqn. (2).

$$\ln k_2 = \ln A - E_A/RT \qquad (2)$$

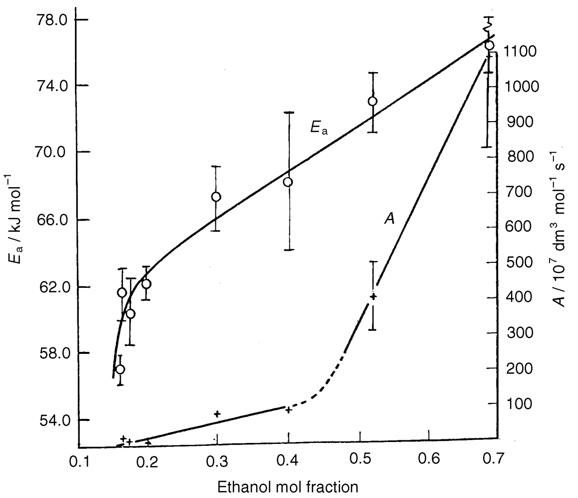

Fig. 3 Apparent (Arrhenius) activation energy (E_a) and pre-exponential factor (A) for the alkaline hydrolysis of ethyl benzoate in ethanol–water mixtures of various composition

The results are given in Table 3 in the supplementary material and are shown in Fig. 3. The graphs seem to reveal profound changes of E_A at the water-rich end of the solvent composition scale and of A at the middle of the scale. Both E_A and A appear to have distinctly different slopes at those solvent compositions. This seems to support the prediction of solvent effects of a structural nature, which stemmed from the work of Winstein and Fainberg[10] on the solvolysis of *tert*-butyl chloride in the same solvent system. Such effects have since been extensively reviewed by Blandamer.[11]

The inadequacy of linear correlation of ln k_2 with $1/T$ has also been reported by Moelwyn-Hughes in the case of methyl chloride.[9] In view of this restriction in the present cases, resort has had to be made to computer fitting by the method of least-squares orthogonal polynomials based on eqn. (3) at constant

$$-\ln k_2 = f(T) \qquad (3)$$

ethanol mol fractions. To guard against artefacts, the fitted polynomials were terminated and tested for goodness of fit by means of F- and t-tests, and by inspection of the standard deviation and residuals. Unfortunately, in a very few instances, there were small departures of the actual ethanol mol fractions (X) from those fixed by design to apply throughout the temperature range. In such cases, the required ln k_2 values were obtained by computerised interpolation, again using empirical orthogonal polynomial fitting based on eqn. (4).

$$-\ln k_2 = f(-\ln X) \qquad (4)$$

The parameters of eqns. (3) and (4) are given in Tables 4–6 of the supplementary material.

The electrostatic effects on reaction rates were briefly examined by fitting the data graphically to the equation of Amis and Quinlan[12,13] based on a model of ion–dipolar molecule interactions leading to the formation of the activated complex. Generally, the plots of $-\ln k_2$ *vs.* $1/D$, where D is the relative permittivity, for the different temperatures show more linearity in the case of the *p*-nitrobenzoate than that of the benzoate. Furthermore, the latter shows a break around 0.2 ethanol mol fraction with steeper slopes below this composition.

Analysis of kinetic data in the context of solvent effects is known to be complex, partly because several factors come into play together and may not all be separable, and partly because of inadequate understanding of the solvent structure and the existence of a number of alternative models for it. However, thermodynamic functions of activation are a powerful tool for such analysis and the transition state theory is the most popular for such studies. This subject is well covered in a review by Engberts.[14]

Structural factors arise mainly from solute–solvent interactions in both the initial and activated states. The intrusion of the solute results in the replacement of solvent–solvent forces by solute–solvent forces within the cybotactic region. This may also have implications on the binary solvent structure beyond this region. The initial and activated states may enhance water structure and the enhanced structure is extremely sensitive to temperature. Relative solvation of the initial and activated states superimposes a $\Delta H^{\ddagger}$ contribution upon the intrinsic bond-breaking and -making energies. Solvation of the two states is also reflected in $\Delta S^{\ddagger}$ through the changes in translational and rotational degrees of freedom of solvent molecules, hence the dominance of the entropy effect over rate constants. Dramatic changes affecting $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are less manifest in $\Delta G^{\ddagger}$ because of enthalpy–entropy compensation. Unlike $\Delta S^{\ddagger}$, $\Delta C_p{}^{\ddagger}$ does not have the disadvantage of inherent contributions due to steric factors, and should therefore be very useful for revealing the specific role of solvent reorientations—and their temperature dependence—in rate processes. Unfortunately, for $\Delta C_p{}^{\ddagger}$ data to be useful, the accuracy of k_2 data would need to be 0.2% or better.

Finally, since solute polarity is an important factor in solute–solvent interactions the *p*-nitrobenzoate ester with approximately double the dipole moment of the benzoate ester has been chosen for comparison in this study with the added interest of testing for any structural effects due to dispersion forces at the nitro group. Unfortunately, solubility limitations have prevented measurements below the 0.16 ethanol mol fraction. However, tentative calculations of the activation parameters as functions of solvent composition do show extrema in the cases of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both esters with some remarkable differences between the two at certain temperatures, presumably due to the *p*-nitro group. Since the validity of these features depends largely on the degree of the polynomial chosen for eqn. (3) above, there is the danger of such features being mere artefacts despite the careful statistical basis of that choice. More work is therefore needed to substantiate such interesting variations, preferably with even higher accuracy of k_2 than has hitherto been achieved. Unfortunately, the opportunity for this is not available for us.

Experimental

The purification of esters, solvents and other materials has been described in the earlier publication.[1] The rates of the hydrolysis reactions were determined by the improved titrimetric technique.[6] The advantages of this technique lie in the special design of the reaction vessel shown in Fig. 4. It consists of three compartments, C_1, C_2 and C_3. One of the two reacting solutions is placed in C_1 and the other in C_2. The pH electrodes (glass/calomel assembly) are inserted into C_3. The compartments C_1 and C_2 communicate *via* a B10 socket fitted with a solution-retaining plug P. C_3 communicates with the reaction flask C_2 *via* a capillary tube and has a side arm at the top which is used either for sucking the solution up into C_3 for pH measurement during the titration or for bubbling pre-saturated purified nitrogen through the solution in C_2 for mixing.

In contrast to commonly used methods where one reactant is thermostatted in a flask and the other run in from a pipette, this design has the advantage that it enables: (*i*) both reactants to be thermostatted, in the same vessel, before mixing; (*ii*) the time-of-mixing error to be reduced to a relatively insignificant value; (*iii*) an inert atmosphere of nitrogen to be maintained over the reaction mixture throughout; (*iv*) the reaction to be quenched and the excess acid to be back-titrated in the same reaction vessel, thus eliminating the volume, temperature and time errors inherent in pipette sampling of the reaction mixture and of quenching in a separate flask.

The alkali used was ensured to be carbonate-free through *in situ* ion-exchange treatment prior to its introduction into the vessel *via* a semi-micro burette. This is rendered feasible by a specially designed auxiliary set-up incorporating the automatic burette and an ion-exchange column packed with a strong hydroxide resin, with protection of the alkali solution against atmospheric CO_2 by means of self-indicating soda-lime guard tubes. The excess acid after quenching was titrated against the same carbonate-free alkali using a pH meter. In the present study, the precision of the pH readings was ± 0.005 unit. The end-point was determined graphically from the differential plots of pH *vs.* $V + 1/2\ \Delta V$ (derived from the pH *vs.* V titration curve) with an accuracy of ± 0.002 ml. In all the kinetic runs, the total volume of the reaction mixture was designed to be 100.00 ml.

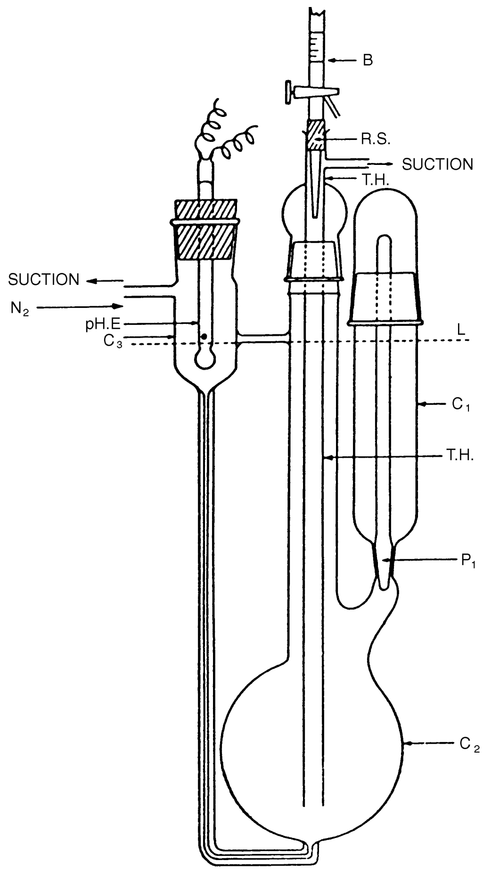

Fig. 4 Reaction and titration vessel for kinetic runs

With C_3 stoppered and the plug P removed, the clean dry vessel was purged with nitrogen. With plug P inserted and nitrogen flowing slowly, the aqueous alkali solution was run into C_2 and the equivalent amount of ethanolic ester solution into C_1. Purified ethanol was run into C_2 (*via* C_3), in order to achieve the same required solvent composition in C_2 as in C_1. The compartment C_1 was stoppered, the pH electrode assembly inserted in C_3 and the burette detached from the titration head TH. The latter was stoppered and the vessel placed in the thermostat bath. A slow stream of nitrogen was maintained through C_2 for *ca.* 20 min. The flow rate was increased momentarily for efficient mixing and the plug P removed to start the reaction. The flow of nitrogen was slowed down.

Near the halflife time, plug P was inserted and the appropriate volume of the quenching hydrochloric acid solution was delivered into C_1. The nitrogen flow was increased momentarily and plug P then removed. This instant was the termination time. The flow of nitrogen was stopped and the vessel was taken out of the bath. The plug P and the walls of the compartment C_1 were washed with CO_2-free purified water into the solution in C_2 and the burette was attached to the titration head TH.

The excess acid was titrated, the solution being sucked up the titration head repeatedly in between readings during the titration to ensure that any traces of alkali were transferred to the bulk of the solution in C_2. Successive portions of the solution in C_2 were simultaneously sucked up into C_3 in between alkali additions until successive pH readings were consistent within the limit of the titration error. A slow stream of nitrogen was passed through in the course of the titration for mixing and for maintaining a CO_2-free atmosphere.

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